Nutrient Enrichment and Its Effects on the Phytoplankton Populations of the Standing Freshwaters of the Shetland Islands

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DEDICATION

This work is dedicated to my mother

Winifred Hennessy (McQueen)

(1926-1978)

and to my friend

Lorraine Wilson

(1967-1994)

ABSTRACT

During the period 1989-1990, phytoplankton blooms were observed in three lochs on Mainland Shetland. Land improvement procedures were taking place in each of the three drainage basins involved. The standing freshwaters of the Shetland Islands constitute a limited resource, having amenity value in terms of brown trout fishing, potable water supply and nature conservation. There was therefore concern that deterioration in water quality might be occurring as a result of fertiliser usage within loch catchment areas. In order to investigate this hypothesis, studies of current water quality, phytoplankton and macrophyte community structure, soil and sediment characteristics were undertaken.

Of the thirty one lochs examined, only six were oligotrophic in nature. This indicated that twenty five lochs were at risk of developing excessive algal growth, as once total phosphorus levels exceed 10 μg P L^{-1}, this becomes increasingly likely. In addition, monitoring of loch inflow waters of five drainage basins indicated that in catchment areas incorporating improved grassland, cattle/dairy farming and septic tanks, P concentrations were higher than those of both the receiving waters and the inflows in other watersheds with little anthropogenic influence.

Examination of data collected from thirty one lochs on phytoplankton taxa and numbers, combined with information on environmental parameters measured, indicated that certain phytoplankton were associated with particular water column conditions. Green algae were advantaged where enriched waters were relatively high in total phosphorus (TP) and total ammoniacal nitrogen (TAN). Of the blue green algae, *Anabaena* was found to be successful at the highest concentrations of TP and TAN, in association with low total oxidised nitrogen (TON) levels.

Macrophyte community structure was not found to be a useful means to characterise water column trophic status in the sites investigated. Examination of the macrophyte communities was not therefore used in assessing the susceptibility of waters to development of high phytoplankton biomass. This lack of explanation was partly due to the direct influence of sediment quality on macrophyte community structure. Many sediments represent an accessible nutrient source, whilst other types of bottom deposit

may either retain low levels of available nutrients, or inhibit macrophyte colonisation. The types of macrophyte which tend to grow in oligotrophic water bodies have little effect on nutrient cycling, whereas those associated with nutrient rich waters may act as nutrient "pumps" from sediment to water column.

P adsorption tests indicated that soils with an organic content of >80% were likely to retain little of the P added to them. Low soil pH (pH <4.00) also had a deleterious effect on P retention capacity. P adsorption tests with sediment from four lochs indicated that P retention within the upper 5 cm was related to organic content and magnitude of previous P additions. Soils and sediments rich in Ca, Mg or Fe and low in organic content retain a higher proportion of the P applied to them, than those poor in cations and high in organic matter. The more organic soils and sediments also release P which has been added to them previously.

After considering the literature on ameliorative measures in enriched loch systems, it was concluded that implementation of appropriate catchment management procedures in order to prevent development of nutrient enrichment difficulties was a more appropriate approach than attempting to improve water quality after enrichment has occurred. Using an established model, existing P loadings from five drainage basins were estimated. In the watershed with the highest proportion of the catchment undergoing pasture improvement, P export coefficients were found to be greatest.

The combined data from inflow water quality, soil and sediment nutrient retention and estimates of nutrient runoff indicate that the freshwaters of Shetland are clearly susceptible to enrichment. The deleterious effects which result are those of excessive phytoplankton growth. In order to prevent further deterioration of water quality, caution must be exercised in the management of both point and non-point nutrient discharges in the future.

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CHAPTER 1: GENERAL INTRODUCTION

1.1 INTRODUCTION

1.1.1 Physical processes influencing in development of primary production in freshwater lakes

1.1.1.1 Formation of lakes

Various mechanisms of lake formation are responsible for basin shape. Lake morphometry influences development of primary production in standing freshwaters as it determines the potential area of macrophyte colonisation and the volume of water receiving sufficient light to support photosynthesis. Drift and solid geology of a lake catchment area are important in determining lake sediment characteristics and water chemistry. The three main classifications of lake basin are referred to as rock, barrier and organic in origin (Maitland, 1990) and are created in essentially different ways.

Erosion of the Earth's surface through glacial action can result in formation of rock basins. Geomorphological indentations caused by ice scour and or alternate freezing and thawing of water allow formation of lacustrine features when ice melts. A glacial lake may also be formed if ice melts on erosional deposits associated with an ice sheet. Examples of lakes formed by glacial action are the Great Lakes of North America (Strahler and Strahler, 1973). Rock basins are also located in areas of previous volcanic activity. Collapse of rock structures created by lava flows, or sites of eruption, collect water from the surrounding watershed to form volcanic lakes, *e.g.* Crater Lake, Oregon, USA and Lake Kivu, East Africa (Strahler and Strahler, 1973). Movements of tectonic plates in the Earth's crust may form depressions along fault lines, at sites of folding processes or subsidence. In areas of upward movements of the surface, where plates are colliding, changing hydrological patterns can result in creation of new water bodies, in addition to those occurring due to stranding of marine basins. Standing waters formed by such processes are termed tectonic lakes, *e.g.* Lake Victoria and Lake Nyasa in East Africa (Strahler and Strahler, 1973). In areas where geological strata consist largely of sodium chloride, calcium sulphate, aluminium or ferric hydroxides and limestone, surface erosion and subsidence due to disappearance of supporting structures may occur as a consequence of dissolution of these minerals. The resulting lakes are known as solution lakes and include Deep Lake, Florida (Butzer, 1976). Depressions in the Earth's surface occurring as a result of meteorite collision account for the final category of rock basins (Butzer, 1976).

Barrier basins are formed by natural damming processes such as the blockage of a valley by lava flows or the erosional products of glaciers (moraine), flowing waters (alluvium) or wind (loess). For example, Slide Lake, Madison River, Nebraska was formed after a landslide (Strahler and Strahler, 1973).

Organic basins are those occurring because of the action of living organisms. Damming may occur as a result of formation of dense vegetation growth, a coral atoll, beaver activity, or reservoir creation by man (Wetzel, 1983).

1.1.1.2 Light in lakes

The amount of radiation energy falling as incident light upon an aquatic system depends on time of year, time of day, latitude and altitude of the site, climatic, atmospheric and local weather conditions. Only 1.5% of light which is vertical in incidence is lost (Maitland, 1990), but quantity of light reflected obviously increases with increasing angle of incidence, such as occurs during early morning or evening and during winter in temperate regions. Under these conditions, the depth to which light pervades the water column is shallow. Penetration of water by light not reflected at the surface is further dissipated through absorbance by matter in solution or suspension, as well as by water itself. Approximately 53% of light penetrating the water surface is converted to thermal energy within the upper 1 m of water column (Wetzel and Likens, 1990). Shorter wavelengths of light generally penetrate further, but light intensity decreases logarithmically with depth (Maitland, 1990). Depth of the water column is also important as shallow lakes are more likely to have significant quantities of resuspended material present and more likely to exhibit light effects due to sediment characteristics.

1.1.1.3 Distribution of heat energy in lakes

Lakes are often characterised by their mixis *i.e.* the process of physical circulation of the water column, through temperature dependent water density changes. Whereas pure ice has a low specific gravity and therefore floats, at a temperature of approximately 4°C, water is at its maximum density. Consequently, water of this temperature sinks (Wetzel, 1983). The nature of heat distribution and consequent stratification in lakes falls into several categories. Amictic lakes are located at high latitudes and altitudes only. There is no water circulation in these lakes, which remain

permanently ice covered and below 4°C on an annual basis. In cold monomictic lakes, seasonal ice formation occurs, winter temperature remaining greater at depth. Mixis is initiated in summer, temperature never exceeding 4°C during this season. Warm monomictic lakes are found mostly in areas of tropical climate, thermal stratification taking place in summer and circulation occurring the remainder of the year when temperature is never below 4°C (and normally considerably higher). Equatorial oligomictic lakes occur only in areas where incoming solar radiation continually maintains water temperature significantly in excess of 4°C. Stratification is disturbed infrequently by wind mixing only. Under conditions of strong chemical stratification, inhibition of lake mixis may occur, despite uniform water temperature. This type of lake is termed meromictic. In contrast, holomictic or polymictic lakes are continually mixed.

In temperate regions, such as the UK, a dimictic regime dominates. In autumn, water temperature is greater than 4°C and full mixing occurs. Inverse stratification is present in winter and as in cold monomictic lakes, ice often forms at the surface. As temperatures rise above 4°C in spring, overturn is initiated, wind mixing the entire water column. Thermal stratification takes place in summer owing to greater heating of surface waters. The warmest layer nearest the lake surface is the epilimnion and is separated from the colder deeper water, or hypolimnion, by a zone of rapidly changing temperature, the metalimnion. Circulation is then maintained in the epilimnion by wind action. The hypolimnion circulates separately, induction of mixing occurring through movement of the back current of the epilimnion or by internal seiches (Macan and Worthington, 1990). In a shallow lake, mechanical mixing through wind action makes it possible for the entire water column to be of constant temperature, regardless of season. However, in deeper, narrower lake basins, the restricted surface area:volume ratio encourages formation of discrete masses of water of different temperatures.

1.1.1.4 Effects of physical factors on plant growth

Hydrodynamic considerations, such as water column stratification, turbulence and water exchange rate, together with light intensity and temperature, all influence phytoplankton productivity. As photosynthetically active radiation (PAR) decreases with depth, phytoplankton biomass will be proportionally higher in broad, shallow

lakes than in narrow, deep basins. Similarly, the whole water column may be heated to constant temperature in a shallow lake, so stimulating greater algal growth when considering it in relation to lake mass. In lakes where stratification occurs, phytoplankton growth tends to be concentrated in the epilimnion. As growth proceeds, nutrient levels become limiting and high phytoplankton biomass may lead to light limitation. During periods of wind induced turbulence, additional nutrient supplies from the hypolimnion are distributed throughout the water column. This may stimulate algal growth, but limitation of biomass is imposed by continual removal of phytoplankton from the photic zone. Volume of a lake basin in comparison to volume of water supply from its catchment determines flushing rate of a body of water, which in turn influences time available to phytoplankton for growth. This is because flushing rate determines length of time available for water and sediment interactions, for concentration of nutrients from the watershed, loss of nutrients from the catchment through lake outflow and rate of loss of particulate matter (including phytoplankton) to sediment and outflow.

1.1.2 Nutrients of major importance to aquatic plant growth

Water chemistry is influenced by sediment and catchment characteristics and is of considerable importance to phytoplankton productivity and population dynamics. Four other major elements are considered to be significant in determining productivity of freshwater systems: Si, N, P and C.

1.1.2.1 Silicon

Silica (SiO_2) is a requirement of all phytoplankton for protein and carbohydrate synthesis (Reynolds, 1986), but is of major significance to diatoms and some species of Chrysophyceae and Xanthophyceae (Round, 1973). In diatoms, a pair of siliceous frustules are necessary for strengthening the cell wall and in chrysomonads, silica is used to construct protective scales (Reynolds, 1986). Although fragile diatoms such as *Rhizosolenia* may dissolve after death, silica cycling in lakes may be complicated by the permanent loss of assimilated silica to sediments because of the insolubility of phytoplankton structures. Such structures are soluble only in very acid (Wetzel, 1983) or peaty conditions in the water and sediments (Round, 1973), where silica solubility is increased by humic acids and formation of iron- and aluminium-silicate-humic complexes (Wetzel, 1983).

At the time of maximum diatom growth (spring in temperate lakes), lake waters exhibit a notable decrease in concentration of dissolved silica (Lund, 1950) Although species succession may occur in response to this, it is generally unlikely that low levels of silica inhibit diatom cell growth in freshwaters (Boney, 1989). Silicates are abundant components of mineral structures of rocks, therefore silica is continually supplied from catchment soils and geology. It is likely that other nutrients such as P and N become limiting before silica decreases to concentrations which would restrict phytoplankton growth.

1.1.2.2 Carbon

Carbon (C) cycling in lakes may be described as following the processes of photosynthesis, grazing, detritus formation and subsequent release of dissolved organic compounds from products of death and excretion of aquatic organisms (Moss, 1980). Bacterial transformations have a varying, but important role in C assimilation in lakes. In terms of plant uptake for photosynthesis, there are species, especially mosses, which can utilise C in its dissolved carbon dioxide (CO_2) form. Aquatic angiosperms may recycle respiratory CO_2 through their lacunar systems. However, many species have the ability to incorporate H_2CO_3 into cellular processes, rather than CO_2. This is important as inorganic C compounds exist in a series of equilibria as follows:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows HCO_3^- + H^+ \rightleftarrows CO_3^{2-} + H^+$$

The relative quantities of CO_2, H_2CO_3, bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) influence pH changes in the water. A change in the proportion of one of these compounds shifts the equilibrium, so that photosynthetic utilisation of CO_2 can lead to increased pH, so allowing formation of $CaCO_3$ or $MgCO_3$ (Wetzel, 1983). When pH is < 4, CO_2 and H_2CO_3 are the inorganic C species present in the water column. In contrast, at pH 10, CO_3^{2-} formation is enhanced, little or no CO_2 or H_2CO_3 being present (Moss, 1980). In temperate lakes, during times of peak photosynthesis in summer, temporary shortages in CO_2 can be compensated for by plant species capable of assimilation of C from H_2CO_3, although a metabolic cost will obviously be incurred. Increases in concentration of CO_2 in hypolimnetic waters cannot occur until water column overturn. Although there is a continual C source from the atmosphere, temporary dissolved CO_2 shortages due to photosynthesis or low levels in hard water lakes (*i.e.* lakes which have high concentrations of Ca^{2+} and or Mg^{2+} ions) may

nevertheless lead to changes in plant community structure.

1.1.2.3 Nitrogen

Nitrogen (N) in freshwaters exists in the following forms (Forsberg, 1977):

(1) molecular N_2 in solution

(2) dissolved inorganic ammoniacal compounds NH_4^+ and NH_3 and oxidised forms of nitrate (NO_3^-) and nitrite (NO_2^-)

(3) dissolved N in complex organic compounds of biological origin such as peptides, purines, amines, amino acids and urea

(4) N which is particulate in nature through assimilation into the structure of organisms within the water column or catchment area

N may also be present as inorganic forms which have been adsorbed to organic matter (Wetzel, 1983), although most inorganic N salts are not readily bound to clay minerals or organic matter in the sediments (Riemer, 1984).

N is necessary to aquatic organisms for formation of amino acids and proteins. Organic N compounds also function in plant nutrition through their ability to act as chelators. Soluble chelator complexes supply algae with metal ions such as iron (Fe^{3+}) and molybdenum (Mo^{3+}) (Moss, 1980). Owing to the lower energy cost of utilising more complex forms of N, most primary producers have the ability to use dissolved organic N. Preference then falls to NH_4^+ followed by NO_3^- then NO_2^- (Forsberg, 1977). However, bacterial uptake accounts for much of the dissolved organic N, particularly of smaller molecules *e.g.* amino acids, as they outcompete algae, especially when organic N sources in the water column are at low concentrations (Moss, 1980).

Relative amounts of different N sources in freshwaters are dependent upon the processes of nitrification, denitrification, ammonification and N fixation. Ammonium (NH_4^+) is generated within lakes as a product of heterotrophic bacterial break down of organic matter (Salisbury and Ross, 1978). Generally it exists as NH_4^+ and undissociated NH_4OH, molecular breakdown being dependent upon pH and temperature (Wetzel, 1983). Nitrification involves conversion of N in a reduced state (NH_4^+) through oxidation stages to NO_3^-. These steps involve bacteria, fungi and autotrophic organisms. Through molybdenum dependent enzyme systems, the

converse of this process is carried out in aquatic plants. Denitrification also occurs through biochemical reduction of oxidised N in bacterial oxidation of organic matter (Wetzel, 1983).

Molecular N can be used only by prokaryotic microorganisms which can reduce N_2 to NH_4^+ in the process termed N-fixation (Salisbury and Ross, 1978). In many temperate lakes, this form of N is relatively unimportant. Greater concentrations are likely to occur in P-enriched systems where N-fixing algae have become important (Moss, 1980). Increased phytoplankton biomass stimulated by P addition to the system can result in other sources of N being exhausted, so favouring development of a large population of N-fixers.

1.1.2.4 Phosphorus

Phosphorus (P) is the element which most commonly limits primary production in freshwater ecosystems (Wetzel, 1983). Total P (TP) in the water column consists of particulate P (PP) and dissolved P. PP may be further subdivided according to its source. PP of a physicochemical nature comes from catchment rocks and soils and may be present adsorbed to inorganic complexes such as clays, carbonates and ferric hydroxides. P may also be found attached to organic matter. Organic P assimilated in aquatic organisms commonly exists as nucleic acids, phosphoproteins, esters of enzymes, vitamins and nucleotide phosphates (Wetzel, 1983). Organic P may also be transported to a lake ecosystem from life forms within the drainage basin. Inorganic water soluble P is present in the water column on organic or adsorptive colloids, in polyphosphates and as phosphate ions (PO_4^{3-}, $H_2PO_4^-$, HPO_4^{2-}) (Moss, 1980).

1.1.3 Plant communities in temperate lake systems

1.1.3.1 Phytoplankton growth and succession in freshwater lakes

In temperate lakes, the relationships between physical and chemical parameters of standing freshwater bodies result in an annual succession, with phytoplankton species and abundance changing seasonally (Lund, 1950). During winter, lake water conditions of lower thermal input, light intensity and availability, the phytoplankton present are predominantly Bacillariophyceae and Chrysophyceae. These are usually present in low numbers (NCC, 1990). Overwintering cells of species which become abundant in spring (*e.g.* diatoms and desmids) comprise much of the plant life within

the water column at this time (Boney, 1989).

With increasing light and water temperature levels in spring, a bloom dominated by diatom species occurs, with algae utilising nutrients released from the hypolimnion to the whole water column during spring overturn. Depletion of this nutrient store, through increased water temperature and formation of a thermocline in summer results in catastrophic reduction ("crash") of the spring population (Jeffries and Mills, 1990). Lake phytoplankton communities may exhibit productivity peaks of green, blue-green and dinoflagellate species throughout summer to autumn (NCC, 1990). There may be great species diversity in the epilimnion, resulting from biological pressures on the phytoplankton population. Cryptophyceae may be present in large numbers, along with different forms of green algae, desmids, unicellular and colonial flagellates and non-flagellates (Boney, 1989). In Scotland, there may be periods of dominance by Chrysophyceae (Bailey-Watts and Duncan, 1981a).

When hypolimnetic water mixes with the epilimnion during autumn, a further phytoplankton peak may be stimulated by higher nutrient concentrations, despite reduced light intensity and water temperatures. Blue-green algae may flourish in autumn before grazing, greater mixing and a less favourable light climate reduces numbers to winter levels.

Biological processes within the water column exert a "top down" pressure on phytoplankton communities. Examples of these are grazing by zooplankton or predation by fish, destruction of algal cells by disease or parasites, and competition between species for available resources.

1.1.3.2 Macrophyte zonation in freshwater lakes

Rooted aquatic plants occupying the area from lake shore to the littoral zone have developed a number of anatomical and physiological adaptations to their environment. The exposure of the rhizosphere to anaerobic conditions in the sediment and changes in lake water level (the latter being especially important in summer in reservoir waters), are important in defining aquatic plant community structure. Area of lake sediment available for colonisation is dependent upon lake basin shape together with depth of light penetration. Primary production of rooted plants in the littoral zone of

a deep lake with steeply sloping sides and large volume, will be relatively small in comparison to that in a shallow lake.

Plants which grow in the land-water interface may be divided into three groups depending upon situation within this gradient (Wetzel, 1990). These categories are (a) emergent, (b) floating leaved and (c) submersed. Outwith this classification are free-floating macrophytes, which do not root in sediment and include species of *Lemna* and *Utricularia*. Emergent plants such as species of *Scirpus*, *Phragmites* and *Typha* are found growing both above and below the water level. These plants are generally perennials of a rhizomatous or cormous nature which are located in the region where the water table range is approximately -0.5 m to +1.5 m (Wetzel, 1983). Floating leaved macrophytes have leaves which reside on the water surface despite petiole (*e.g. Nuphar* and *Nymphaea* species) or petiole plus stem attachment (*e.g. Potamogeton natans*) to rhizomes in the sediment (Wetzel, 1983; Moss, 1980). These plants are mainly angiosperms and may be present to a water depth of *c.* 3.0 m.

Submersed plants comprise a diverse group, which exhibit considerable variability in leaf form both within and between species and include pteridophytes (*e.g. Isoetes*), mosses (*e.g. Fontinalis*) and stoneworts (*e.g. Chara*) as well as flowering plants. They occur between the water line and the depth at which light becomes limiting.

1.1.4 Nutrient enrichment in standing freshwaters

Nutrient enrichment, or eutrophication, may be defined as "natural or "man-made"" and "is the response in water to overenrichment by nutrients, particularly phosphorus and nitrogen." (OECD, 1982).

Natural waters may receive increased nutrient loadings from anthropogenic sources such as industrial developments, sewage systems, forestry and agriculture. Nutrients from agricultural sources include those from fertiliser, silage and dairy waste. Such artificial inputs of nutrients cause eutrophication to proceed at a higher rate than would occur naturally. General characteristics of lakes of different nutrient status are presented in Table 1.1 (Maitland, 1990) and Table 1.2 (Ratcliffe, 1977), where lakes of low and high water nutrient concentrations are referred to as oligotrophic and eutrophic respectively, the term mesotrophic indicating the intermediate state.

Table 1.1 General characteristics of dystrophic, oligotrophic and eutrophic lakes (Maitland, 1990)

Characteristic	Dystrophic	Oligotrophic	Eutrophic
Basin shape	small, shallow	narrow, deep	broad, shallow
Lake substrate	peaty silt	stony,inorganic silt	fine, organic silt
Lake shoreline	stony, peaty	stony	weedy
Water transparency	low	high	low
Water colour	brown	green or blue	yellow or green
Dissolved solids	low poor in Ca	low poor in N	high much N and Ca
Suspended solids	low	low	high
Dissolved oxygen	high	high	high at surface low under ice or thermocline
Phytoplankton	few species low numbers	many species low numbers Chlorophyceae typical	few species high numbers Cyanophyceae typical
Macrophytes	few species some abundant in shallow water	few species rarely abundant found in deep water	many species abundant in shallow water
Zooplankton	few species low numbers	many species low numbers	few species high numbers
Zoobenthos	few species low numbers	many species low numbers	few species high numbers
Fish	very few species often none	few species Salmonidae characteristic	many species especially Cyprinidae

Table 1.2 **General characteristics of lakes of different trophic states (Ratcliffe, 1977)**

Trophic state	Alkalinity (meq L^{-1})	Winter pH	Water colour	Productivity
Dystrophic	0-0.04	<6.0	brown peat stained	extremely low limited by low nutrient concentration and light penetration
Oligotrophic	0-0.2	6.0-7.0	clear	low, limited by low nutrient concentrations
Mesotrophic	0.2-0.6	*c.*7.0	slight green algal colouration	moderate to high possibly some hypolimnetic oxygen depletion during summer in deeper lakes
Eutrophic	>0.6	>7.0	often discoloured by algae	high, hypolimnetic oxygen depletion in deeper lakes
Marl (calcareous)	>2.0	>7.4	extremely clear	extremely low phytoplankton production high macrophyte production
Brackish	high ionic concentration	variable	usually clear	variable phytoplankton, generally sparse

Dystrophic lakes are those which are yellow/brown in colour, owing to the influence of organic soils in the catchment area.

Lakes formed in rock basins of glacial, volcanic or tectonic origin frequently exhibit the characteristics of deep water, nutrient deficiency, poor sediment and stony shores (although volcanic areas may also produce rich lakes). Often anthropogenic influence is minimal, as areas where these types of lakes predominate are generally inhospitable. Nutrient status therefore remains low. In contrast, lakes of low mean depth occurring on sedimentary rocks or deposits of wind, alluvium or glacial drift, have naturally enriched waters due to the supply of nutrients from catchment geology. Suitability of surrounding land for agriculture increases the potential for artificially enhanced inputs from such sources as fertiliser run-off and sewage from centres of population, leading to enrichment of these water bodies (Granberg, 1986; Kauppi *et al.*, 1990). Although sedimentation is a natural process in lakes, it is accelerated in catchments such as these. Accretion of littoral sediment and subsequent development of macrophyte communities, may result in further sediment accumulation. Basin shape is also important as it influences the effect of sediment characteristics on the overlying water and *vice versa*. In shallow lakes a greater proportion of water mass is in contact with the sediment. Similarly, mean depth:volume ratio is important in considering effects of solar radiation on a lake, the latter being the energy source responsible for driving production in aquatic systems.

Potential for P recycling is partly dependent upon the sediment area:water volume ratio. Limited opportunities for P recycling occur in narrow, deep basins, compared with shallow, broad basins. In oxygenated waters, it is possible for an aerobic surface layer of sediment to act as a sink for P with formation of trivalent iron phosphate and trivalent iron hydroxide. In nutrient enriched productive waters, there is the possibility that oxygen depletion in the hypolimnion will result in an anoxic sedimentary environment. Consequently, destruction of this barrier layer may occur when oxygen is absent from hypolimnetic waters. Ferric iron may then be reduced to more soluble ferrous iron, thereby leading to release of P from sediment to hypolimnion. The released P may then become available to the entire water column at overturn (Mortimer, 1941). As a consequence of depleted oxygen reserves, there may also be elevated concentrations of ammoniacal N through reduction of oxidised

sources and metal ions *e.g.* Fe^{2+} and Mn^{2+}. Therefore, in addition to importation of nutrients from the drainage basin, plant growth in enriched waters may also be supported through internal lake sources of sediment nutrient release.

Increasing nutrient concentrations in lakes can cause significant augmentation of biomass of macrophytes, periphyton and phytoplankton. Enhanced algal growth in particular may result in deterioration of water quality through changes in pH, transparency, dissolved oxygen concentrations and suspended solids within the water column. Increased productivity and phytoplankton numbers occur in eutrophic water bodies (Tables 1.1 and 1.2). Table 1.3 (Wetzel, 1983), synthesised from published information (Hutchinson, 1967), illustrates general associations between water type and phytoplankton groups present in the water column. In oligotrophic waters, desmids, diatoms, dinoflagellates and chrysophytes tend to dominate phytoplankton assemblages, whereas in nutrient enriched waters certain diatoms and blue-green algae generally assume dominance. Species of cyanobacteria have been found to produce poisons (NRA, 1990). Therefore, through eutrophication, water quality can also deteriorate because of the development of populations of toxin producing phytoplankton in the water column.

1.1.5 The freshwater resources of the Shetland Islands

Morphometric characteristics of Shetland water bodies are such that the smaller lochs have high area:depth ratios whilst conversely, larger lochs possess lower area:depth ratios, when compared with lochs on the Scottish mainland (George and Maitland, 1984). Of the freshwater lochs in the Shetland Islands, Loch of Cliff has the greatest catchment area, Loch of Strom the largest surface area, but Loch of Girlsta contains the greatest volume of water (Murray and Pullar, 1908). However, when morphometric characteristics of the large Shetland lochs are examined in a global context, or even in terms of Scottish water bodies, they are relatively small (Table 1.4). From a study of Ordnance Survey 1:63 360 scale maps, the total number of standing freshwaters in Shetland is 1569 (Lyle and Britton, 1985).

Table 1.3 Phytoplankton associated with different lake types (Wetzel, 1983)

Trophic status	Characteristics	Phytoplankton of water type Dominant	Present
Oligotrophic	slightly acid; very low salinity	*Staurastrum*, *Staurodesmus*	*Sphaerocystis*, *Gloeocystis*, *Rhizosolenia*, *Tabellaria*
Oligotrophic	neutral to slightly alkaline; nutrient poor	diatoms especially *Cyclotella* and *Tabellaria*	some *Asterionella* spp., some *Melosira* spp., *Dinobryon*
Oligotrophic	neutral to slightly alkaline; nutrient poor	*Botryococcus* or *Oocystis*	diatoms
Oligotrophic	neutral to slightly alkaline; generally nutrient poor *e.g.* shallow Arctic lakes	dinoflagellates especially *Peridinium* spp., *Ceratium* spp.	small chrysophytes, cryptophytes and diatoms
Oligotrophic	neutral to slightly alkaline; nutrient poor or seasonally nutrient poor	chrysophytes especially *Dinobryon*, some *Mallomonas*	chrysophytes *e.g. Synura*, *Uroglena*; *Tabellaria*
Mesotrophic or Eutrophic	neutral to slightly alkaline; annual dominants or seasonally under eutrophic conditions	dinoflagellates, some *Peridinium* spp. and *Ceratium* spp.	many phytoplankton including *Glenodinium*
Eutrophic	usually alkaline lakes with nutrient enrichment	diatoms much of the year especially *Asterionella* spp., *Fragilaria crotonensis*, *Stephanodiscus*, *Melosira granulata*	many phytoplankton especially greens and blue-greens during warm periods; desmids if dissolved organic matter relatively high
Eutrophic	usually alkaline; nutrient enriched common in warmer periods in temperate lakes or perennially in tropical lakes	blue-green algae especially *Microcystis*, *Aphanizomenon*, *Anabaena*	other blue-green algae; euglenophytes if organically enriched or polluted

Table 1.4 **Morphometric characteristics of large lakes of Shetland, Scotland, Europe and the World**

Lake	Location	Volume (km^3)	Surface area (km^2)	Mean depth (m)	Max depth (m)	Ref
Caspian Sea	Russia	79,319	436,400	182	946	1
Baikal	Siberia	23,000	31,500	730	1741	
Tanganyika	Africa	18,940	34,000	557	1470	
Superior	North America	12,000	83,300	144	307	
Constance	Germany	49.3	540	91	252	
*Balaton	Hungary	1.8	596	3.0	4.0	
Windermere	England	0.35	14.8	24.0	67.0	
*Tjeukemeer	Holland	0.03	20.0	1.5	3.0	
Lomond	Scotland	2.6	71.1	37.0	189.9	2
Awe	Scotland	1.2	38.5	32.0	93.6	
Ness	Scotland	7.5	56.4	132.0	229.8	
Morar	Scotland	2.3	26.3	86.6	310.0	
Shiel	Scotland	0.8	19.6	40.5	128.0	
Girlsta	Shetland	0.009	0.91	9.6	22.6	3
Strom	Shetland	0.003	1.34	2.1	4.0	
Cliff	Shetland	0.003	1.04	3.3	6.4	
Spiggie	Shetland	0.003	0.98	3.5	12.5	

KEY:

* approximate figures

1 Goldman and Horne (1983)
2 Smith *et al.* (1981)
3 George and Maitland (1984)

The density of standing freshwater bodies in Shetland compared with mainland Britain is therefore relatively high, accounting for as much as 30% of the land area in North Roe (Britton, 1974) and at least 3% of the land area in the Shetland Island group as a whole (Lyle and Smith, 1994). However, compared with the other regions of Scotland, in terms of numbers, accumulated area and volume, the Shetland region is relatively poor in freshwater resources (Lyle and Smith, 1994). The standing freshwaters of Shetland are therefore important, as they represent a limited resource in the Scottish context.

1.1.5.1 Water quality problems in the Shetland Islands

From 1989-1990, the Environmental Health Department of Shetland Islands Council (SIC), in its capacity as River Purification Authority (RPA), received reports of excessive algal growth in three lochs on Mainland Shetland. Of these, only one, Strand Loch (NGR: HU 432 460), had given any previous indication of possible problems, having for some years exhibited substantial growth of filamentous algae. During 1989, Turdale Water (NGR: HU 307 529) was found to have a dense population of algae. Although this was not investigated further, a bloom forming in mid May 1990 was diagnosed as being mainly *Anabaena* which is potentially toxicto fish and mammals. This was present for approximately two weeks before a period of weather associated with a zone of high pressure ended and the nuisance algae dispersed. A second bloom occurring in mid July, 1990, at Punds Water (NGR: HU 325 757), was also identified as being a dense colony of *Anabaena*. Finally, a late season "pea soup" was found at Strand Loch on 28-29 September, 1990.

Although SIC information on land use indicated that a significant nutrient input to Strand Loch from sewage and agricultural sources such as silage was likely, Turdale Water had possibly only one septic tank discharge and Punds Water had none. The lack of obvious point sources of nutrients at Turdale and Punds Water, together with the knowledge that Strand Loch had not previously suffered phytoplankton blooms, led to consideration of the possibility that fertilisation of land to improve sheep grazing (reseeding) might stimulate dense phytoplankton populations, as all three catchments had ongoing reseeding operations.

1.1.5.2 Land use in Shetland

According to statistics (SIC, 1991) for the period 1971 to 1990, the amount of land used for grassland and crops in the Shetland Islands increased from 8,407 to 12,840 ha. Rough grazing also increased from 129,019 to 130,736 ha, although greater areas were in use during the early/mid 1980s. It may be that the difference from early to mid 1980s was a result of rough grazing being converted to grassland; from 1986-1989 approximately the same area of land was lost from rough grazing as was gained to grassland.

As part of SIC's 10-year Agricultural Plan, the Council's Charitable Trust operated an agricultural loans scheme which began in 1982. Grants are also available from the Scottish Office Agriculture and Fisheries Department (SOAFD); those not qualifying for SOAFD grants may apply for a 50% grant from SIC. In practice, most aid comes from SOAFD (G. Petrie, SOAFD, *pers. comm.*, 1991). Reseeding development projects in 1989 were approved for 3664.4 ha at a gross cost to the SIC loans scheme of £1,238,152.

1.1.5.2.1 Reseeding procedures

A standard method of reseeding is implemented for those receiving SOAFD grants. Most of the work is carried out by a contractor; therefore adjacent tracts of land owned by different grant holders are often treated at approximately the same time. As a consequence of this practice total fertiliser load to a particular catchment may be increased substantially. SOAFD recommend procedures for land regeneration which are also the qualifying criteria for grant aid and include heavy harrowing or discing, application of lime, additions of fertiliser and finally, provision of grass seeds. Application of at least 5 t of limestone per hectare is compulsory unless soil is found to require less by the College of Agriculture. A balanced compound fertiliser must then be used, providing at least 110 kg per hectare of nutrients as N, P_2O_5 and potash, before a subsequent addition of 150 kg P_2O_5 as ground mineral phosphate or basic slag per hectare. Fertiliser additions are made during May, June and July and seeds are broadcast before 31st July. Proportions of Kent Wild White Clover, Aberystwyth White Clover and Huia White Clover are stipulated and use of lower grade seed prohibited. In the second year, balanced compound fertiliser must again be applied, providing at least 110 kg nutrients as described above per hectare. Grant

aid is not provided in cases where nitrogenous fertiliser alone is applied in the second year.

According to the Scottish Agricultural College, the time of surface seeding is usually during early to mid July when increasing humidity and showers, together with warm, moist soil promote efficient germination and growth of grass and clover. Provision of lime and fertiliser plus any cultivation occurs prior to sowing while the weather is dry. Initial nutrient addition therefore occurs coincidentally with early summer phytoplankton growth in the lochs.

1.1.6 Problems of algal blooms for water supply authorities

Increased algal biomass can cause significant problems for potable water supply authorities. Water treatment filters may become blocked and it is possible for algal toxins to pass into the consumer supply. Wholesomeness of water received at the tap can deteriorate badly with respect to taste and odour. Table 1.5 lists algae which have been associated with polluted water, filter clogging, taste, odour (APHA, 1989) and toxicity problems (NRA, 1990). Finally, when considering public health issues, the production of trihalomethanes (THMs) can occur with chlorination of cyanophyte infested waters.

Blue-green algae and humic substances which are present in peaty lochs produce THMs as carcinogenic by-products of traditional disinfection methods. Present EC legislation provides a low non-statutory guideline of 1 $\mu g\ L^{-1}$ rather than a standard (Foster *et al.*, 1991). Water authorities in England have been investigating alternative treatment processes to chlorination in order to alleviate THM problems. It is now generally accepted that treatment with ozone and granular activated carbon deals with THM precursors and removes taste and odour problems. Ozone is a powerful oxidant which alters organic substances in raw supply water to produce aldehydes, ketones and acids which are more biodegradable. This process increases available organic carbon which can be removed in a subsequent biological treatment stage (Foster *et al.*, 1991).

Table 1.5 **Algae associated with polluted water, filter clogging, taste and odour problems (APHA, 1989) and toxicity (NRA, 1990)**

Polluted water	Filter clogging	Taste and odour	Toxicity
Phormidium	*Synedra*	*Tabellaria*	*Anabaena*
Carteria	*Asterionella*	*Anabaena*	*Microcystis*
Lepocinclis	*Tribonema*	*Uroglenopsis*	*Oscillatoria*
Lyngbya	*Oscillatoria*	*Synedra*	*Nostoc*
Gomphonema	*Trachelomonas*	*Ceratium*	*Cylindrospermum*
Stigeoclonium	*Rivularia*	*Gomphosphaeria*	*Aphanizomenon*
Chlorella	*Cyclotella*	*Synura*	
Microcystis	*Chlorella*	*Pandorina*	
Oscillatoria	*Navicula*	*Volvox*	
Tetraedron	*Dinobryon*	*Dinobryon*	
Nitzschia	*Tabellaria*	*Aphanizomenon*	
Anabaena	*Diatoma*	*Peridinium*	
Euglena	*Spirogyra*	*Hydrodictyon*	
Spirogyra	*Fragilaria*	*Microcystis*	
Chlamydomonas	*Palmella*	*Nitella*	
Merismopedia	*Closterium*	*Mallomonas*	
	Microcystis	*Staurastrum*	
	Anabaena	*Asterionella*	
	Cymbella		

1.1.7 Control of water quality in Scottish standing freshwaters

The River Purification Authorities (RPAs) are the primary regulatory organisations responsible for water quality in fresh and coastal waters in Scotland. These RPAs are constituted of seven River Purification Boards and three island councils. RPA criteria for maintaining freshwater resources in Scotland involve the setting of an environmental quality objective (EQO). An EQO is decided depending upon the present or predicted amenity value of the water body, based on water quality parameters. Environmental Quality Standards (EQS) are then set in accordance with the EQO and appropriate EC Directive on water quality criteria (*e.g.* if the objective is to support freshwater fish life, Directive 78\659\EEC would be consulted). In the absence of EC directives, standards such as those of the European Inland Fisheries Advisory Commission (EIFAC) may be employed. However, where EC standards do exist, these must be met regardless of other guidelines. Where a water body has more than one usage, compliance must be with the most stringent user requirements. In the case of interconnected water bodies (*e.g.* the catchments of Brow-Spiggie and Tingwall-Asta), it is required that upstream water quality is of a standard sufficient to meet all downstream EQS.

In cases of identifiable point or diffuse effluents to water bodies, the discharger must apply to the RPA for Consent to Discharge under the Control of Pollution Act (1974), Part 2, Section 34. Conditions for Consent to Discharge are set by RPAs with reference to maintaining the appropriate EQS for that water body. Information relating to the discharge is therefore required on such parameters as nutrient loading, concentration of metals and biochemical oxygen demand (BOD) of the intended discharge before Consents can be granted.

However, practices relating to the application of fertiliser on forest or agricultural land do not require clearance from RPAs. In order to limit such activities, a request to the Secretary of State would be required, stating application of fertiliser as a prescribed activity under Section 31(4), Schedule 23 of the Water Act (1989). Forth River Purification Board (FRPB) (*pers. comm.*) indicated that this situation was under reconsideration by RPAs, both locally and nationally, but that the Secretary of State would ultimately decide on applicability of regulations to these activities. Two RPAs in Scotland (Clyde and North East) (*pers. comm.*) considered that data they possessed

indicated no cause for concern with regard to these inputs. Scottish Natural Heritage (*pers. comm.*) foresee no change in current circumstances under present Government policy.

However, in small loch systems such as those of Shetland, it is possible that any addition of nutrients from fertilised land may have an impact on receiving water bodies. In small drainage basins, it is conceivable that the fertilised area may make up a considerable proportion of total catchment area. In shallow lakes, the sediments already represent a potentially important internal nutrient source as a consequence of low mean depth and wind mixing. Although little information exists concerning integrated catchment studies of the fate of agricultural fertiliser, possible deleterious effects of forestry practises are well documented (Bailey-Watts *et al.*, 1987a).

1.1.8 Project aims

The potable water supplies of the Shetland Islands rely upon water treatment systems which are largely unsuitable for dealing with waters affected by algal blooms. In addition to this, there are at present no guidelines as to an acceptable level of algal toxin present in a potable water supply. The water supply in Shetland is not on a grid system, therefore no alternative water source exists for a community should abstraction from a reservoir be interrupted because of increased algal biomass. A full investigation was therefore undertaken to assess the following points:

(a) present status of water quality in Shetland Island lochs

(b) susceptibility of Shetland standing waters to excessive primary production problems associated with nutrient enrichment

(c) the potential for fertiliser applications on land to cause nutrient enrichment of standing freshwaters

(d) possible preventative or remedial measures to preserve water quality should problems of elevated plant productivity occur.

1.1.8.1 Catchments chosen for study

The first year of the project consisted of a broad study to enable the classification of lochs and soils and identification of five catchment areas for more detailed investigation in the second and third years. Lochs from all over Shetland were chosen for the baseline study; from Mainland, Unst, Yell, Fetlar, Whalsay, Bressay and Papa

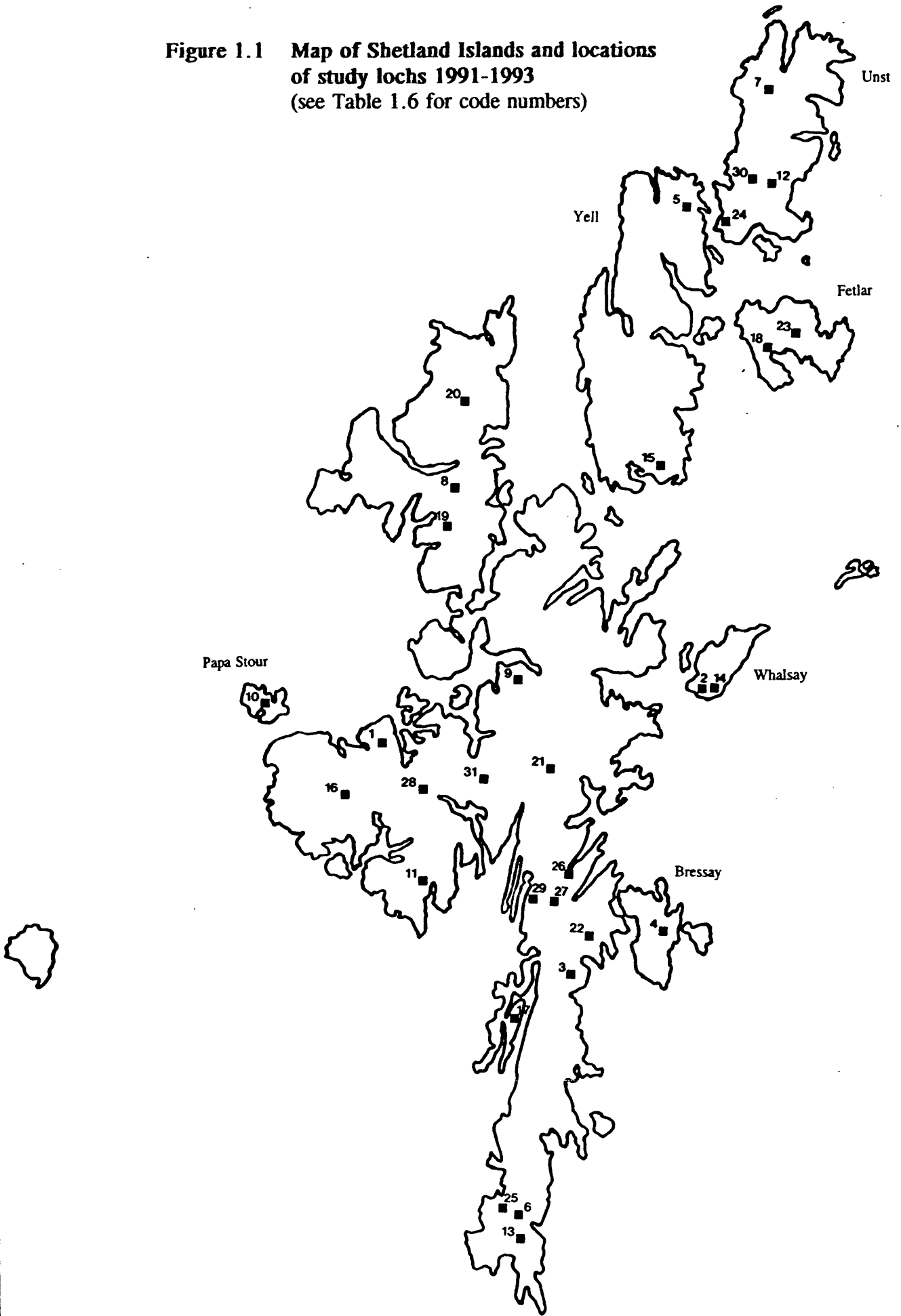
Table 1.6 Freshwater lochs in Shetland included in 1991 survey

Water body	Map reference	Amenity value
1 Arthurs Loch	HU 270 565	WS (West Burrafirth)
2 Bu Water	HU 548 620	WS (Whalsay)
3 Loch of Brindister	HU 433 370	F WS (Gulberwick/Quarf)
4 Loch of Brough	HU 513 407	F WS (Bressay)
5 Loch of Brough	HP 530 029	F WS (Cullivoe)
6 Loch of Brow	HU 384 157	SSSI
7 Loch of Cliff	HP 600 120	F
8 Eela Water	HU 330 785	WS (Sullom Voe/Northmavine)
9 Loch of Gonfirth	HU 385 623	WS (Voe)
10 Gorda Water	HU 167 607	WS (Papa Stour)
11 Gossa Water	HU 303 457	F WS (Skeld)
12 Helliers Water	HP 610 047	F WS (Unst)
13 Loch of Huesbreck	HU 389 139	WS (Sumburgh)
14 Loch of Huxter	HU 556 622	F WS (Whalsay)
15 Loch of Kettlester	HU 513 806	WS (Burravoe/South Yell)
16 Lunga Water	HU 234 527	F WS (Walls)
17 Mill Pond	HU 386 334	WS (Burra Isle)
18 Papil Water	HU 604 904	F
19 Punds Water	HU 325 757	F
20 Roer Water	HU 336 863	F WS (Sullom Voe/ Northmavine)
21 Sand Water	HU 416 545	F SSSI
22 Sandy Loch	HU 450 403	F WS (Lerwick/Scalloway)
23 Skutes Water	HU 623 920	F WS (Fetlar)
24 Loch of Snarravoe	HP 570 015	F
25 Loch of Spiggie	HU 371 170	F SSSI
26 Strand Loch	HU 432 460	F
27 Loch of Tingwall	HU 417 430	F SSSI
28 Turdale Water	HU 307 529	
29 Loch of Ustaness	HU 399 434	F WS (Whiteness/Weisdale)
30 Loch of Watlee	HP 593 055	F WS (Unst)
31 Whitelaw Loch	HU 385 540	WS (Aith)

KEY:

Numbers 1-31 refer to Figure 1.1
SSSI Site of Special Scientific Interest
WS potable water supply loch
F trout angling (from Burrows and Hoseason, 1982)

Figure 1.1 Map of Shetland Islands and locations of study lochs 1991-1993
(see Table 1.6 for code numbers)



Stour (Table 1.6 and Figure 1.1). This was in order to reflect effects of different catchment geologies (the geology of Shetland is complex and variable), soil types and management practices in the results. All twenty one water supply lochs were visited, whilst ten sites were chosen as they were of interest to SIC for the following reasons. Papil Water on Fetlar, Lochs of Cliff and Snarravoe on Unst had all supported fish farm operations; Lochs of Tingwall, Brow and Spiggie and Sand Water were Sites of Special Scientific Interest, whilst Turdale Water, Strand Loch and Punds Water were included as the three "problem" lochs mentioned previously. The five lochs chosen for further study in 1992 and 1993 were Loch of Gonfirth, Helliers Water, Loch of Tingwall, Sandy Loch and Turdale Water.

CHAPTER 2: LIMNOLOGY AND WATER QUALITY OF SHETLAND FRESHWATER LOCHS

2.1 INTRODUCTION

2.1.1 Chemical status of Shetland waters

There has been much interest in small lakes in Scandinavia and North America, especially those high in water colour (Jackson and Schindler, 1975; Jones, 1990; 1992a). In contrast, little work has been carried out on the standing waters of Shetland and much of the data collected to date remains unpublished. The status of fresh waters in the Islands has been estimated from information on geology of catchment areas (Table 2.1). The majority of lochs are those which are highly coloured (yellow/brown) by peaty substances, such as humic and fulvic acids. Britton (1974) claims these water bodies are characterised by low nutrient concentrations, low biological productivity and are generally small, for with increasing size it becomes more likely that mineral soils will form part of the catchment. However, waters of this lake type tend to exhibit higher total P concentrations than comparable clear water lakes (Hutchinson, 1957; Wetzel, 1983), but phytoplankton production and biomass development is frequently lower than expected from the P concentration. This being the case, many Shetland lochs, although largely free from anthropogenic influences, may be expected to exhibit relatively high nutrient concentrations.

It is possible that in highly humic lakes an appreciable proportion of phosphate P may be present as part of a dissolved humic matter-Fe-P complex, rather than immediately biologically available phosphate P (Jones *et al.*, 1988). Free phosphate can be progressively released from these complexes as ambient free phosphate P concentration declines, thereby possibly providing a long term buffer against P deficiency (Jones *et al.*, 1990). In shallow and/or nutrient-rich lakes of this type, phosphorus release from the peaty sediments is dependent upon mineralisation of organic matter (Sinke *et al.*, 1990). As a large reservoir of dissolved organic carbon exists in humic waters, higher microbial activity may be sustained, so allowing nutrient regeneration through the food chain (Jones *et al.*, 1990).

Table 2.1 Classification of Shetland Island lochs according to geology (Britton, 1974)

Loch type	Number of lochs	% of total
Dystrophic	547	34.7
Oligotrophic	661	41.9
Mesotrophic	212	13.4
Eutrophic	111	7.0
Brackish	45	2.8
Marl	1	0.1

Table 2.2 **Range of water quality parameters from 53 lochs in Shetland (Carter and Bailey-Watts, 1981)**

Nutrient	Concentration
NO_3-N	trace - 100 μg N L^{-1}
NH_3-N	trace - 400 μg N L^{-1}
PO_4-P	trace - 400 μg P L^{-1}
SiO_2-Si	trace - 2 mg Si L^{-1}

Carter and Bailey-Watts (1981) undertook a synoptic survey of Shetland lochs. In a wide range of lochs, P concentration was found to be similar to, or in excess of, that of inorganic N (Table 2.2). This situation may encourage algae which fix N (*i.e.* certain species of cyanobacteria), although once enrichment occurs, dependent upon relative quantities of N and P, this advantage may be lost. Subsequently, non N-fixing cyanophytes may bloom and in cases of great hypernutrification, green phytoplankton may dominate. As N levels are generally low in Shetland lochs, the addition of a N+P+K fertiliser, rather than P alone may be important, as it is possible that in some circumstances primary production may be N-limited.

2.1.2 Aims

Before management decisions regarding land use in catchment areas of Shetland freshwater lochs are possible, it is necessary to know the current limnological status of the water bodies concerned. From the information on ranges of nutrient levels in Shetland lochs of Carter and Bailey-Watts (1981), it is likely that a variety of water types exist, water quality being influenced by different geology, soil type and land use. When current status of a water body has been determined, it is possible to recognise its amenity value and therefore attempt to comprehend the limitations to be imposed on nutrient inputs. The aims of this section of work were therefore as follows.

(a) Determine the status of the thirty one lochs in terms of a number of different physical and chemical variables, *i.e.* conduct a synoptic survey of these water bodies.

(b) Compare results of the synoptic survey with existing standards of water quality required for drinking water and for the purpose of supporting freshwater fish.

(c) Using existing standards, classify the water bodies surveyed in terms of trophic status and likelihood of phytoplankton blooms.

(d) From the first year's data, select five water bodies incorporating a range of water types for further study. Examine variation in total P and chlorophyll *a* concentrations, during the period of the year when phytoplankton growth is expected to be elevated, *i.e.* from March to October.

(e) Ascertain whether inflow waters of selected water bodies are likely sources of nutrient enrichment.

2.2 MATERIALS AND METHODS

2.2.1 Field procedures

During summer 1991, each of the thirty one lochs was visited on three occasions. Three sites were chosen mid water in each water body. Water collection was undertaken using a Van Dorn self closing sampler throughout the survey. Depending on water depth, samples were taken at 0, 2 and 5 m (Table 2.3). These samples were composited, except for subsamples taken for discrete measurements of pH and conductivity (HMSO, 1980). Dissolved oxygen and temperature readings were recorded *in situ* to water collection depth, whilst light readings were taken with a PAR meter to 1 m depth only. The oxygen probe was of the Mackereth type and was agitated continuously whilst readings were taken using a pHOX Model 62 oxygen meter. The light attenuation coefficient (LAC) was calculated according to Moss (1980):

$$(\ln I_o - \ln I_z)/z = \eta$$

where:

I_o PAR reading in surface water

I_z PAR reading at depth

z depth of PAR reading

η negative extinction coefficient (light attenuation coefficient)

Variables of 1991 water samples measured in the laboratory were pH and conductivity values, total phosphorus (TP), total dissolved phosphorus (TDP) and dissolved reactive phosphorus (DRP) concentrations, total ammoniacal nitrogen (TAN), total oxidised nitrogen (TON), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K) levels, colour and chlorophyll *a* (chl *a*).

Sampling in 1992 was more detailed and intensive; five visits were made from March to October, to each of the five study lochs, the entire water column being studied at the same three sites per water body as used in the 1991 survey (Table 2.3). Discrete samples and readings of dissolved oxygen and temperature were taken at intervals from surface to deep water. In 1993, lochs were visited on four occasions between March and October, sampling continuing as in 1992, though at one site only (with the exception of Loch of Tingwall where there was one site in each of the two basins)(Table 2.3).

Table 2.3 Sites and dates of water sampling 1991, 1992 and 1993 (all sampling carried out between 09:00 and 16:30)

1991

Site	Depth (m)	Date
Arthurs Loch	0	16/07/91, 14/08/91, 25/09/91
Bu Water	0	15/07/91, 18/08/91, 28/09/91
Loch of Brindister	0, 2	12/07/91, 17/08/91, 18/09/91
Loch of Brough (Bressay)	0	16/07/91, 22/08/91, 27/09/91
Loch of Brough (Yell)	0	17/07/91, 21/08/91, 28/09/91
Loch of Brow	0	13/07/91, 22/08/91, 20/09/91
Loch of Cliff	0, 2	18/07/91, 20/08/91, 22/09/91
Eela Water	0, 2	21/07/91, 16/08/91, 26/09/91
Loch of Gonfirth	0, 2, 5	20/07/91, 16/08/91, 26/09/91
Gorda Water	0	22/07/91, 27/08/91, 01/10/91
Gossa Water	0	16/07/91, 14/08/91, 20/09/91
Helliers Water	0	18/07/91, 20/08/91, 22/09/91
Loch of Huesbreck	0, 2	14/07/91, 17/08/91, 18/09/91
Loch of Huxter	0, 2	15/07/91, 18/08/91, 28/09/91
Loch of Kettlester	0	17/07/91, 19/08/91, 21/09/91
Lunga Water	0, 2	20/07/91, 14/08/91, 25/09/91
Mill Pond	0	13/07/91, 15/08/91, 27/09/91
Papil Water	0, 2	19/07/91, 25/08/91, 23/09/91
Punds Water	0, 2	21/07/91, 16/08/91, 26/09/91
Roer Water	0	25/07/91, 28/08/91, 29/09/91
Sand Water	0	15/07/91, 15/08/91, 19/09/91
Sandy Loch	0	12/07/91, 15/08/91, 18/09/91
Skutes Water	0	19/07/91, 23/08/91, 23/09/91
Loch of Snarravoe	0, 2	17/07/91, 21/08/91, 22/09/91
Loch of Spiggie	0, 2	14/07/91, 17/08/91, 18/09/91
Strand Loch	0	13/07/91, 15/08/91, 19/09/91
Loch of Tingwall	0, 2, 5	13/07/91, 26/08/91, 19/09/91
Turdale Water	0	15/07/91, 14/08/91, 25/09/91
Loch of Ustaness	0	24/07/91, 28/08/91, 29/09/91
Loch of Watlee	0	18/07/91, 20/08/91, 22/09/91
Whitelaw Loch	0	23/07/91, 29/08/91, 30/09/91

1992 and 1993 water sampling locations

Water body	Site	Depth (m)	Sampling dates for each site and depth
Loch of Gonfirth	1	0, 2, 5, 10	23/03/92
	2	0, 2, 5, 10, 15, 20	11/05/92
	3	0, 2, 5, 10, 15	23/06/92
			20/08/92
			07/10/92

Table 2.3 (cont.)

Water body	Site	Depth (m)	Sampling dates for each site and depth
Loch of Gonfirth			
	2	0, 2, 5, 10, 15, 20	22/03/93
			20/05/93
			25/07/93
			03/10/93
Helliers Water	1	0	19/03/92
	2	0	12/05/92
	3	0	20/06/92
			23/03/93
			23/05/93
			28/07/93
			02/10/93
Loch of Tingwall	1	0, 2, 5, 10	22/03/92
	2	0, 2, 5, 10, 15, 20	13/05/92
	3	0, 2, 5, 10, 15	24/06/92
			22/08/92
			08/10/92
	1	0, 2, 5, 10	24/03/93
	2	0, 2, 5, 10, 15, 20	21/05/93
			26/07/93
			04/10/93
Sandy Loch	1	0, 2	21/03/92
	2	0, 2, 5	10/05/92
	3	0, 2, 5	20/06/92
			21/08/92
			10/10/92
	3	0, 2, 5	21/03/93
			22/05/93
			27/07/93
			01/10/93
Turdale Water	1	0	18/03/92
	2	0	12/05/92
	3	0	18/06/92
			21/08/92
			09/10/92
			24/03/93
			22/05/93
			29/07/93
			05/10/93

Records of Secchi disc depth were taken instead of light readings in 1993. Variables of 1992 and 1993 samples determined in the laboratory were pH, conductivity, alkalinity, TP, TDP, DRP and chl *a* levels. Samples of loch inflow and outflow waters were taken during each visit from May 1992 to October 1993 (Positions marked in Figure 3.1). The same parameters were measured in these samples as in the loch samples, with the exception of chl *a* concentration.

Bathymetric surveys of the five study lochs were carried out in May, 1992. This was conducted using a Lowrance X16 echosounder and motorised boat. Depending upon the surface area of the water body, between six and thirteen sounding tracks were taken in each loch. A "flying start" (Håkanson, 1981) was practised for each transect. From an identifiable point on the shoreline, direction was maintained using a compass reading. Constant engine speed was sustained during all soundings. Echosoundings were conducted parallel and at right angles to the shoreline. Depth contours were then constructed using the echogram and the appropriate 1:25 000 OS map for each loch.

2.2.2 Treatment and storage of samples

All bottles involved in sample collection and storage were pre treated in 1.2 M HCl. Polyethylene sampling bottles were rinsed in deionised water then thoroughly rinsed in loch water prior to use. Water for TP analysis was decanted into iodised polyethylene bottles rinsed with deionised, double distilled and sample water. Rinsing procedure was the same for all other storage bottles. Subsamples for metals analysis were decanted into polyethylene bottles. Water samples were filtered through prewashed 0.45 μm cellulose nitrate papers (1991) or 1.2 μm GF/C papers (1992 and 1993) shortly after sampling and stored for measurement of dissolved parameters at the laboratory. Filtrate was stored in polyethylene bottles. All filtered samples were stored frozen in darkness until analysis.

2.2.3 Laboratory measurement of environmental parameters

All glassware utilised in the following techniques was pretreated with 1.2 M HCl then Decon 90 P-free detergent before rinsing in deionised and double distilled water.

2.2.3.1 Alkalinity

A 100 mL sample was decanted into a conical flask. A few drops of BDH 4.5

indicator were added to the sample and titration carried out using 0.01 M HCl to the pink pH 4.5 end point. The first sample of each loch water titrated to pH 4.5 was retained for reference colour. Volume of acid titre was multiplied by a factor of 0.1 in order to express results in terms of meq L^{-1}.

2.2.3.2 Phosphorus

Total phosphorus (TP), total dissolved phosphorus (TDP) and dissolved reactive phosphorus (DRP) determinations were performed with 15 mL aliquots of sample, TP analyses being carried out on unfiltered water, TDP and DRP on filtrate. After a sulphuric acid/potassium persulphate digestion in an autoclave for 30 minutes at 15 p.s.i. (Phillips, 1985a), TP and TDP were measured spectrophotometrically as DRP using a molybdenum blue complex technique with ascorbic acid as the reducing agent (Phillips, 1985a). Absorbance was read at 690 nm, using a 4 cm cell. All DRP results were colour corrected.

2.2.3.3 Nitrogen

Total ammoniacal nitrogen (TAN) was determined using an automated technique based on Method F, HMSO (1982a). Hypochlorite was generated *in situ*, by alkaline hydrolysis of sodium dichlorocyanurate. Ammonia and hypochlorite were reacted with a phenolic compound *i.e.* the salicylate ion, to form a blue colour. Sodium nitroprusside was used as the catalyst and trisodium citrate was utilised as a complexing agent to prevent interference from metals such as Mg. Total oxidised nitrogen (TON) was determined using an automated technique modified from Method D, HMSO (1982b). Nitrate was reduced to nitrite by passing samples through a copper coated cadmium coil, after addition of ammonium chloride. TON was subsequently measured as nitrite using an NED/sulphanilamide procedure. TAN and TON were determined simultaneously, using a Technicon II autoanalyser at 640 and 70 nm respectively.

2.2.3.4 Calcium and magnesium

Ca and Mg determinations were carried out by atomic absorption spectroscopy, using a direct air acetylene flame technique after installation of appropriate lamp, wavelength and slit width and optimisation of lamp alignment for each element. All samples were diluted to within standard range. All solutions including distilled water

blanks were made up to have a final concentration of 1% strontium (Sr), using $SrCl_2(6H_2O)$ and of 1% 'Spectrosol' grade nitric acid (HNO_3). Standards were made by dilution of Spectrosol stock 1000 mg Ca L^{-1} and 1000 mg Mg L^{-1} to within the ranges 1-5 mg Ca L^{-1} and 0.1-0.5 mg Mg L^{-1} respectively. Samples for Ca analysis were diluted (sample volume:water volume) 1:1 to 1:19, those for Mg determinations generally 1:9, though by as much as 1:49. All dilutions were carried out with distilled water.

2.2.3.5 Sodium and potassium

Concentrations of Na and K in water were determined by flame emission spectroscopy. Standards for Na determinations were made by dilution of Ciba Corning 1000 mg Na L^{-1} stock to within the range 10-50 mg Na L^{-1}, whilst those for K measurement were in the range 1-5 mg K L^{-1}, having been diluted from Ciba Corning 1000 mg K L^{-1} stock. For each element, the most concentrated standard was aspirated and the machine set to give a reading of 100 units. Similarly a distilled water blank was used to set the instrument to zero. Samples were diluted where necessary to within standard range. All dilutions were carried out using distilled water.

2.2.3.6 Colour

The colour in filtered water samples was measured spectrophotometrically at 400 nm (HMSO, 1984), using 4 cm cells.

2.2.3.7 Chlorophyll *a*

Chl *a* was used as an estimate of phytoplankton biomass within the water column. Up to 2 L of water was filtered through a 1.2 μm GF/C filter paper. The filter paper was then stored frozen in darkness until analysis. Chl *a* was extracted from each filter paper using 14 mL 100% methanol neutralised with $MgCO_3$. Methanol was added to centrifuge tubes containing the filter papers. These tubes were subsequently heated in a water bath at 62 $\pm$2°C for 5 minutes. Centrifuge tubes were then shaken and placed in a centrifuge for 5 minutes at 3,000 rpm. Absorbance of each chl *a* extract was measured spectrophotometrically at wavelengths 665 nm and 750 nm, using 4 cm glass cuvettes. To correct for phaeophytin, 11 mL of extract was then decanted into a test tube and 0.11 mL 3% HCl added. After 5 minutes, this extract was neutralised

with 0.11 mL 0.3 M dimethylaniline (organic base in methanol). Each extract was then reread at 665nm and 750nm to allow correction for phaeophytin. Chl *a* concentration was then calculated using the equation of HMSO (1983), modified for the particular conditions of the techniques used. The equation was as follows:

$$\text{Chl } a = (13.9 \times (3.0 (A_h - A_j)) \times v) / dV$$

where:

A_h absorbance of extract at 665 nm, minus extract absorbance at 750 nm

v initial volume of extract (mL)

d cell path length (cm)

V sample volume (mL)

13.9 constants associated with properties of

3.0 the solvent, methanol

$$A_j = ((v + 0.22) \times A_i) / v$$

where:

v volume of acidified extract (mL)

0.22 total volume of additions to the acidified extract (mL)

A_i absorbance of acidified extract at 665 nm minus absorbance of acidified extract at 750 nm

2.2.3.8. Presentation of survey data

Data from each loch and each environmental variable were summarised using the range or mean (± 2 standard errors) (n=3).

2.3 RESULTS

2.3.1 Water chemistry and physical characteristics of Shetland lochs in 1991

All ± values accompanying mean values given in the following text represent ± 2 standard errors (± 2 s.e.). Similarly, Figures 2.1-2.8 present the parameter mean ± 2 s.e..

2.3.1.1 Dissolved oxygen concentration and temperature (Table 2.4)

In 1991, daytime dissolved oxygen concentrations measured ranged from 6.5 mg L^{-1} (63.7%) in Lunga Water during August, to 12.5 mg L^{-1} (116.4%) in Loch of Brow in September.

Table 2.4 **Ranges of summer water column temperatures and dissolved oxygen concentrations in the 31 lochs of the 1991 survey**

Water body	Temperature (°C)		Dissolved oxygen (mg O_2 L^{-1})	
	min	max	min	max
Arthurs Loch	9.6	17.7	6.9	11.6
Bu Water	8.9	16.1	9.1	11.4
Loch of Brindister	12.2	15.0	9.3	10.9
Loch of Brough (Bressay)	9.0	14.7	9.3	10.8
Loch of Brough (Yell)	8.3	15.9	9.1	11.2
Loch of Brow	12.1	15.2	10.4	12.5
Loch of Cliff	11.6	16.7	8.7	10.7
Eela Water	10.4	15.4	9.0	10.6
Loch of Gonfirth	10.8	15.2	9.3	10.4
Gorda Water	8.3	15.7	9.0	11.4
Gossa Water	12.1	16.6	6.7	11.3
Helliers Water	11.0	16.3	9.8	10.9
Loch of Huesbreck	12.0	16.1	10.4	12.3
Loch of Huxter	9.7	16.0	8.8	11.2
Loch of Kettlester	11.6	17.7	9.3	10.8
Lunga Water	10.8	15.6	6.5	11.1
Mill Pond	9.1	15.2	9.5	10.9
Papil Water	10.9	16.6	8.9	11.1
Punds Water	10.0	15.7	8.9	10.7
Roer Water	8.8	14.2	9.4	10.7
Sand Water	11.8	16.1	9.3	10.9
Sandy Loch	11.8	15.4	9.0	11.0
Skutes Water	9.7	15.9	9.5	10.4
Loch of Snarravoe	11.6	16.8	9.0	10.9
Loch of Spiggie	12.5	15.8	8.8	11.2
Strand Loch	12.4	16.1	10.0	11.6
Loch of Tingwall	12.4	16.1	9.4	10.6
Turdale Water	9.9	16.8	7.1	11.2
Loch of Ustaness	10.6	14.9	9.2	10.6
Loch of Watlee	11.3	17.7	9.3	10.7
Whitelaw Loch	7.4	14.2	10.0	11.3

Only three readings of < 7.0 mg L^{-1} were observed, the remaining two occurring in Arthurs Loch (6.9 mg L^{-1}, 68.4%) and Gossa Water (6.7 mg L^{-1}, 66.4%) during August. Temperature was at its lowest recorded level of 7.4°C in Whitelaw Loch during the September sampling visit. Maximum temperature observed in 1991 was 17.7°C, which was measured in Arthurs Loch and Lochs of Kettlester and Watlee in July. Water temperature was generally highest in July, decreasing to lower levels in September. Exceptions were Strand Loch and Lochs of Brow and Whitelaw. Temperature remained approximately the same in July and August in Loch of Brow, whereas higher temperatures were recorded in August than July in Strand Loch and Loch of Whitelaw.

2.3.1.2 Light attenuation (Table 2.5)

Light penetration was greatest in Gorda Water and Loch of Snarravoe, which each had a mean LAC of 0.09. However, light penetration was poor in several of the lochs studied. On average, the LAC was > 3.00 in Mill Pond, Lochs of Strand, Brough (Yell) and Brow, Sand Water and Sandy Loch. Mill Pond was the darkest of these water bodies, with a mean LAC of 4.94. Intermediate between waters of relatively low and high light penetration were those with a mean LAC of between 1.00 and 2.00 *i.e.* Bu, Gossa and Turdale Water, Lochs of Ustaness and Kettlester.

2.3.1.3 pH (Table 2.6)

The highest recorded mean summer pH was 9.38 in Loch of Brow. Gorda Water was found to have the lowest mean summer pH of 5.49. All measurements of pH of Roer Water and Loch of Ustaness were also < 6.00. Although the pH of Mill Pond exceeded pH 6.00 during the 1991 study, mean summer pH in this water body was 5.83. Lochs in this study were mostly either between pH 6.00 and pH 7.00 or in the range pH 7.00 to pH 8.00. The more acid water bodies were Arthurs, Sandy and Whitelaw Lochs, Lochs of Brough (Bressay, Yell), Gonfirth and Kettlester, Bu, Eela, Lunga and Gossa Water. Lochs of Brindister and Huxter and Punds Water were all near neutral pH. Average water column pH values which were more alkaline in nature were those of Lochs of Cliff, Huesbreck, Snarravoe, Spiggie, Tingwall and Watlee, Helliers, Papil, Sand, Skutes and Turdale Water and Strand Loch. Strand Loch water had a great pH range of pH 7.00 in September to pH 8.06 in August.

Table 2.5 **Ranges of light attenuation coefficients and water colour determined in the surface waters of the 31 lochs of the 1991 survey**

Water body	Light attenuation coefficient			Water colour (absorbance at 400 nm)		
	min	max	mean	min	max	mean
Arthurs Loch	0.08	0.25	0.25	0.027	0.126	0.069
Bu Water	0.33	1.48	1.29	0.340	0.401	0.379
Loch of Brindister	0.16	1.17	0.90	0.185	0.198	0.191
Loch of Brough (Bressay)	0.06	0.36	0.19	0.045	0.099	0.068
Loch of Brough (Yell)	2.44	3.76	3.32	0.457	0.643	0.527
Loch of Brow	0.17	3.62	3.14	0.079	0.125	0.100
Loch of Cliff	0.06	0.60	0.33	0.106	0.186	0.135
Eela Water	0.15	0.69	0.41	0.153	0.180	0.164
Loch of Gonfirth	0.11	0.52	0.47	0.114	0.122	0.118
Gorda Water	0.07	0.14	0.09	0.014	0.040	0.027
Gossa Water	0.39	1.72	1.51	0.275	0.323	0.299
Helliers Water	0.07	0.24	0.16	0.030	0.066	0.046
Loch of Huesbreck	0.06	0.19	0.12	0.141	0.166	0.152
Loch of Huxter	0.19	0.30	0.26	0.228	0.280	0.246
Loch of Kettlester	0.53	1.29	1.06	0.272	0.417	0.330
Lunga Water	0.17	0.73	0.51	0.192	0.208	0.200
Mill Pond	1.78	5.33	4.94	0.434	0.887	0.610
Papil Water	0.10	0.47	0.26	0.044	0.079	0.056
Punds Water	0.11	0.30	0.29	*	*	*
Roer Water	0.10	0.13	0.11	0.048	0.118	0.080
Sand Water	0.35	3.45	3.09	0.300	0.578	0.459
Sandy Loch	2.76	3.54	3.27	0.490	0.530	0.506
Skutes Water	0.08	0.46	0.25	0.037	0.219	0.100
Loch of Snarravoe	0.08	0.09	0.09	0.052	0.056	0.054
Loch of Spiggie	0.11	0.57	0.38	0.057	0.064	0.060
Strand Loch	0.46	5.01	4.53	0.174	0.525	0.298
Loch of Tingwall	0.08	0.64	0.47	0.063	0.068	0.065
Turdale Water	0.71	2.42	1.97	0.201	0.620	0.355
Loch of Ustaness	0.12	1.28	1.01	0.105	0.110	0.108
Loch of Watlee	0.12	0.19	0.16	0.086	0.152	0.108
Whitelaw Loch	0.24	1.17	0.79	0.142	0.305	0.229

KEY: * missing data

Table 2.6 **Summer water column pH and conductivity in the lochs of the 1991 survey**

Water body	pH			Conductivity (μS cm^{-1})		
	min	max	mean	min	max	mean
Arthurs Loch	6.54	6.90	6.75	250	268	261
Bu Water	5.97	7.24	6.84	317	340	328
Loch of Brindister	6.40	7.27	7.00	200	246	225
Loch of Brough (Bressay)	6.39	6.62	6.48	307	429	357
Loch of Brough (Yell)	5.96	6.83	6.63	238	296	273
Loch of Brow	8.40	9.80	9.38	441	463	449
Loch of Cliff	7.29	7.41	7.37	324	349	334
Eela Water	6.13	6.56	6.41	194	206	199
Loch of Gonfirth	6.20	6.52	6.34	167	274	205
Gossa Water	6.35	6.71	6.51	259	266	263
Gorda Water	5.09	5.82	5.49	418	455	438
Helliers Water	6.78	7.44	7.30	269	319	290
Loch of Huesbreck	7.70	7.88	7.81	563	695	633
Loch of Huxter	6.30	7.48	7.07	298	331	317
Loch of Kettlester	6.48	6.65	6.56	241	269	259
Lunga Water	6.20	6.38	6.27	221	228	225
Mill Pond	5.51	6.11	5.83	347	397	366
Papil Water	7.34	7.55	7.35	342	369	353
Punds Water	6.56	7.06	6.93	246	259	251
Roer Water	5.57	5.79	5.69	164	181	175
Sand Water	6.88	7.23	7.11	151	242	205
Sandy Loch	6.25	6.90	6.77	241	255	248
Skutes Water	7.26	7.90	7.61	316	403	368
Loch of Snarravoe	7.15	7.61	7.48	364	396	379
Loch of Spiggie	7.44	7.94	7.72	569	617	594
Strand Loch	7.00	8.06	7.80	256	17410	10795
Loch of Tingwall	7.11	7.86	7.72	328	380	355
Turdale Water	7.18	7.97	7.69	257	318	295
Loch of Ustaness	5.64	5.67	5.65	227	252	242
Loch of Watlee	7.53	7.64	7.59	335	376	352
Whitelaw Loch	6.22	6.59	6.38	176	195	188

The smallest variation in pH values was observed in Loch of Ustaness, the range being from pH 5.64 in July to pH 5.67 in August.

2.3.1.4 Conductivity (Table 2.6)

Mean summer conductivity in Shetland lochs ranged from 175 μS cm^{-1} in Roer Water to 10795 μS cm^{-1} in Strand Loch. Conductivity in Whitelaw Loch and Eela Water was < 200 μS cm^{-1}. The majority of water bodies studied had conductivity values of between 200 μS cm^{-1} and 300 μS cm^{-1}. In this category were Arthurs and Sandy Lochs, Lochs of Brindister, Brough (Yell), Gonfirth, Ustaness and Kettlester and Gossa, Helliers, Lunga, Punds, Sand, and Turdale Water. With higher conductivity of between 300 μS cm^{-1} and 400 μS cm^{-1} were Lochs of Brough (Bressay), Cliff, Huxter, Snarravoe, Tingwall and Watlee, Mill Pond, Skutes and Bu Water. Conductivity was observed between 400 μS cm^{-1} and 500 μS cm^{-1} in Loch of Brow and Gorda Water. The highest conductivities measured, with the exception of Strand Loch, were 594 μS cm^{-1} in Loch of Spiggie and 633 μS cm^{-1} in Loch of Huesbreck. Variation in conductivity occurred throughout the summer, those with the greatest changes in conductivity being Lochs of Brough (Bressay) ($\pm$30.0), Gonfirth ($\pm$28.1) and Huesbreck ($\pm$108.5), Sand ($\pm$22.5) and Skutes Water ($\pm$21.6) and Strand Loch ($\pm$4349.0).

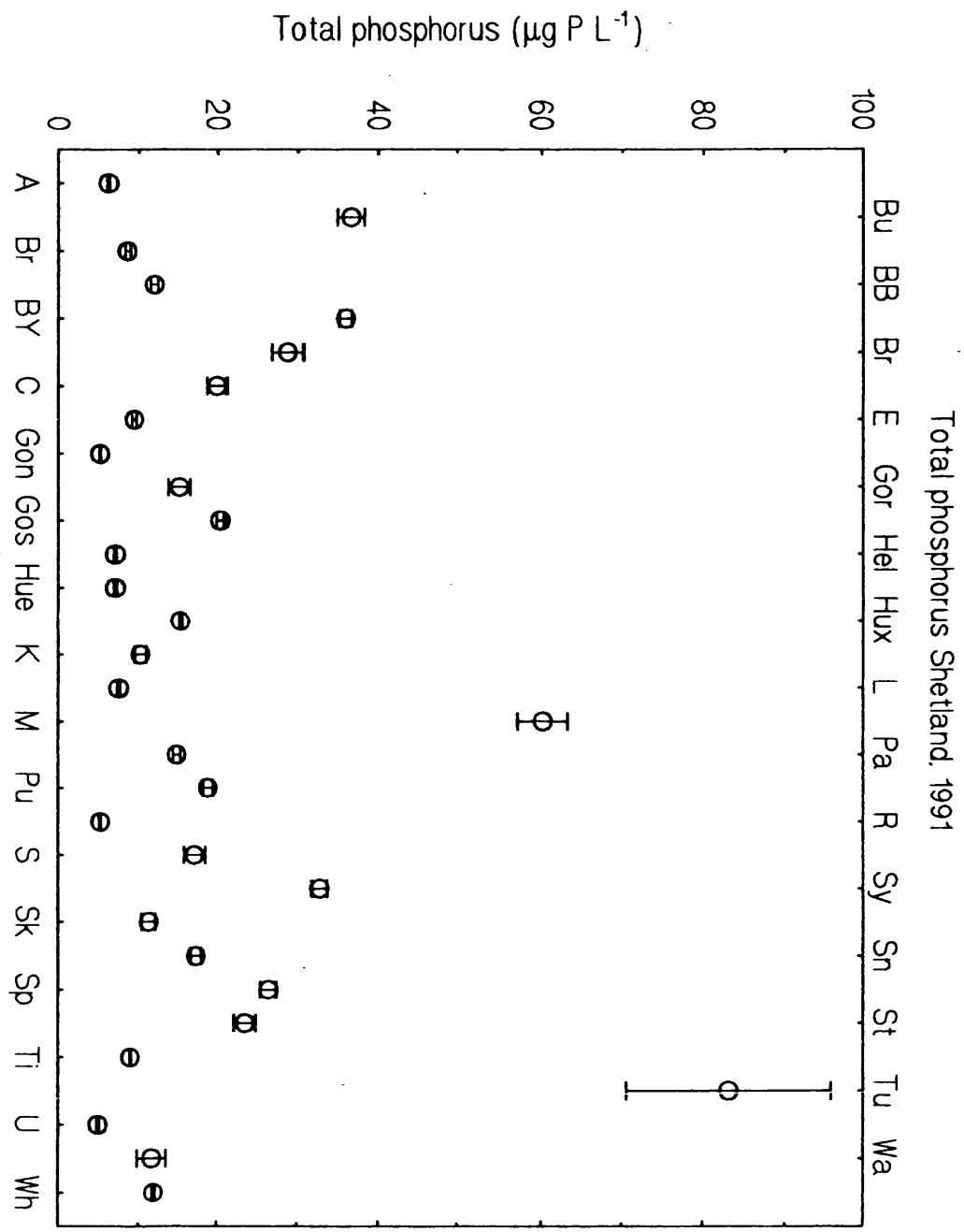
2.3.1.5.1 Total phosphorus (Figure 2.1)

Ten of the lochs in this study exhibited mean summer TP concentrations of < 10 μg P L^{-1}. There was very little variation throughout the summer in water TP concentrations in these low TP lochs, which comprised Arthurs Loch, Lochs of Brindister, Gonfirth, Huesbreck, Tingwall and Ustaness, Eela, Helliers, Roer and Lunga Water. Of these water bodies, Loch of Ustaness was most TP poor, having an average concentration of 5.0 μg P L^{-1}. Loch of Gonfirth TP concentration varied least between sampling dates (mean: 5.2 μg P L^{-1} $\pm$0.16). Other lochs in which TP concentration varied little were Loch of Huxter, Whitelaw Loch and Eela Water, although TP concentrations were higher in Lochs of Huxter and Whitelaw than those lochs above. Greatest mean summer water TP concentration was determined for Turdale Water (mean: 83.2 μg P L^{-1} $\pm$25.2), which also had the most variation in its TP concentration.

KEY TO FIGURES 2.1-2.8:

Loch name	Loch Code
Arthurs Loch	A
Bu Water	Bu
Eela Water	E
Gorda Water	Gor
Gossa Water	Gos
Helliers Water	Hel
Loch of Huxter	Hux
Loch of Brow	Br
Loch of Gonfirth	Gon
Loch of Snarravoe	Sn
Loch of Spiggie	Sp
Loch of Cliff	C
Loch of Brough (Bressay)	BB
Loch of Huesbreck	Hue
Loch of Brough (Yell)	BY
Loch of Kettlester	K
Loch of Watlee	Wa
Loch of Brindister	Bri
Loch of Ustaness	U
Loch of Tingwall	Ti
Lunga Water	L
Mill Pond	M
Papil Water	Pa
Punds Water	Pu
Roer Water	R
Sand Water	S
Sandy Loch	Sy
Skutes Water	Sk
Strand Loch	St
Turdale Water	Tu
Whitelaw Loch	Wh

Figure 2.1 Mean summer total phosphorus levels in the thirty one Shetland lochs studied in 1991 (n=3)



Sandy Loch, Mill Pond, Bu Water, Lochs of Brow and Brough (Yell), all exhibited sufficient variation between sampling visits that the standard errors of the mean TP concentrations coincided with those of Turdale Water, thus indicating the high TP levels in these water bodies.

2.3.1.5.2 Total dissolved phosphorus (Figure 2.2)

Though present at lower concentrations, TDP levels followed a similar pattern to TP concentrations. Generally, less variation of water TDP concentrations was evident between sampling dates than had been in TP levels, although Turdale Water (mean: 59.2 μg P L^{-1} $\pm$26.5), Strand Loch (mean: 11.8 μg P L^{-1} $\pm$3.0) and Mill Pond (mean: 30.8 μg P L^{-1} $\pm$3.5) exhibited high deviations from their mean values. Average summer water TDP concentration was greatest in Turdale Water, followed by Mill Pond and Sandy Loch (mean: 30.3 μg P L^{-1} $\pm$0.5), whilst Bu Water, Lochs of Brough (Yell) and Brow also had elevated levels of TDP in comparison to the remaining study sites. The lowest level of TDP was determined in Loch of Ustaness, which had both the smallest summer average TDP concentration of 2.8 μg P L^{-1} and the minimum individual TDP concentration for one sampling date of 1.5 μg P L^{-1}. Seven other lochs contained $<$ 5 μg P L^{-1} on average, these water bodies being Arthurs Loch, Lochs of Brindister, Gonfirth, Huesbreck and Watlee, Roer and Helliers Water.

2.3.1.5.3 Dissolved reactive phosphorus (Table 2.7)

Generally, the concentration of DRP in the lochs studied was $<$ 1 μg P L^{-1}. There were few exceptions. In July, Eela and Gorda Water, Loch of Snarravoe and Whitelaw Loch had DRP levels of 1.3 μg P L^{-1}, 2.9 μg P L^{-1}, 4.1 μg P L^{-1} and 2.4 μg P L^{-1} respectively. During September, DRP was again detected in Loch of Snarravoe at 1.3 μg P L^{-1}. In Turdale Water, DRP levels ranged from $<$ 1 μg P L^{-1} in July, to 90.8 μg P L^{-1} in September.

2.3.1.6.1 Total oxidised nitrogen (Table 2.8)

The highest mean water column TON concentration in 1991 was 254 μg N L^{-1} for Loch of Gonfirth. Three other water bodies had mean TON of $>$ 100 μg N L^{-1}. These were Roer Water, Sandy Loch and Loch of Ustaness which had average water TON levels of 139 μg N L^{-1}, 129 μg N L^{-1} and 144 μg N L^{-1} respectively.

Figure 2.2 Mean summer total dissolved phosphorus levels in the thirty one Shetland lochs studied in 1991 (n=3)

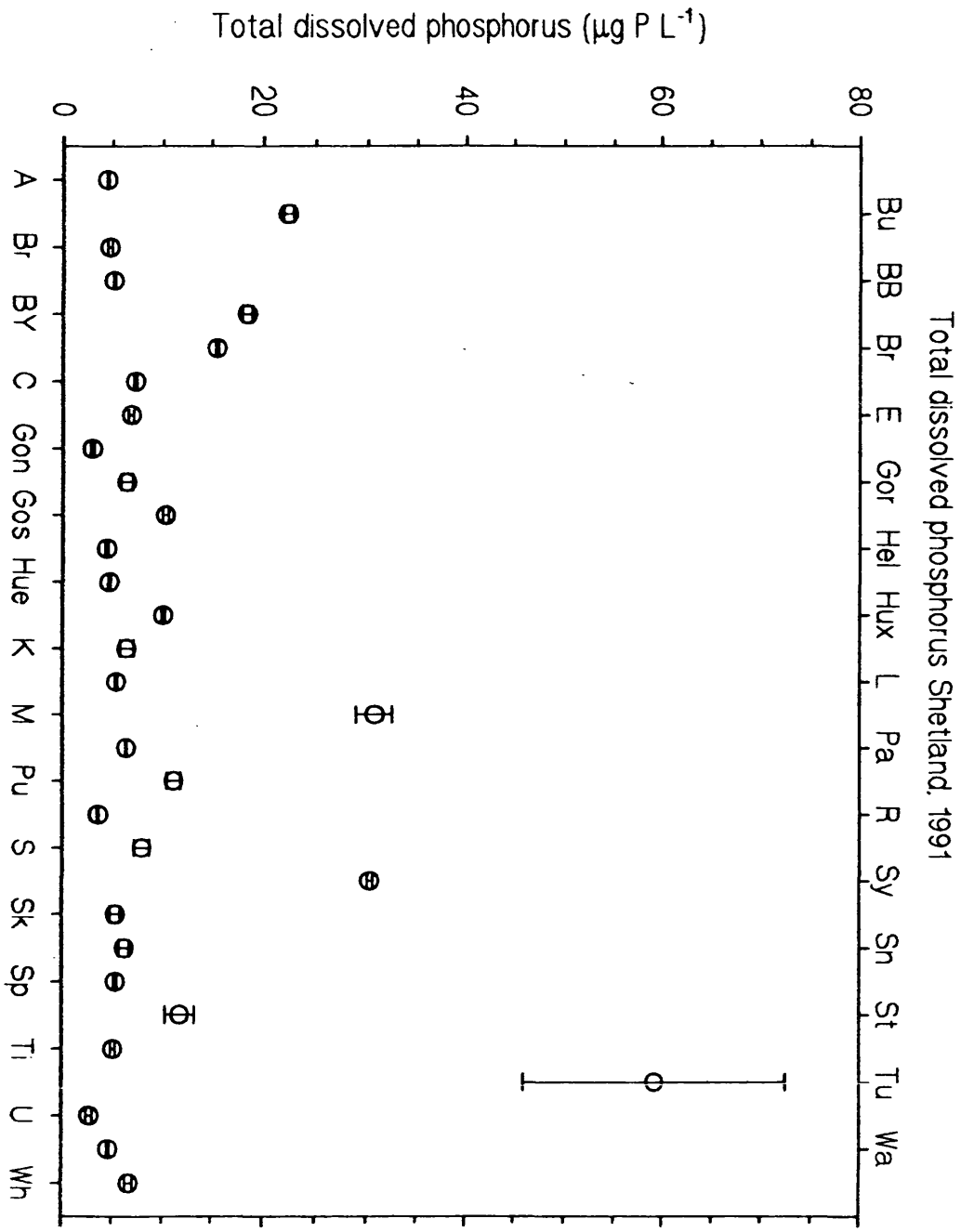


Table 2.7 Range of dissolved reactive phosphorus concentrations present in the thirty one lochs studied in summer 1991 (n=3)

Site	Range (in μg P L^{-1})
Arthurs Loch	all <1.0
Bu Water	<1.0-2.9
Loch of Brindister	all <1.0
Loch of Brough (Bressay)	all <1.0
Loch of Brough (Yell)	all <1.0
Loch of Brow	all <1.0
Loch of Cliff	all <1.0
Eela Water	<1.0-1.3
Loch of Gonfirth	all <1.0
Gorda Water	<1.0-2.9
Gossa Water	all <1.0
Helliers Water	all <1.0
Loch of Huesbreck	all <1.0
Loch of Huxter	all <1.0
Loch of Kettlester	all <1.0
Lunga Water	all <1.0
Mill Pond	all <1.0
Papil Water	all <1.0
Punds Water	all <1.0
Roer Water	all <1.0
Sand Water	all <1.0
Sandy Loch	all <1.0
Skutes Water	all <1.0
Loch of Snarravoe	<1.0-4.1
Loch of Spiggie	all <1.0
Strand Loch	all <1.0
Loch of Tingwall	all <1.0
Turdale Water	<1.0-90.8
Loch of Ustaness	all <1.0
Loch of Watlee	all <1.0
Whitelaw Loch	<1.0-2.4

Note: limit of detection 1.0 μg P L^{-1})

Table 2.8 **Range of total organic nitrogen concentrations present in the thirty one lochs studied in summer 1991 (n=3)**

Site	Range (in $\mu g\ N\ L^{-1}$)
Arthurs Loch	<5-11
Bu Water	all <5
Loch of Brindister	80-85
Loch of Brough (Bressay)	all <5
Loch of Brough (Yell)	<5-51
Loch of Brow	all <5
Loch of Cliff	7-13
Eela Water	58-74
Loch of Gonfirth	249-258
Gorda Water	all <5
Gossa Water	<5-17
Helliers Water	all <5
Loch of Huesbreck	<5-40
Loch of Huxter	<5-11
Loch of Kettlester	<5-82
Lunga Water	82-116
Mill Pond	13-161
Papil Water	<5-7
Punds Water	18-20
Roer Water	111-169
Sand Water	<5-18
Sandy Loch	114-159
Skutes Water	all <5
Loch of Snarravoe	<15-10
Loch of Spiggie	all <5
Strand Loch	40-87
Loch of Tingwall	<5-13
Turdale Water	<5-42
Loch of Ustaness	134-154
Loch of Watlee	<5-13
Whitelaw Loch	<5-9

Note: limit of detection 5.0 $\mu g\ N\ L^{-1}$

TON levels in Loch of Brindister, Eela and Lunga Water and Strand Loch were greater than those of the remaining lochs with the exceptions of Turdale Water, Loch of Kettlester and Mill Pond, each of which exhibited high variability in TON concentration between sampling trips. The majority of water bodies in the 1991 study were low in TON with twenty two lochs having an average TON concentration of < 20 μg N L^{-1}. The lowest mean TON levels occurred in the following waters which had mean summer TON concentrations of < 5 μg N L^{-1}: Lochs of Brough (Bressay), Brow, Snarravoe and Spiggie, Bu, Gorda, Helliers, Papil and Skutes Water.

2.3.1.6.2 Total ammoniacal nitrogen (Figure 2.3)

Generally, there was a high degree of variation in TAN concentrations in individual lochs between sampling dates. Greatest mean summer TAN concentration was in Mill Pond (Mean 103.0 ±55.7), followed by Turdale Water (Mean 101.0 ±32.7). Several water bodies had mean TAN levels which were 20-40 μg N L^{-1} *i.e.* were intermediate in comparison with values for other lochs in the study. Loch of Brough (Yell) and Punds Water exhibited average values of 63.0 μg N L^{-1} ±0.9 and 55.7 μg N L^{-1} ±2.4, respectively, with little variation around the mean. Lochs of Brough (Bressay), Brow, Huxter and Spiggie, Gorda, Gossa and Sand Water, Sandy and Strand Lochs and Mill Pond also had intermediate mean TAN concentrations, but high variability over the summer. Lowest mean summer TAN concentrations found for waters in the study were for Arthurs Loch (16.0 μg N L^{-1} ±0.9), Loch of Ustaness (13.7 μg N L^{-1} ±2.0) and Roer Water (13.3 μg N L^{-1} ±1.1), with little variation occurring through the summer.

2.3.1.7.1 Calcium (Figure 2.4)

The highest mean Ca concentration (196.8 mg Ca L^{-1} ±152.1) was calculated for Strand Loch. The highest mean recorded for a water body which did not have a direct sea water input was 68.5 mg Ca L^{-1} ±9.4 for Loch of Huesbreck. Lochs of Tingwall, Brow and Spiggie and Turdale Water all had mean Ca concentrations which were elevated compared to the remaining lochs, with the exception of Sand Water which showed relatively high variability in its summer Ca concentration range. Twenty four of the lochs studied had mean Ca concentrations of < 10 mg Ca L^{-1}, lowest average Ca levels being recorded in Loch of Ustaness and Whitelaw Loch, both of which had mean Ca concentrations of 2.6 mg Ca L^{-1}.

Figure 2.3 Mean summer total ammonical nitrogen levels in the thirty one Shetland lochs studied in 1991 (n=3)

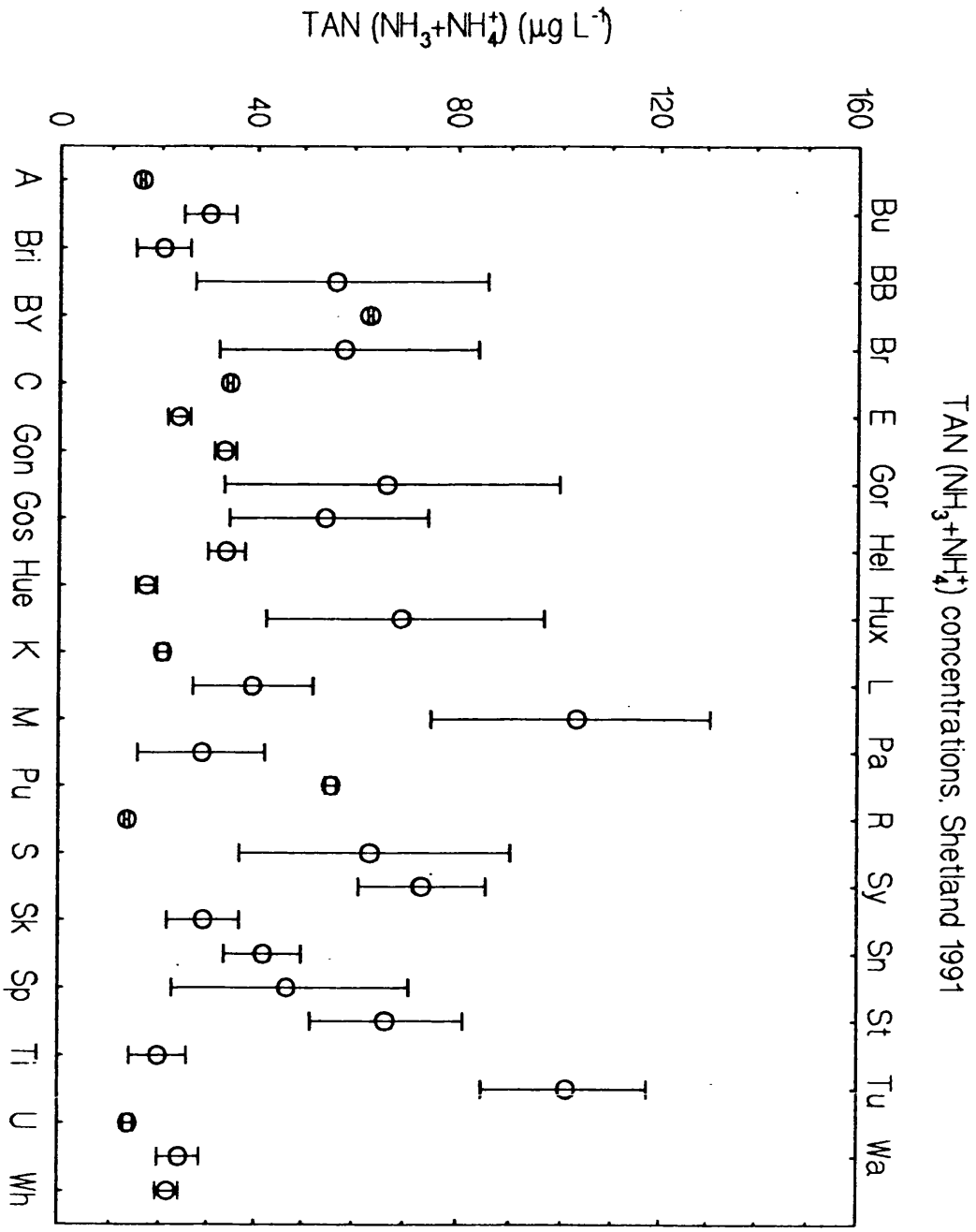
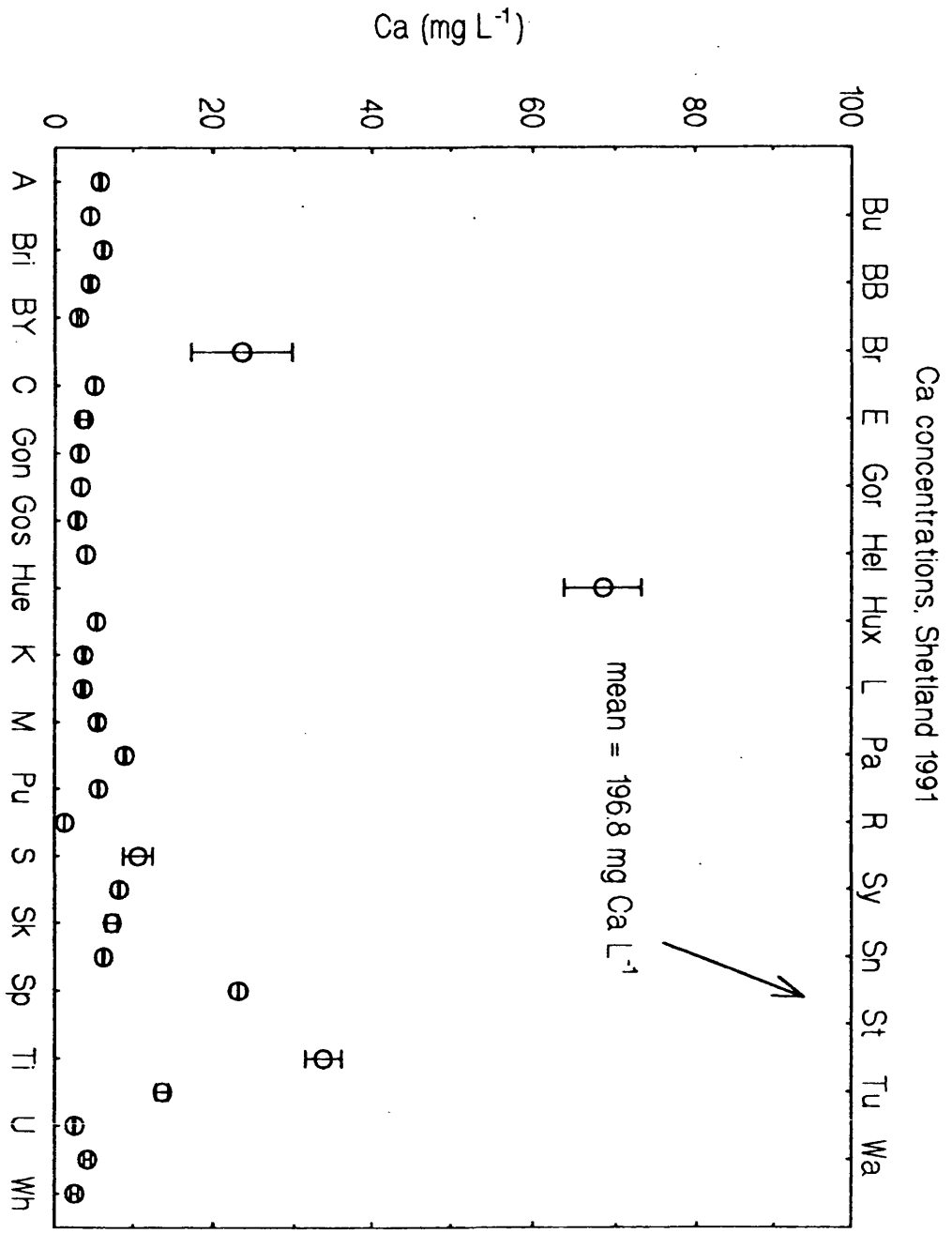


Figure 2.4 Mean summer calcium levels in the thirty one Shetland lochs studied in 1991 (n=3)



2.3.1.7.2 Magnesium (Figure 2.5)

The highest mean Mg concentration for summer 1991 was 177 mg Mg L^{-1} ±252.1 for Strand Loch. There was much variation in Mg content of this water body between July and September. Of the remaining lochs which had no direct sea water input, Loch of Watlee had the highest mean water Mg concentration of 20.3 mg Mg L^{-1}. Lochs of Brow, Cliff, Huesbreck, Snarravoe and Spiggie, Helliers and Skutes Water, all exhibited average water Mg levels of > 10 mg Mg L^{-1}. Minimum average summer water Mg concentration was 3.1 mg Mg L^{-1} for Loch of Gonfirth, the following lochs also having mean Mg levels of ≤ 5.0 mg Mg L^{-1}: Arthurs and Whitelaw Lochs, Lochs of Brindister and Ustaness, Eela, Roer and Sand Water.

2.3.1.7.3 Sodium (Figure 2.6)

Lochs of Brow, Huesbreck and Spiggie, Gorda Water and Mill Pond exhibited mean summer Na concentrations which were > 40 mg Na L^{-1}, although Na levels in Mill Pond fell below this level in September. Maximum average Na concentration was 52.8 mg Na L^{-1} for Loch of Spiggie. Five lochs were observed to have average Na concentrations of < 30 mg Na L^{-1}. These water bodies were Eela, Roer and Sand Water, Whitelaw Loch and Loch of Gonfirth. Minimum calculated mean summer Na concentration was 23.8 mg Na L^{-1} for Sand Water.

2.3.1.7.4 Potassium (Figure 2.7)

The following five lochs had mean summer K concentrations of ≥ 2.0 mg K L^{-1}: Bu, Gorda and Turdale Water, Mill Pond and Loch of Spiggie. The latter exhibited the maximum average water K level of 3.2 mg K L^{-1}. Variation in K levels in Bu Water and Mill Pond was such that the range of concentrations through the summer in these lochs coincided with levels in water bodies with lower mean summer K concentrations *e.g.* Lochs of Huesbreck, Huxter and Tingwall. Four lochs in the study had mean summer K concentrations of ≤ 1.0 mg K L^{-1}. These water bodies comprised Loch of Gonfirth (0.9 mg K L^{-1}), Whitelaw Loch (1.0 mg K L^{-1}), Roer (0.9 mg K L^{-1}) and Sand Water (1.0 mg K L^{-1}).

Figure 2.5 Mean summer magnesium levels in the thirty one Shetland lochs studied in 1991 (n=3)

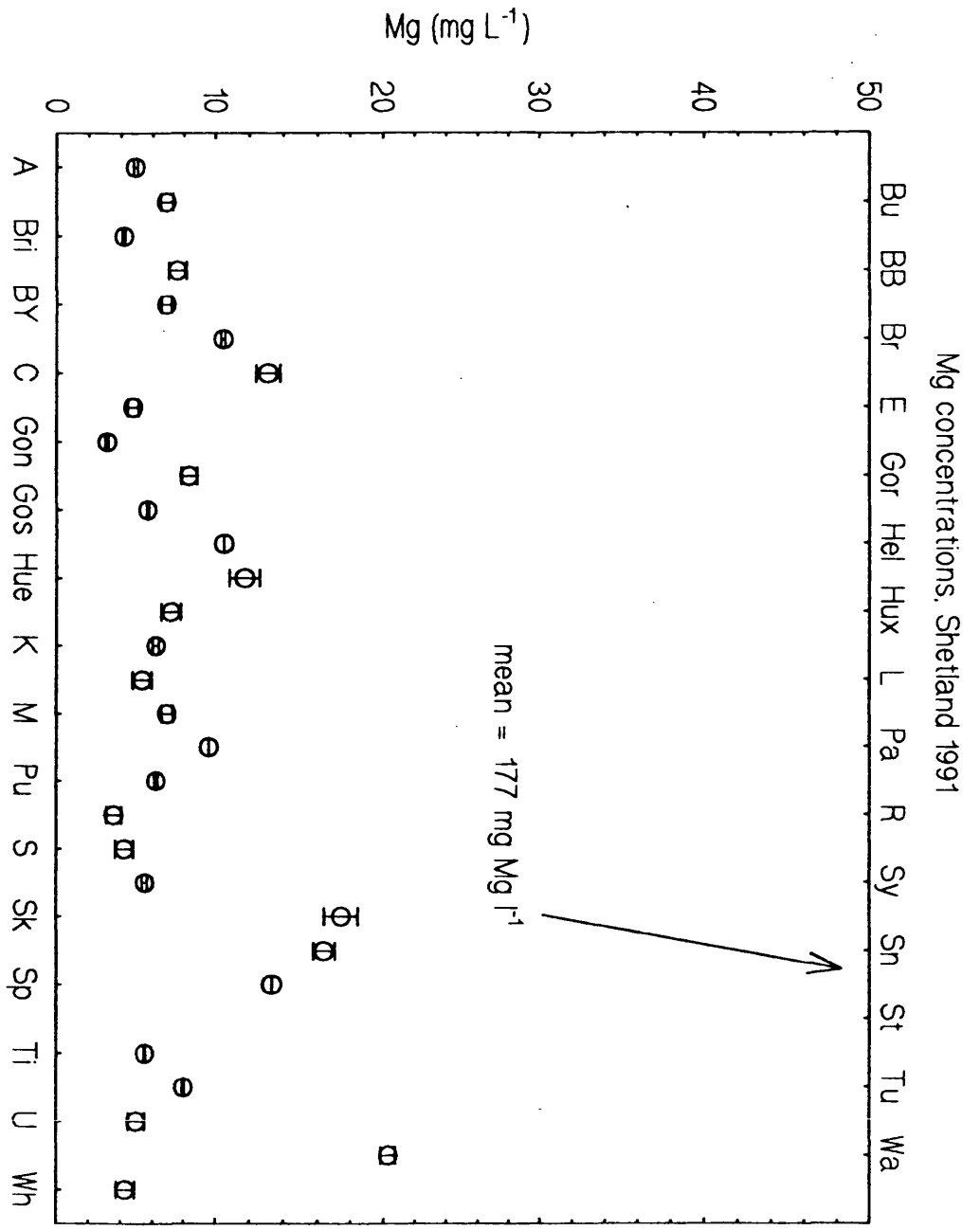


Figure 2.6 Mean summer sodium levels in the thirty one Shetland lochs studied in 1991 (n=3)

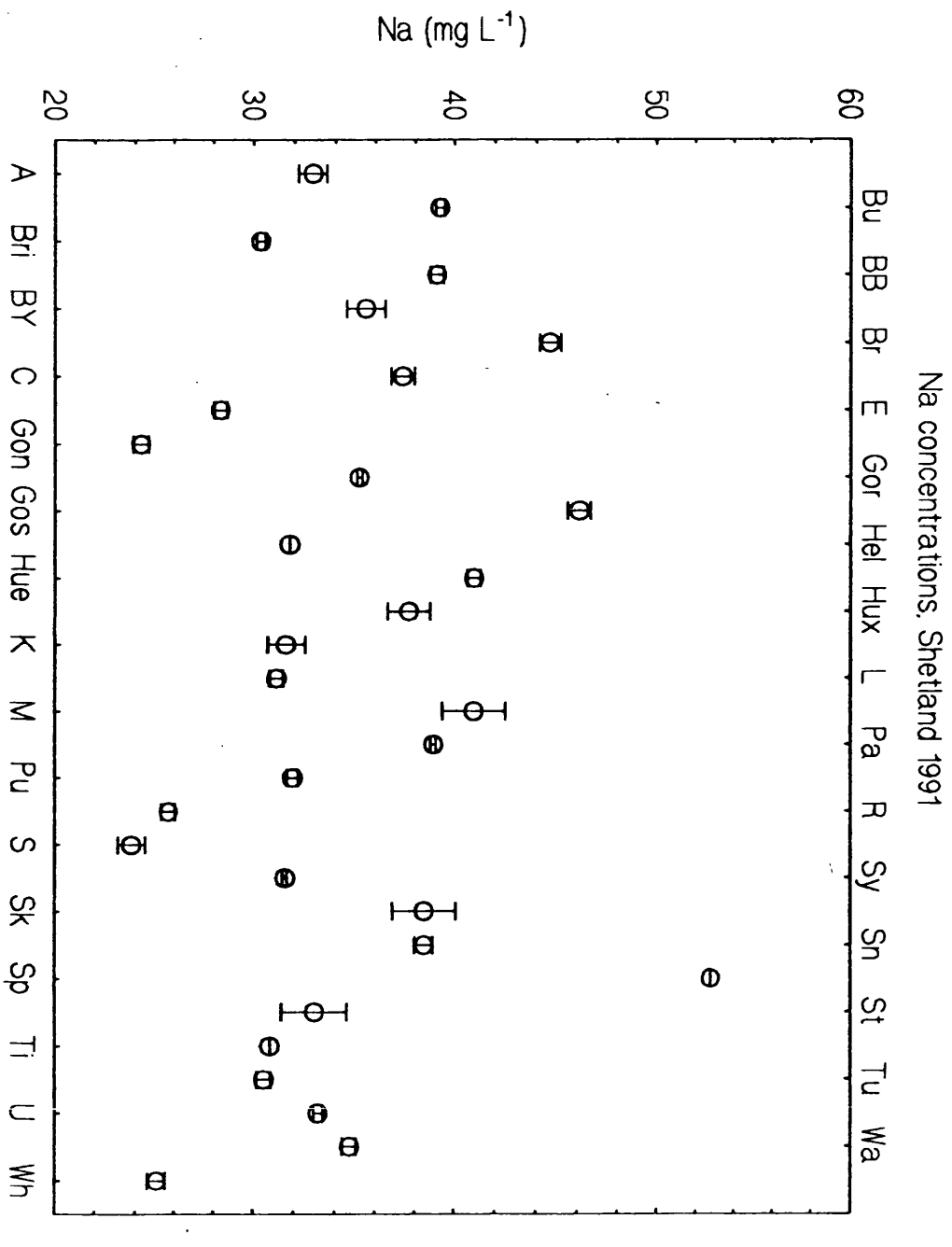
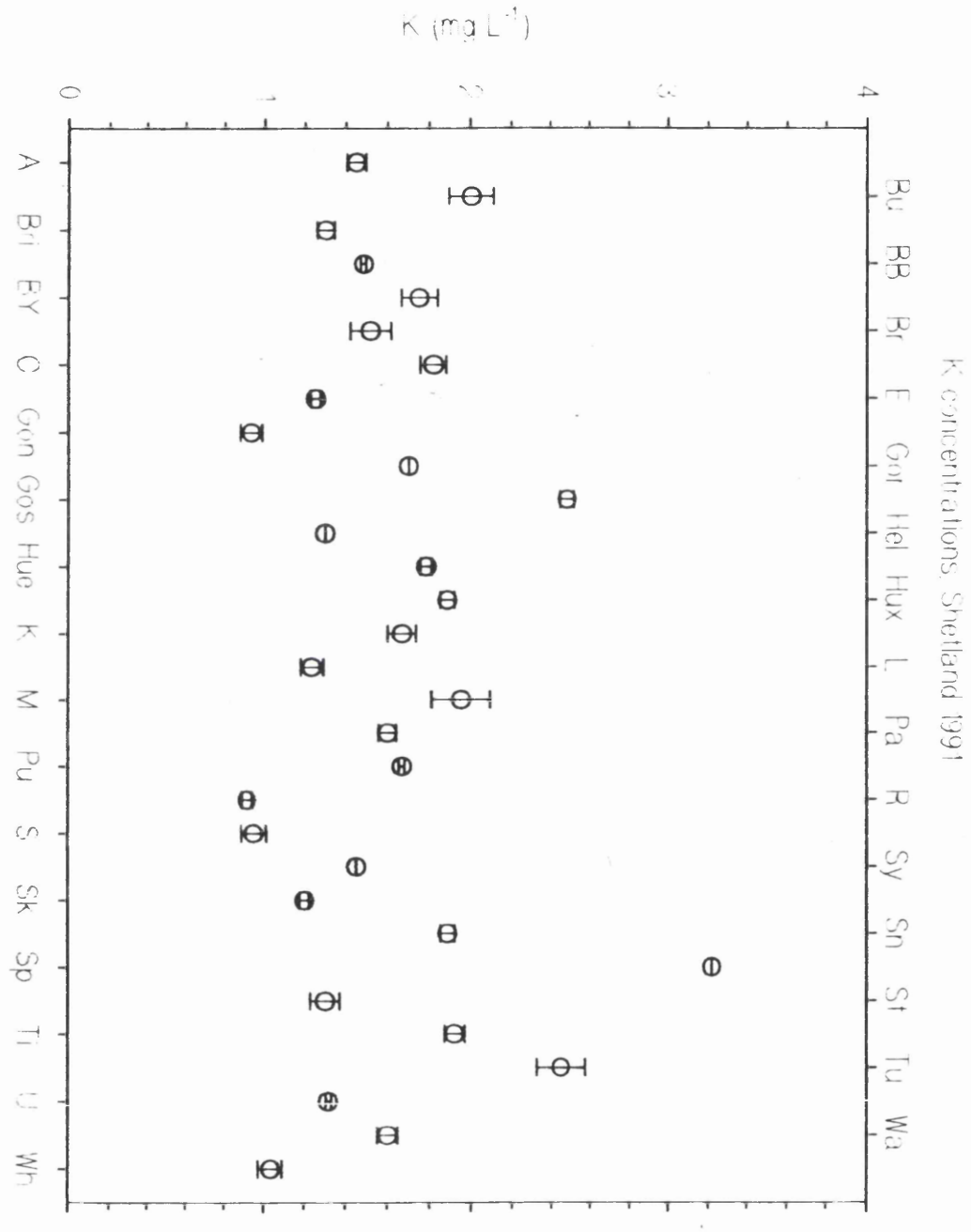


Figure 2.7 Mean summer potassium levels in the thirty one Shetland lochs studied in 1991 (n=3)



2.3.1.8 Colour (Table 2.5)

Water colour at 400nm ranged from 0.014 in Gorda Water to 0.887 in Mill Pond. Other lochs which exhibited at least one colour reading of <0.100 were Arthur's Loch, Helliers, Papil, Roer and Skutes Water, Lochs of Brough (Bressay), Snarravoe, Spiggie, Tingwall and Watlee. Water colour of >0.400 was observed in several water bodies: Lochs of Brough (Yell) and Kettlester, Bu, Turdale and Sand Water, Strand and Sandy Lochs and Mill Pond.

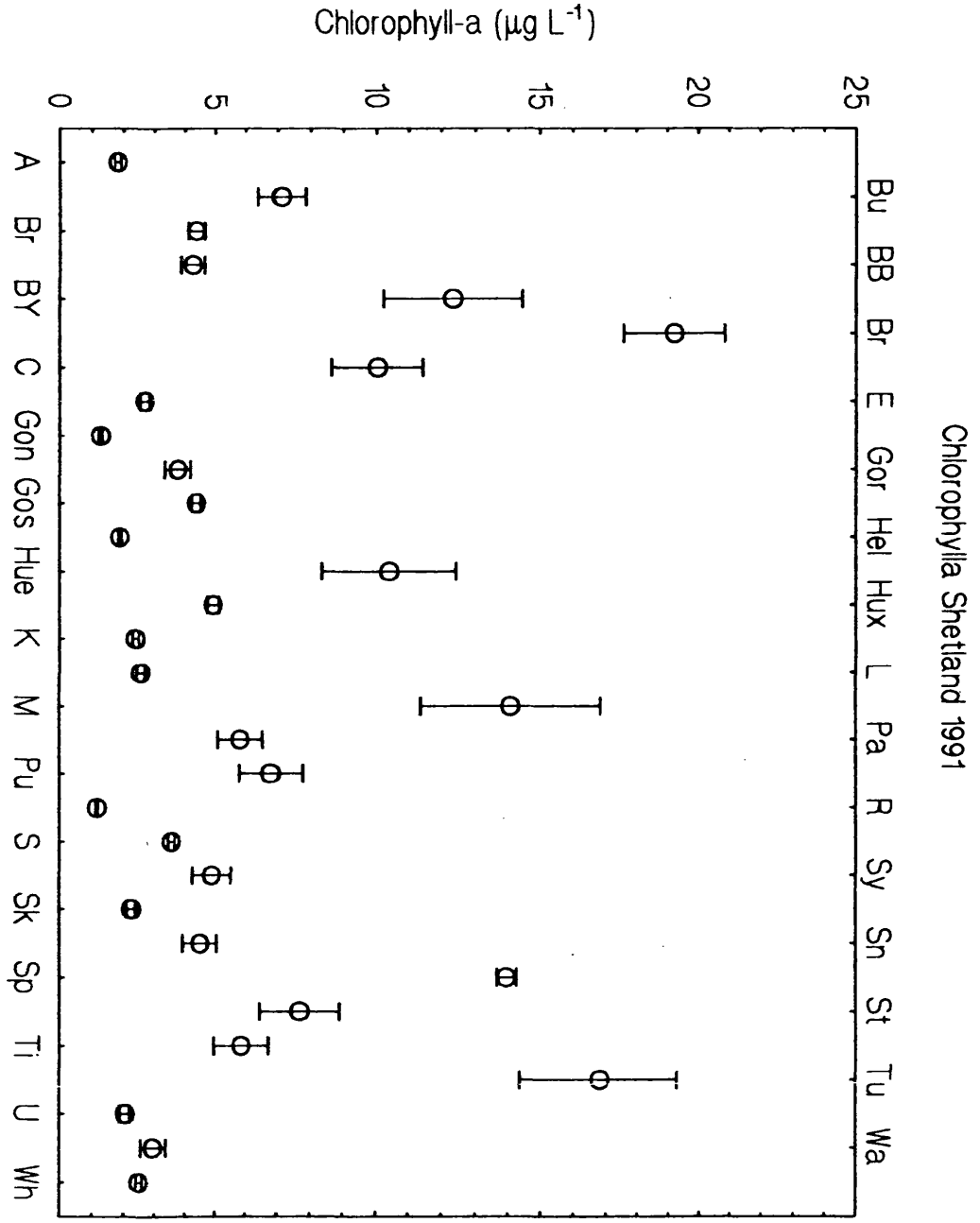
2.3.1.9 Chlorophyll *a* (Figure 2.8)

Lochs with higher mean summer chl *a* levels tended to exhibit greater variability in chl *a* concentrations through the summer than those which were observed to have low levels. Although seven lochs had mean chl *a* concentrations of > 8 μg chl *a* L^{-1}, only those of Lochs of Spiggie and Brow resulted from determinations of chl *a* which all exceeded this level. Chl *a* concentration in the other water bodies of Lochs of Brough (Yell), Huesbreck and Cliff, Turdale Water and Mill Pond was < 8 μg chl *a* L^{-1} during at least one sampling trip. The highest mean water chl *a* concentration was 19.2 μg chl *a* L^{-1} for Loch of Brow. Second to this was 16.8 μg chl *a* L^{-1} for Turdale Water. Lochs with intermediate average levels of chl *a* (2.5-8.0 μg chl *a* L^{-1}), but which were recorded as being variable in chl *a* concentration between July and September were Strand and Sandy Lochs, Papil, Punds and Bu Water and Loch of Tingwall. Minimum average chl *a* concentration was 1.2 μg chl *a* L^{-1}, observed in Roer Water. Arthurs Loch, Loch of Gonfirth and Helliers Water also had mean chl *a* levels of < 2.0 μg chl *a* L^{-1}.

2.3.2 Water chemistry and physical characteristics of the five Shetland lochs studied in 1992 and 1993

The following water bodies were selected for further study as they represented a range of water column conditions: Loch of Gonfirth, Helliers Water, Loch of Tingwall, Sandy Loch, Turdale Water.

Figure 2.8 Mean summer chlorophyll *a* levels in the thirty one Shetland lochs studied in 1991 (n=3)



2.3.2.1 Bathymetry of the five study lochs of 1992 and 1993

Figures 2.9 and 2.10 present maps of the bathymetry of the five study lochs of 1992 and 1993. Table 2.9 shows characteristics of the five study lochs. The shallowest water body was Turdale Water, which was of relatively uniform depth, having a mean depth of 0.9 m. This basin also had the lowest volume of water (58,951 m^3). Helliers Water had the smallest catchment and loch surface area, but had a maximum depth of 2.3 m. The combined volume of the two basins of Loch of Tingwall accounted for the highest volume of water of the five lochs (1,971,770 m^3). Loch of Gonfirth was the deepest water body, mean and maximum depths being 7.8 and 25.5 m respectively. Despite the depth of Loch of Gonfirth, the surface area of Sandy Loch (41.4 ha) meant that the latter was of greater volume.

2.3.2.2 Dissolved oxygen and temperature profiles in the five study lochs during 1992 and 1993

Generally, there was little or no difference in temperature and DO from surface to deep water at the sites. No evidence for stratification was observed in Helliers Water, Turdale Water or Sandy Loch. Profiles exhibiting greatest changes in DO concentration and temperature with depth are presented in Tables 2.10 and 2.11. Owing to instrument malfunction, no readings of DO are available for the August 1992 field visit to Loch of Tingwall. However, temperature remained constant throughout the water column. Greatest changes in temperature and DO concentration in the water column of Loch of Tingwall were noted in July 1993. At Site 1, DO and temperature decreased by only 0.72 mg DO L^{-1} and 0.4°C respectively. DO was supersaturated at all depths. However, between surface and 20 m depth at Site 2, DO was diminished by 4.05 mg DO L^{-1} and temperature decreased by 2.2°C. DO saturation decreased from 115% at surface, to 715 in deep water. Greatest change in temperature and dissolved oxygen occurred between 13 m and 15 m depth (Table 2.10). In Loch of Gonfirth during June 1992 and July 1993, a discontinuity was noted in DO concentration between 13 m and 15 m depth. Temperature change from surface to 20 m depth was 1°C in June 1992 and 1.4°C in July 1993. Diminution of DO concentration from surface to 20 m depth was 2.03 mg DO L^{-1} (21%) in June 1992 and 1.08 mg DO L^{-1} (13%) during July 1993 (Table 2.11).

Figure 2.9 Bathymetric maps of Loch of Gonfirth, Helliers and Turdale Water (depths in metres)

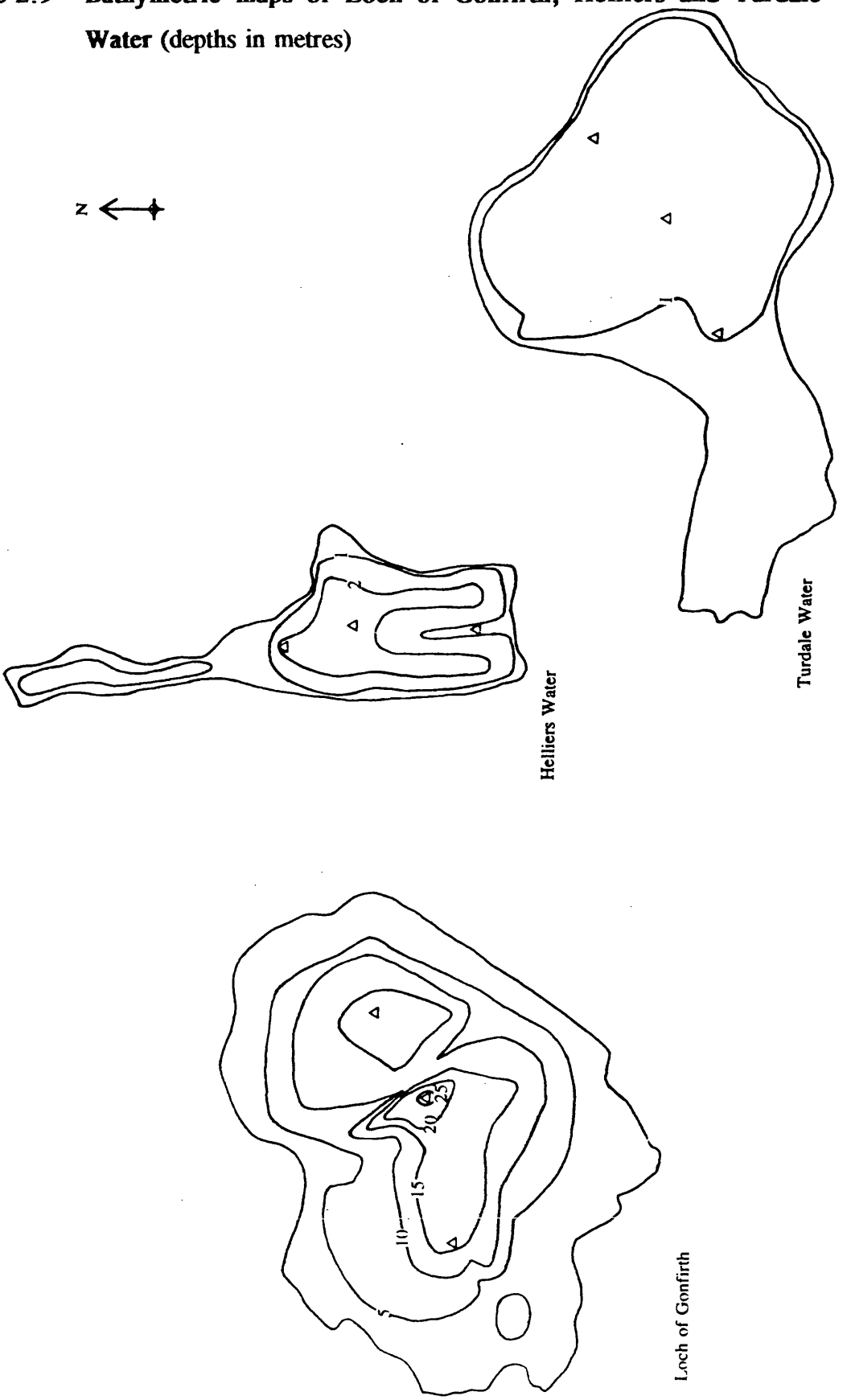


Figure 2.10 Bathymetric maps of Loch of Tingwall and Sandy Loch
(depths in metres)

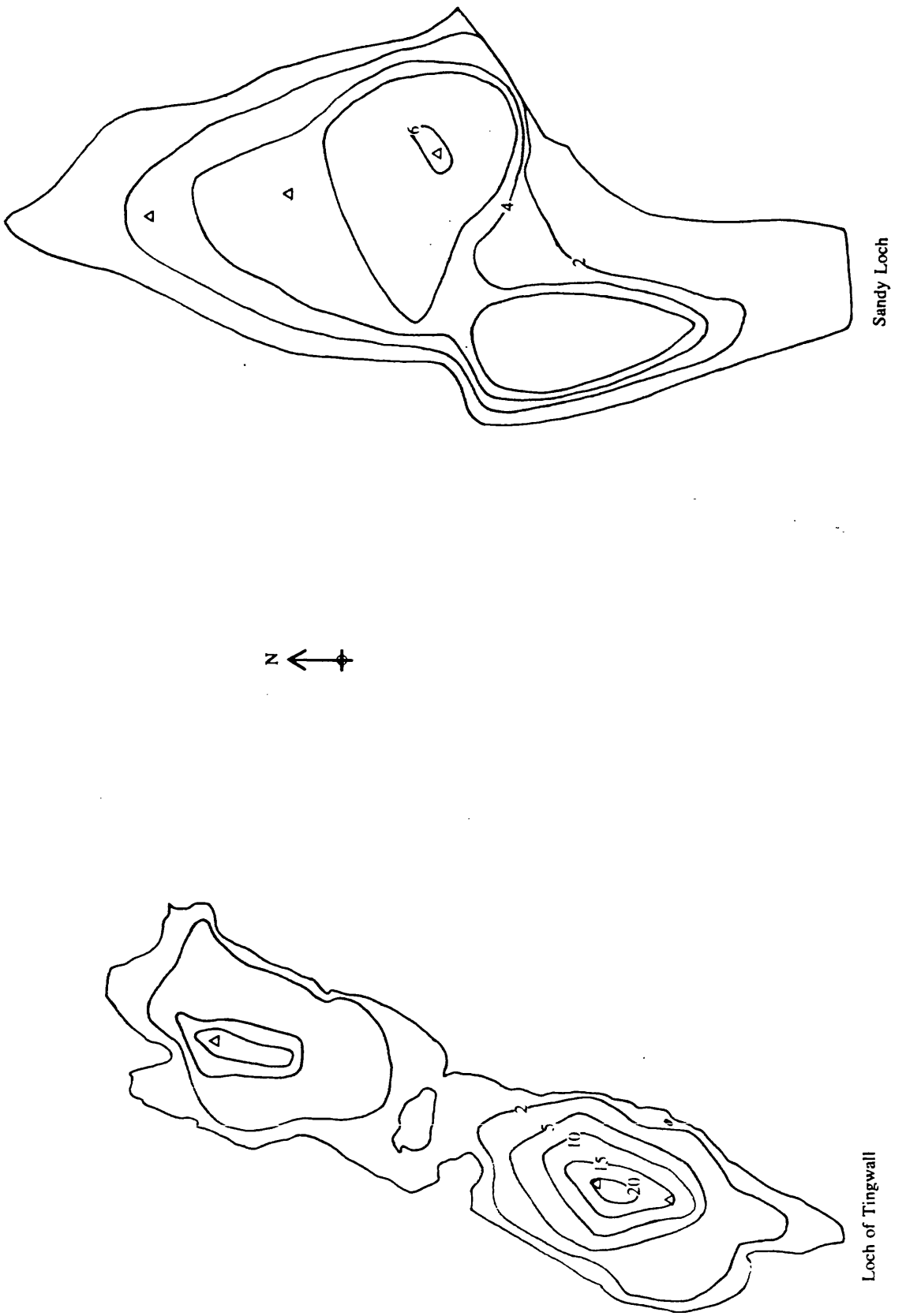


Table 2.9 Physical characteristics of the five lochs studied in 1992 and 1993

Water body	Catchment area (ha)	Loch surface area (ha)	Loch volume (m^3)	Max depth (m)	Mean depth (m)
Helliers Water	40.8	4.4	61,092	2.3	1.4
Loch of Gonfirth	63.6	14.6	1,131,100	25.5	7.8
Loch of Tingwall	309.6	46.3	1,971,770	22.5	4.3
Sandy Loch	287.3	41.4	1,503,058	7.9	3.6
Turdale Water	92.7	6.4	58,951	1.5	0.9

Table 2.10 **Temperature and dissolved oxygen concentration profiles exhibiting incomplete mixing of the water column of Loch of Tingwall (26/07/93)**

Site	Depth (m)	Temperature (°C)	Dissolved oxygen (mg O_2 L^{-1})	(% saturation)
1 (North Basin)	0	14.2	11.38	111.1
	1	14.3	11.42	111.7
	2	14.4	11.49	112.6
	3	14.2	11.42	111.5
	4	14.0	11.32	110.0
	5	14.0	11.12	108.1
	7	13.9	11.04	107.1
	9	13.8	10.87	105.1
	10	13.8	10.66	103.1
2 (South Basin)	0	14.8	11.59	114.6
	1	14.6	11.67	115.0
	2	14.4	11.50	112.7
	3	14.1	11.42	111.2
	4	14.0	11.35	110.3
	5	13.9	11.38	110.4
	7	13.8	11.18	108.1
	9	13.7	11.02	106.4
	11	13.5	10.86	104.4
	13	13.2	10.01	95.6
	15	12.8	9.11	86.2
	17	12.6	8.46	79.7
	19	12.5	7.71	72.5
	20	12.6	7.54	71.0

Table 2.11 **Temperature and dissolved oxygen concentration profiles showing incomplete mixing in Loch of Gonfirth (Site 2)**

Date	Depth (m)	Temperature (°C)	Dissolved oxygen (mg O_2 L^{-1})	(% saturation)
23/06/92	0	12.3	10.85	101.5
	1	12.3	10.83	101.3
	2	12.3	10.82	101.2
	3	12.3	10.86	101.6
	4	12.3	10.90	102.0
	5	12.3	10.90	102.0
	7	12.1	10.86	100.9
	9	12.1	10.87	101.0
	11	11.9	10.73	99.4
	13	11.6	10.72	98.7
	15	11.5	8.87	81.5
	17	11.4	8.76	80.3
	19	11.4	8.63	79.1
	20	11.3	8.82	80.6
25/07/93	0	12.2	11.06	103.2
	1	12.1	11.11	103.4
	2	12.1	11.09	103.3
	3	12.0	11.08	103.0
	4	12.0	11.08	103.0
	5	12.0	11.09	103.1
	7	12.0	11.10	103.2
	9	11.9	11.09	102.8
	11	11.9	11.03	102.2
	13	11.9	11.01	102.0
	15	11.5	10.85	99.6
	17	11.1	10.43	94.9
	19	10.9	10.12	91.7
	20	10.8	9.98	90.2

2.3.2.3 pH, conductivity and alkalinity of waters in 1992 (Table 2.12)

Mean water column pH in Loch of Gonfirth ranged from pH 6.04 in March to pH 6.30 in June. Average water alkalinity in this loch showed its minimum of 0.09 meq L^{-1} in March, buffering capacity being greatest during August and October, when alkalinity was 0.11 meq L^{-1}. In contrast, the highest mean water column conductivity of 222 μS cm^{-1} was recorded in May, the lowest of 173 μS cm^{-1} in October.

In Helliers Water mean pH ranged from pH 6.42 in October to pH 6.87 during May. Highest mean alkalinity was measured as 0.70 meq L^{-1} in August, lowest average alkalinity being 0.14 meq L^{-1} in March samples. The highest conductivity of 350 μS cm^{-1} was also detected in August, whilst the minimum of 252 μS cm^{-1} was recorded in May.

Average water column pH in Loch of Tingwall remained > pH 7.00 throughout the sampling program, ranging from pH 7.52 in June to pH 8.00 in May. Compared with the South Basin, variation in pH was more extreme in the North Basin, where mean pH values extended from pH 7.25 in October, to pH 8.15 in May. Mean conductivity measured for both basins was 362 μS cm^{-1} in March and 377 μS cm^{-1} in August. Again, more extreme mean conductivity values of 352 μS cm^{-1} (March) and 377 μS cm^{-1} (October) were recorded for the North Basin. Mean alkalinity for Loch of Tingwall ranged from 1.06 meq L^{-1} in May to 1.75 meq L^{-1} in August. Greater variability was noted in the South Basin than the North Basin, maximum and minimum values in the former being 1.76 meq L^{-1} (August) and 0.94 meq L^{-1} (May) respectively.

In Sandy Loch, mean water column pH was greatest in May (pH 7.09) and lowest in June (pH 6.79). Minimum conductivity measured was 257 μS cm^{-1} in May, the highest mean conductivity of 271 μS cm^{-1} subsequently being observed in August. Water buffering capacity was poorest in March, when average alkalinity was 0.26 meq L^{-1}. During October, alkalinity was at its highest level (0.38 meq L^{-1}).

Table 2.12 Mean water column pH, conductivity and alkalinity ranges of the five study sites, 1992

Site	pH	Conductivity ($\mu S\ cm^{-1}$)	Alkalinity ($meq\ L^{-1}$)
Loch of Gonfirth	6.04-6.30	173-222	0.09-0.11
Helliers Water	6.42-6.87	252-350	0.14-0.70
Loch of Tingwall (both basins)	7.52-8.00	362-377	1.06-1.75
Sandy Loch	6.79-7.09	257-271	0.26-0.38
Turdale Water	6.50-9.30	256-334	0.26-1.33

Great variation occurred in mean water column pH values for Turdale Water, ranging from pH 6.50 during October to pH 9.30 in June. Mean conductivity readings varied from 256 μS cm^{-1} in March to 334 μS cm^{-1} in August. Mean alkalinity was also highly variable, ranging from 0.26 meq L^{-1} in March to 1.33 meq L^{-1} in August.

2.3.2.4 Phosphorus and chlorophyll *a* concentrations of lochs and their inflows in 1992

Changes in TP, TDP, DRP and chl *a* concentrations over time are presented in Figures 2.11-2.20. These figures represent the water column parameter mean $\pm$ 2 s.e. for each sampling date.

2.3.2.4.1 Loch of Gonfirth

Average water column TP concentration changed little from March to June sampling dates. Maximum recorded TP level was 4.9 μg P L^{-1} in May. This decreased to a minimum of 3.4 μg P L^{-1} determined in samples taken in October. Mean water column TDP concentration was observed to decrease from 3.2 μg P L^{-1} during March to 1.3 μg P L^{-1} in October, greatest change occurring between March and May, when TDP was present in the water column at 2.3 μg P L^{-1} (Figure 2.11). Concentration of DRP in water from Loch of Gonfirth was $<$ 1 μg P L^{-1} in every sample analysed. Mean water column chl *a* concentration increased from its minimum level of 0.5 μg chl *a* L^{-1} in March to peak chl *a* content of 1.8 μg chl *a* L^{-1} in May (Figure 2.12). From May to October average water column chl *a* concentration decreased to 1.3 μg chl *a* L^{-1}. Chl *a* content therefore exhibited a similar pattern to TP concentration during 1992.

2.3.2.4.2 Loch of Gonfirth inflow waters (Table 2.13)

Maximum recorded TP concentration of a Loch of Gonfirth inflow was 23.9 μg P L^{-1}, determined for Inflow 3 during May. A relatively high TP concentration was also found in Inflow 5 at this time (15.6 μg P L^{-1}). Least TP was present in Inflow 1 in May (5.3 μg P L^{-1}). During June, only Inflow 6 had sufficient water flow to allow sampling. TP was determined at 5.3 μg P L^{-1} in this inflow. In August TP concentration ranged from 7.2 μg P L^{-1} in Inflow 1 and Inflow 6 to 9.1 μg P L^{-1} in Inflow 3.

Figure 2.11 Phosphorus levels in Loch of Gonfirth, 1992 sampling season (n=15)

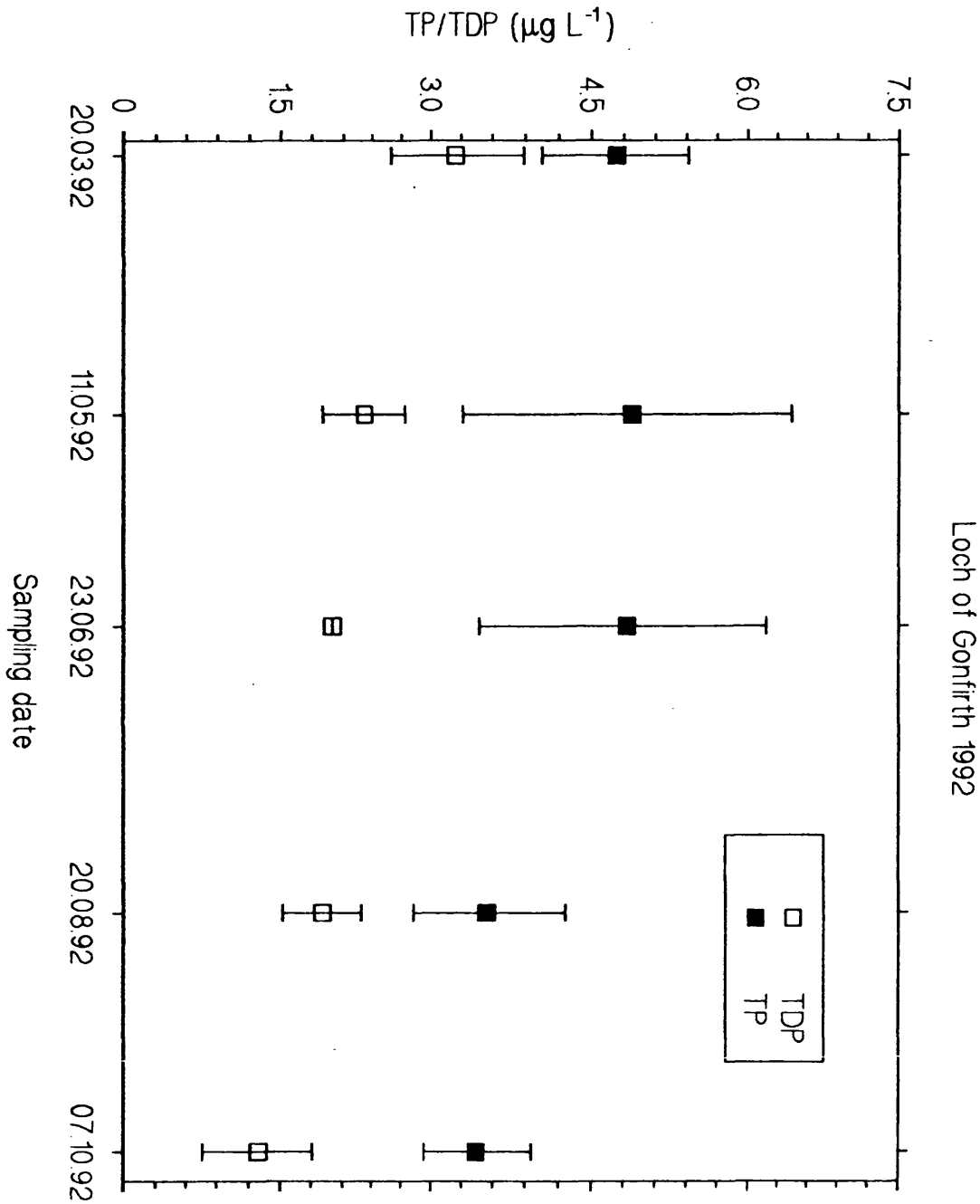


Figure 2.12 Chlorophyll *a* levels in Loch of Gonfirth, 1992 sampling season (n =15)

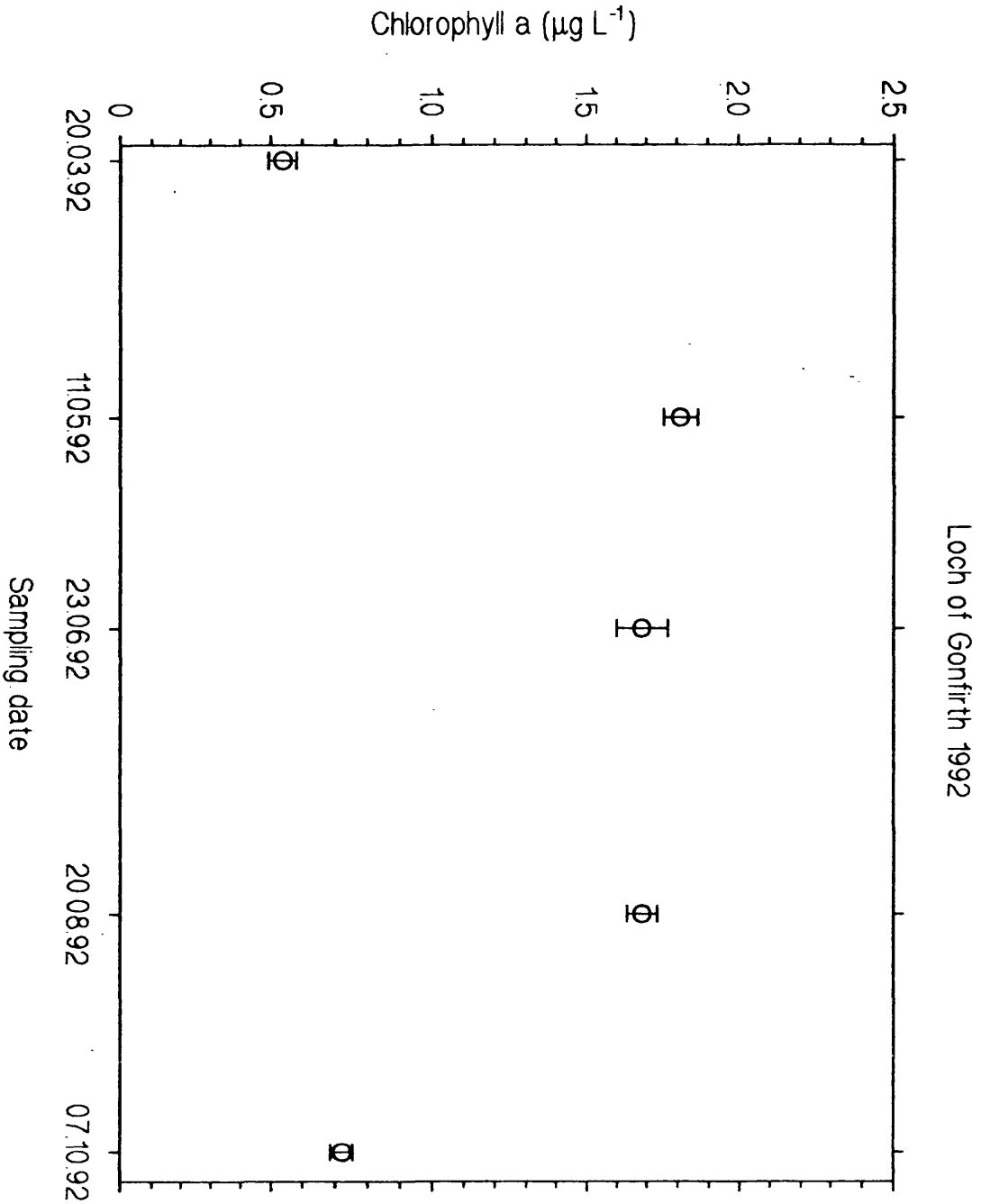


Table 2.13 Inflow water quality for the five study lochs, 1992 (all data reported as $\mu g\ P\ L^{-1}$)

(site details given on Figure 3.1)

Loch of Gonfirth

Site	In 1	In 2	In 3	In 4	In 5	In 6
Date						
20.03.92						
TP						
TDP	no samples taken					
DRP						
11.05.92						
TP	5.3	8.5	23.9	7.8	15.6	n.s.
TDP	3.3	4.6	11.0	6.5	8.4	
DRP	n.d.	n.d.	n.d.	n.d.	n.d.	
23.06.92						
TP	n.s.	n.s.	n.s.	n.s.	n.s.	5.3
TDP						2.7
DRP						n.d.
20.08.92						
TP	7.2	n.s.	9.1	n.s.	n.s.	7.2
TDP	4.0		6.5			6.5
DRP	n.d.		n.d.			n.d.
07.10.92						
TP	5.9	n.s.	n.s.	3.4	5.9	7.8
TDP	5.9			1.5	4.7	4.7
DRP	n.d.			n.d.	n.d.	n.d.

Table 2.13 (cont.)
Helliers Water

Site	In 1	In 2	In 3
Date			
19.03.92			
TP			
TDP	no samples taken		
DRP			
12.05.92			
TP	7.8	16.8	n.s.
TDP	3.3	2.0	
DRP	n.d.	n.d.	
20.06.92			
TP	n.s.	n.s.	10.4
TDP			5.9
DRP			n.d.
21.08.92			
TP	4.0	3.4	n.s.
TDP	1.4	1.4	
DRP	n.d.	n.d.	
10.10.92			
TP	2.7	2.7	n.s.
TDP	n.s.	1.5	
DRP	n.d.	n.d.	

Sandy Loch

Site	In 1	In 2	In 3
Date			
21.03.92			
TP			
TDP	no samples taken		
DRP			
10.05.92			
TP			
TDP	no samples taken		
DRP			
23.06.92			
TP	47.7	n.s.	n.s.
TDP	32.0		
DRP	n.d.		
19.08.92			
TP	48.0	32.1	n.s.
TDP	35.9	16.1	
DRP	n.d.	n.d.	
06.10.92			
TP	64.3	35.7	19.2
TDP	54.2	29.1	14.1
DRP	12.0	n.d.	n.d.

Table 2.13 (cont.)
Loch of Tingwall

Site	In 1	In 2	In 3	In 4	In 5
Date					
22.03.92					
TP					
TDP	no samples taken				
DRP					
13.05.92					
TP	49.6	14.3	14.3	2.1	9.8
TDP	39.0	9.7	6.5	n.s.	n.s.
DRP	n.d.	n.d.	n.d.	n.d.	n.d.
19.06.92					
TP	31.0	18.8	36.1	n.s.	13.6
TDP	21.8	n.s.	12.2		11.6
DRP	n.d.	n.d.	n.d.		n.d.
22.08.92					
TP	27.0	12.3	n.s.	n.s.	11.7
TDP	19.9	11.0			9.7
DRP	n.d.	n.d.			n.d.
08.10.92					
TP	41.4	19.9	n.s.	n.s.	9.7
TDP	27.3	14.1			6.6
DRP	3.8	n.d.			n.d.

Turdale Water

Site	In 1	In 2	In 3	In 4	In 5
Date					
18.03.92					
TP					
TDP	no samples taken				
DRP					
12.05.92					
TP	2223	172	904	1223	n.s.
TDP	1464	150	892	1059	
DRP	971	97	352	733	
18.06.92					
TP	n.s.	120.0	n.s.	n.s.	16.2
TDP		97.7			9.7
DRP		n.d.			n.d.
21.08.92					
TP	n.s.	66.5	n.s.	n.s.	18.0
TDP		51.2			13.6
DRP		n.d.			n.d.
09.10.92					
TP	20.9	119.0	561.0	n.s	1336.0
TDP	12.9	111.0	n.s.		n.s.
DRP	n.d.	69.9	503.4		n.s.

The depths of remaining inflows were too shallow for samples to be taken. During October, Inflow 4A exhibited a concentration of 3.4 μg P L^{-1}. This was the lowest TP concentration determined in Loch of Gonfirth inflow waters. Maximum TP concentration of waters collected at this time was 7.8 μg P L^{-1} in Inflow 6. Greatest TDP levels were found in the same samples as highest TP concentrations. During May, Inflow 3 and Inflow 5 contained 11.0 μg TDP L^{-1} and 8.4 μg TDP L^{-1} respectively, whereas lowest TDP levels in May were observed in Inflow 1 (3.3 μg P L^{-1}). During June TDP concentration was 2.7 μg P L^{-1} in Inflow 6 and a relatively restricted range was noted in August, from 4.0 μg P L^{-1} (Inflow 1) to 6.5 μg P L^{-1} (Inflow 3 and Inflow 6). As with TP, Inflow 4A during October accounted for the lowest recorded concentration of TDP of 1.5 μg P L^{-1}, whilst Inflow 5 and Inflow 6 were each observed to have 4.7 μg TDP L^{-1}, the maximum TDP level for this sampling visit.

2.3.2.4.3 Helliers Water

At 4.8 μg P L^{-1}, mean water column TP concentration was low during March and August. Two peaks were also observed in TP levels, the greater of 9.8 μg P L^{-1} during May, the other of 7.0 μg P L^{-1} in October (Figure 2.13). Average water column TDP concentration did not follow the same pattern as exhibited by TP. Little change in TDP levels occurred between sampling dates. Mean concentration increased from 2.9 μg P L^{-1} in March to the maximum level of 3.3 μg P L^{-1} during May and June. Greatest change was observed from June to August, when TDP concentration decreased to its lowest value of 2.1 μg P L^{-1}. October levels were similar to those found in March. No P was detected in the DRP form in any of the samples collected (Figure 2.13). From 1.9 μg chl *a* L^{-1} March, mean water column chl *a* concentration decreased to 0.9 μg chl *a* L^{-1} in May (Figure 2.14). In comparison, chl *a* levels were elevated in June, average water concentration being 2.7 μg chl *a* L^{-1}. Maximum levels were detected in the October samples. From a concentration of 1.8 μg chl *a* L^{-1} in August, chl *a* levels rose to 3.9 μg chl *a* L^{-1}.

Figure 2.13 Phosphorus levels in Helliers Water, 1992 sampling season (n=3)

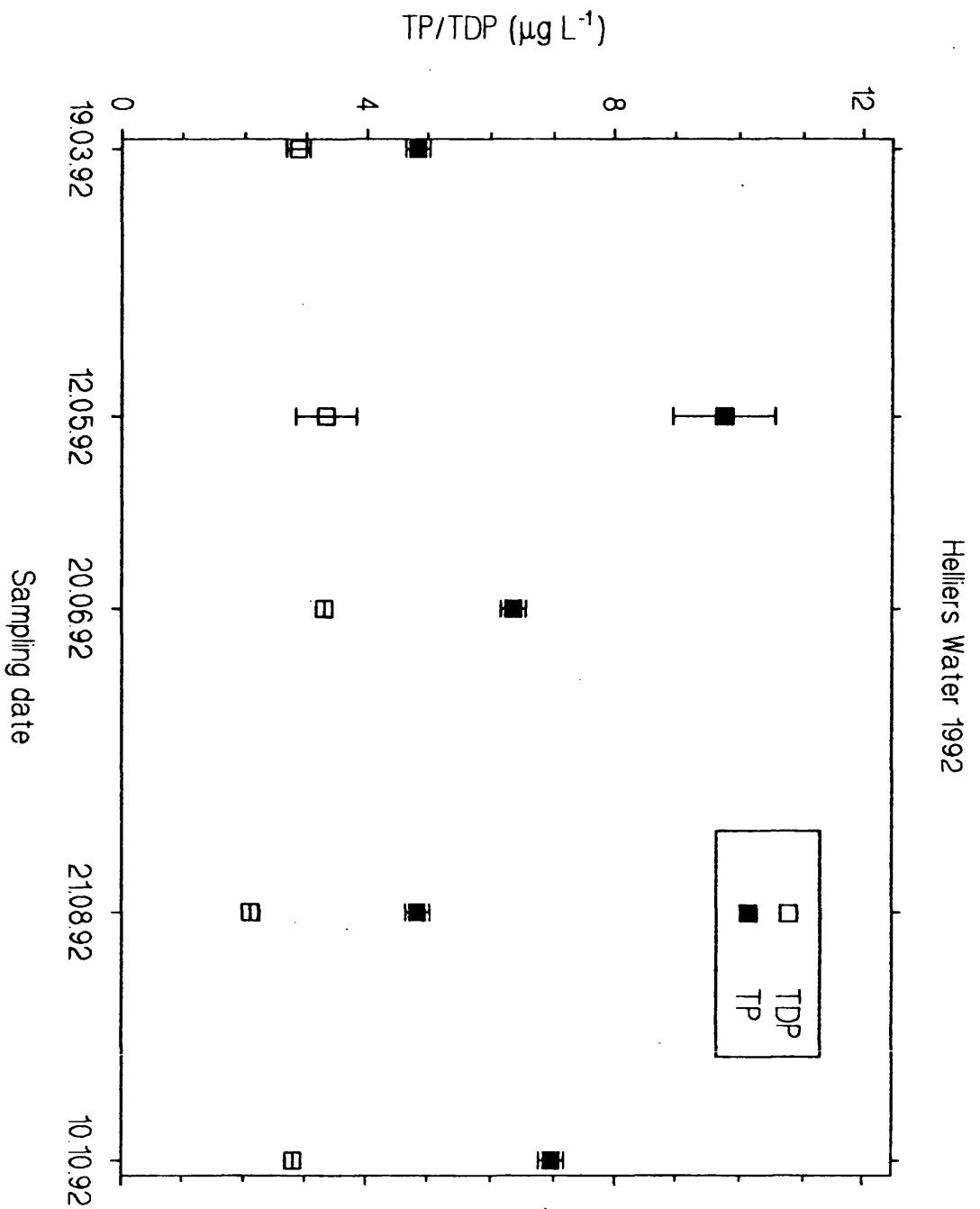
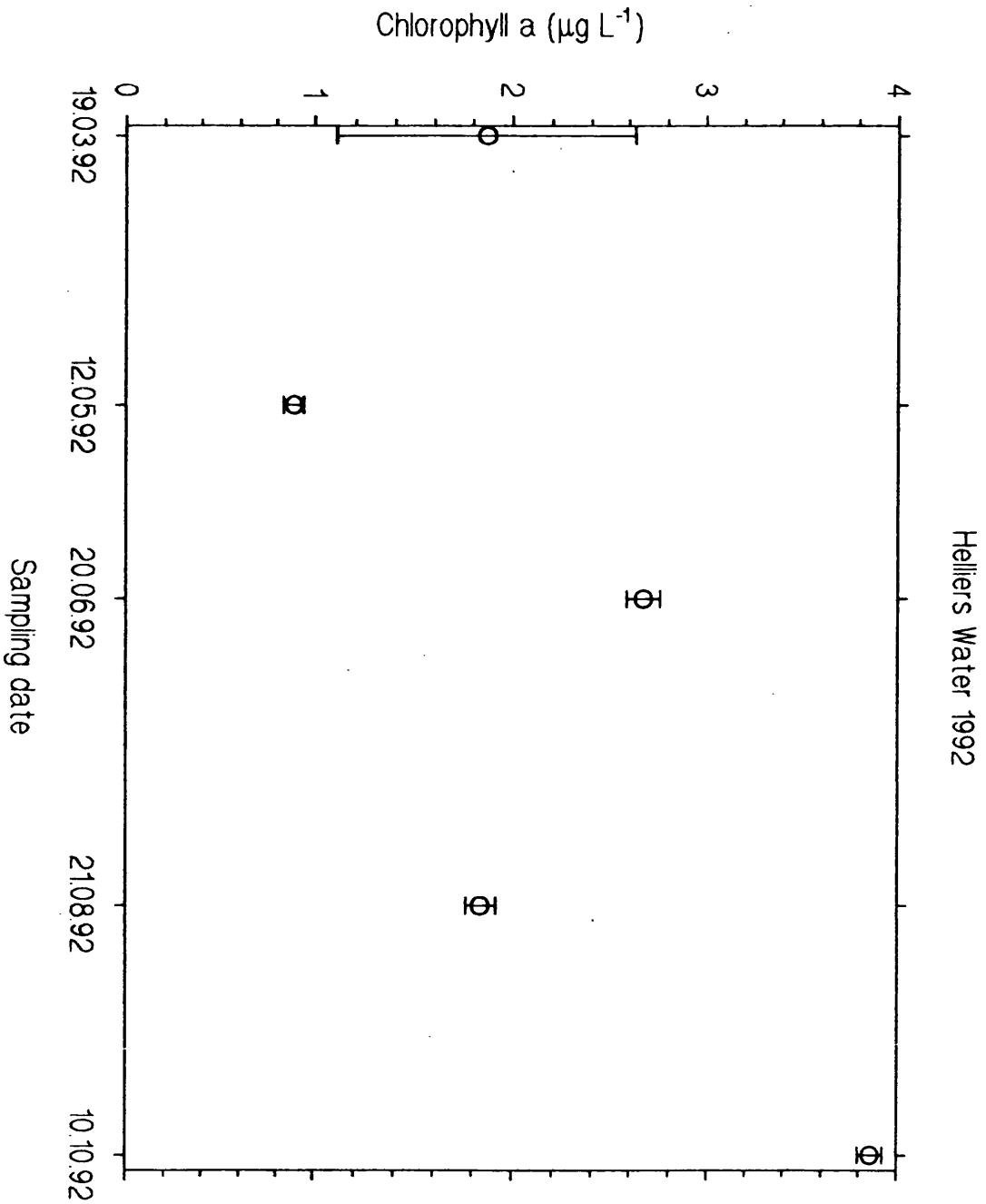


Figure 2.14 Chlorophyll *a* levels in Helliers Water, 1992 sampling season (n=3)



2.3.2.4.4 Helliers Water inflow waters (Table 2.13)

Shortage of water during summer resulted in SIC pumping water from Loch of Watlee to Helliers Water. Although transference of water occurred intermittently from May to August, the inflow from Loch of Watlee was in operation during the June survey only. TP and TDP concentrations in this inflow (Inflow 3) were determined as 10.4 μg P L^{-1} and 5.9 μg P L^{-1} respectively. At this time, Inflow 1 and Inflow 2 had insufficient flow to allow collection of water samples. Concentration of TP in these inflows decreased from March to October, when TP level in each was 2.7 μg P L^{-1}. Maximum concentrations of TP were 7.8 μg P L^{-1} and 16.8 μg P L^{-1} in Inflow 1 and Inflow 2 respectively. TDP concentrations in Inflow 1 ranged from 1.4 μg P L^{-1} in August to 3.3 μg P L^{-1} during May. TDP level in Inflow 2 also ranged from 1.4 μg P L^{-1} in August to 2.0 μg P L^{-1} in May. DRP concentration was < 1 μg P L^{-1} in all inflow water samples analysed.

2.3.2.4.5 Loch of Tingwall

Mean water column TP concentration decreased in both North and South Basins from March to October. In the North Basin, maximum and minimum average TP levels were 20.6 μg P L^{-1} and 10.5 μg P L^{-1} respectively. Mean water TP concentration range in the South Basin was from 14.7 μg P L^{-1} down to 8.5 μg P L^{-1} (Figure 2.15). Mean range for both basins combined was 16.4 μg P L^{-1} to 9.1 μg P L^{-1}. Mean water column chl *a* concentration in Loch of Tingwall North Basin decreased from 8.8 μg chl *a* L^{-1} in March to levels between 3.6 μg chl *a* L^{-1} and 4.2 μg chl *a* L^{-1} during the other sampling visits. South Basin chl *a* concentrations decreased from 8.1 μg chl *a* L^{-1} in March to 1.9 μg chl *a* L^{-1} during May. From this minimum concentration, chl *a* levels increased to 5.7 μg chl *a* L^{-1} in June. During August and October, chl *a* concentration remained at 4.0 μg chl *a* L^{-1}. Average chl *a* range for the entire loch was from 8.3 μg chl *a* L^{-1} in March to 2.5 μg chl *a* L^{-1} in May (Figure 2.16).

2.3.2.4.6 Loch of Tingwall inflow waters (Table 2.13)

The greatest concentration of TP determined for Loch of Tingwall inflow waters was 49.6 μg P L^{-1} in Inflow 1 during May. Inflow 4 exhibited a TP concentration of only 2.1 μg P L^{-1} at this time, which was the minimum measured. In June, greatest TP concentration of 36.1 μg P L^{-1} was found in Inflow 3A, Inflow 5 having the lowest TP concentration at this time of 13.6 μg P L^{-1}.

Figure 2.15 Phosphorus levels in Loch of Tingwall, 1992 sampling season (n=15)

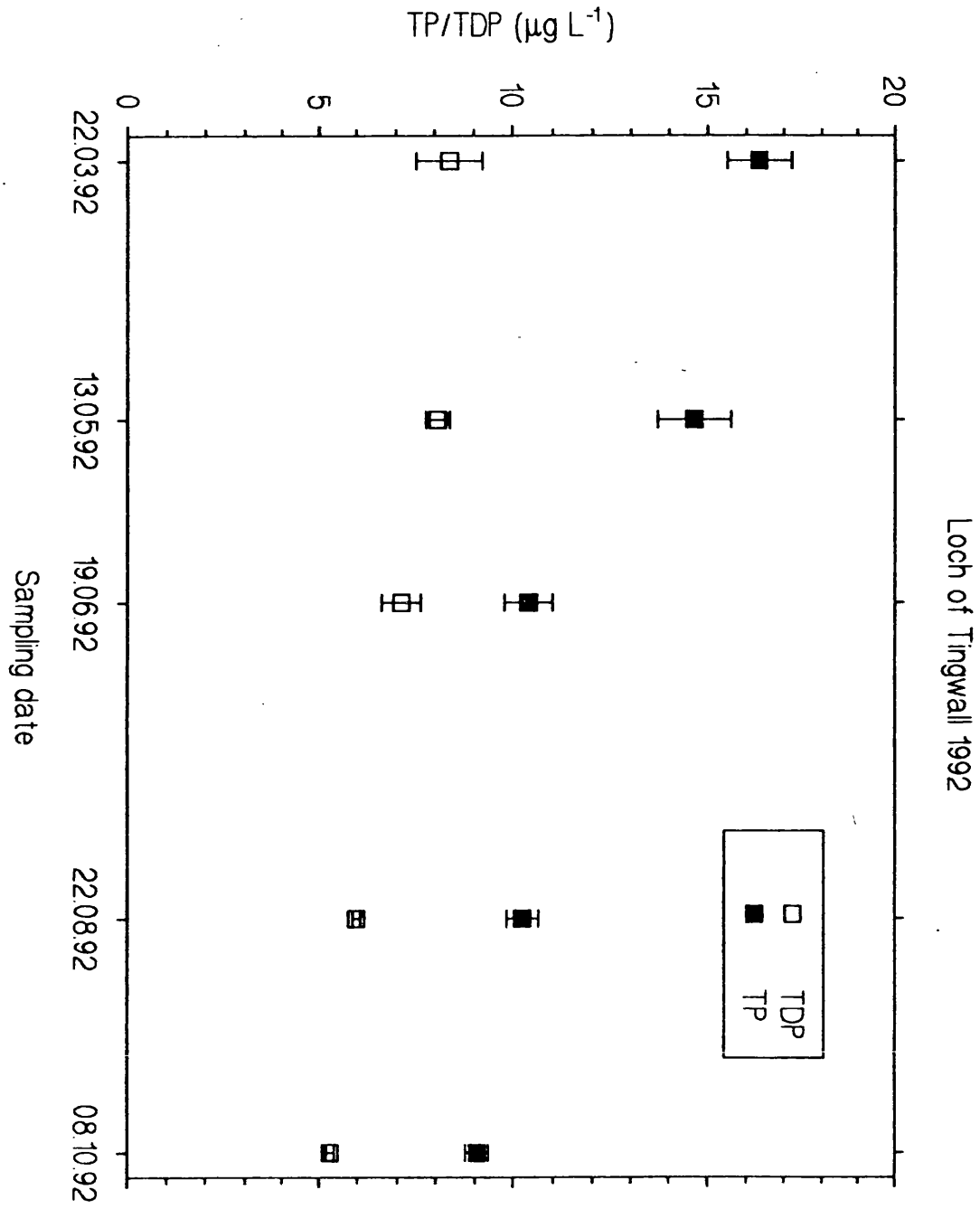
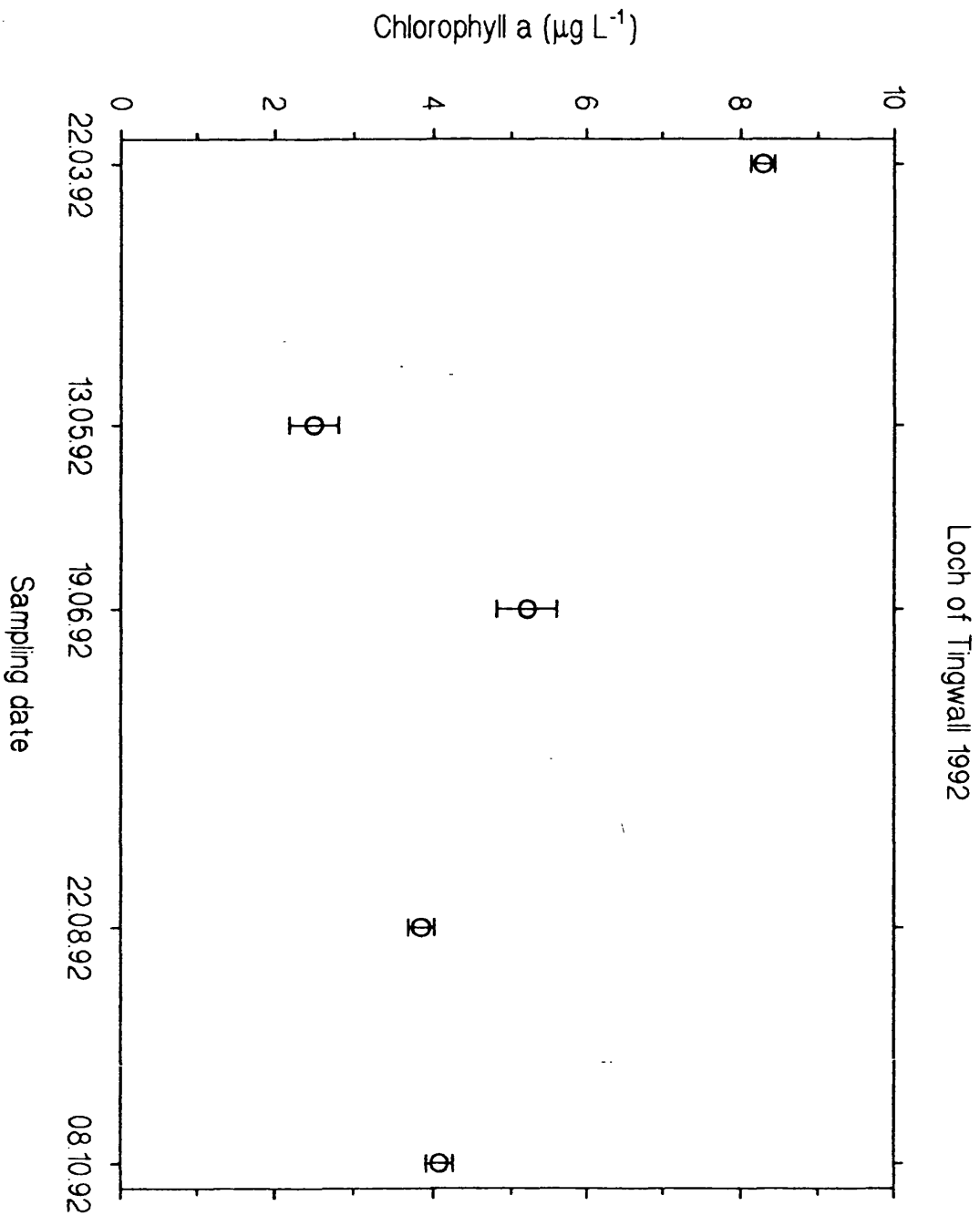


Figure 2.16 Chlorophyll *a* levels in Loch of Tingwall, 1992 sampling season (n=15)



Of samples taken during August and October, TP content was highest in Inflow 1 and lowest in Inflow 5. TP levels ranged from 11.7 μg P L^{-1} to 27 μg P L^{-1} in August and 9.7 μg P L^{-1} to 41.4 μg P L^{-1} in October. TDP levels detected in samples taken in May were greatest in Inflow 1 (39.0 μg P L^{-1}) and least in Inflow 4 (0.9 μg P L^{-1}). As with TP concentrations, samples from Inflows 1 and 4 demonstrated the extremes of TDP levels for all the Loch of Tingwall inflow samples analysed. The following ranges of TDP concentrations were observed in inflow water of the remaining determinations: 11.6 μg P L^{-1} to 31 μg P L^{-1} (June), 9.7 μg P L^{-1} to 27 μg P L^{-1} (August), 6.6 μg P L^{-1} to 41.4 μg P L^{-1} (October). DRP was $<$ 1 μg P L^{-1} in all inflow samples analysed in May, June, August and October, with the exception of Inflow 1, which had a DRP concentration of 3.8 μg P L^{-1} during October.

2.3.2.4.7 Sandy Loch

Average water column TP concentration in Sandy Loch was 33.6 μg P L^{-1} during March, decreasing to 24.8 μg P L^{-1} in June. From this level, mean water column TP then increased to 32.3 μg P L^{-1} in October (Figure 2.17). Average TDP levels decreased from 24.3 μg P L^{-1} in March to a minimum of 12.9 μg P L^{-1} in May. Mean TDP concentration then increased to the maximum of 25.2 μg P L^{-1} in October. During October, DRP was detected at levels of 2.7 μg P L^{-1} and 1 μg P L^{-1} in surface samples from Site 1 and Site 2. Two peaks were noted in chl *a* concentrations in Sandy Loch water samples (Figure 2.18). The first of 8.1 μg chl *a* L^{-1} occurred in May, the second of 11.6 μg chl *a* L^{-1} in August. Lowest mean chl *a* concentration of 2.7 μg chl *a* L^{-1} was detected in October.

2.3.2.4.8 Sandy Loch inflow waters (Table 2.13)

In samples taken from Inflow 1, TP concentration ranged from 47.7 μg P L^{-1} in June, to 64.3 μg P L^{-1} in October. TP concentrations determined in the two samples taken of Inflow 2 waters were 32.1 μg P L^{-1} and 35.7 μg P L^{-1} for August and October, respectively. The October sampling of Inflow 3 exhibited a TP level of 19.2 μg P L^{-1}, of which TDP constituted 14.1 μg P L^{-1}. TDP concentration in Inflow 1 ranged from 32.0 μg P L^{-1} in June to 54.2 μg P L^{-1} in October, whilst that in Inflow 2 was present at 16.1 μg P L^{-1} and 29.1 μg P L^{-1} in August and October respectively.

Figure 2.17 Phosphorus levels in Sandy Loch, 1992 sampling season (n=8)

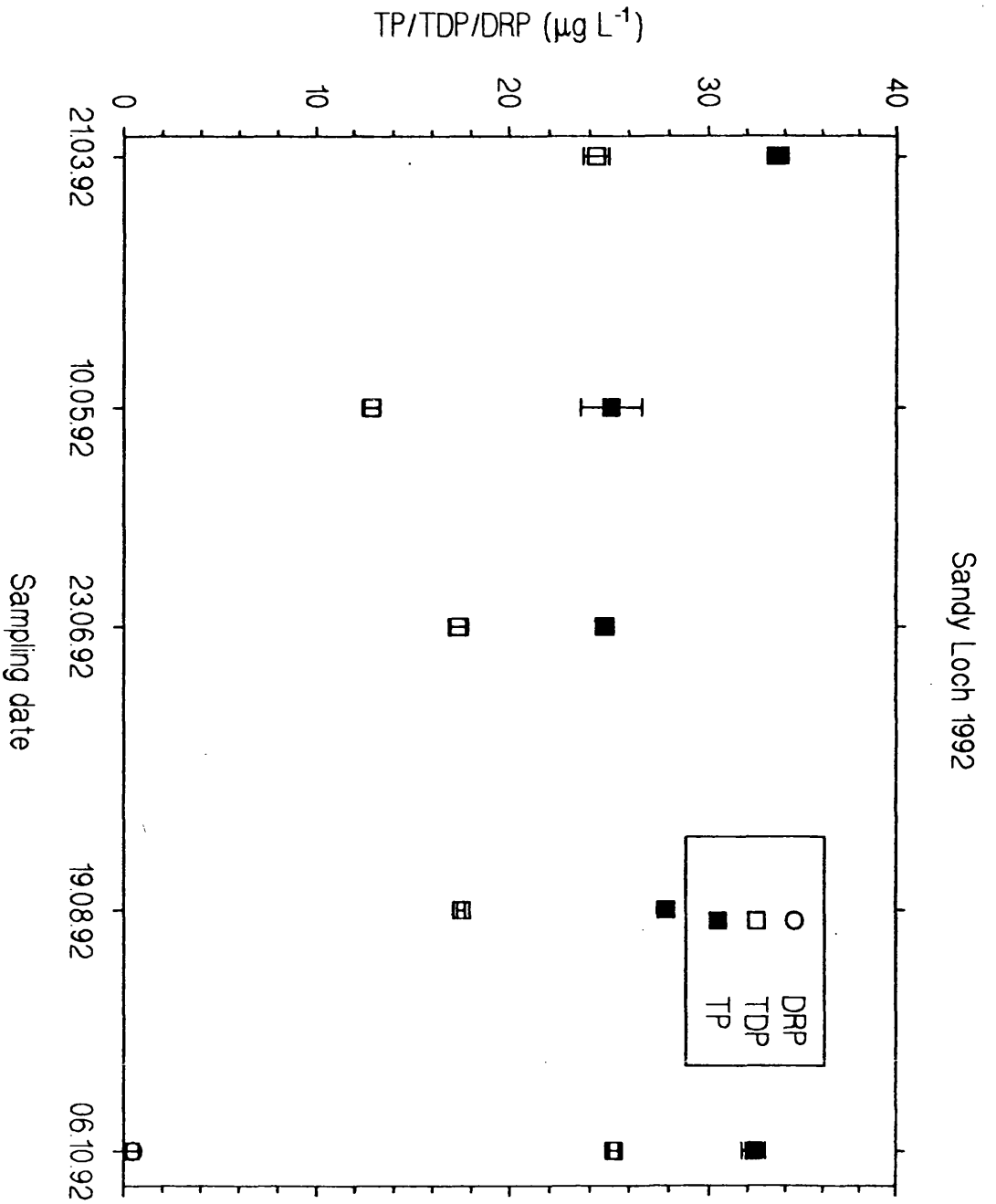
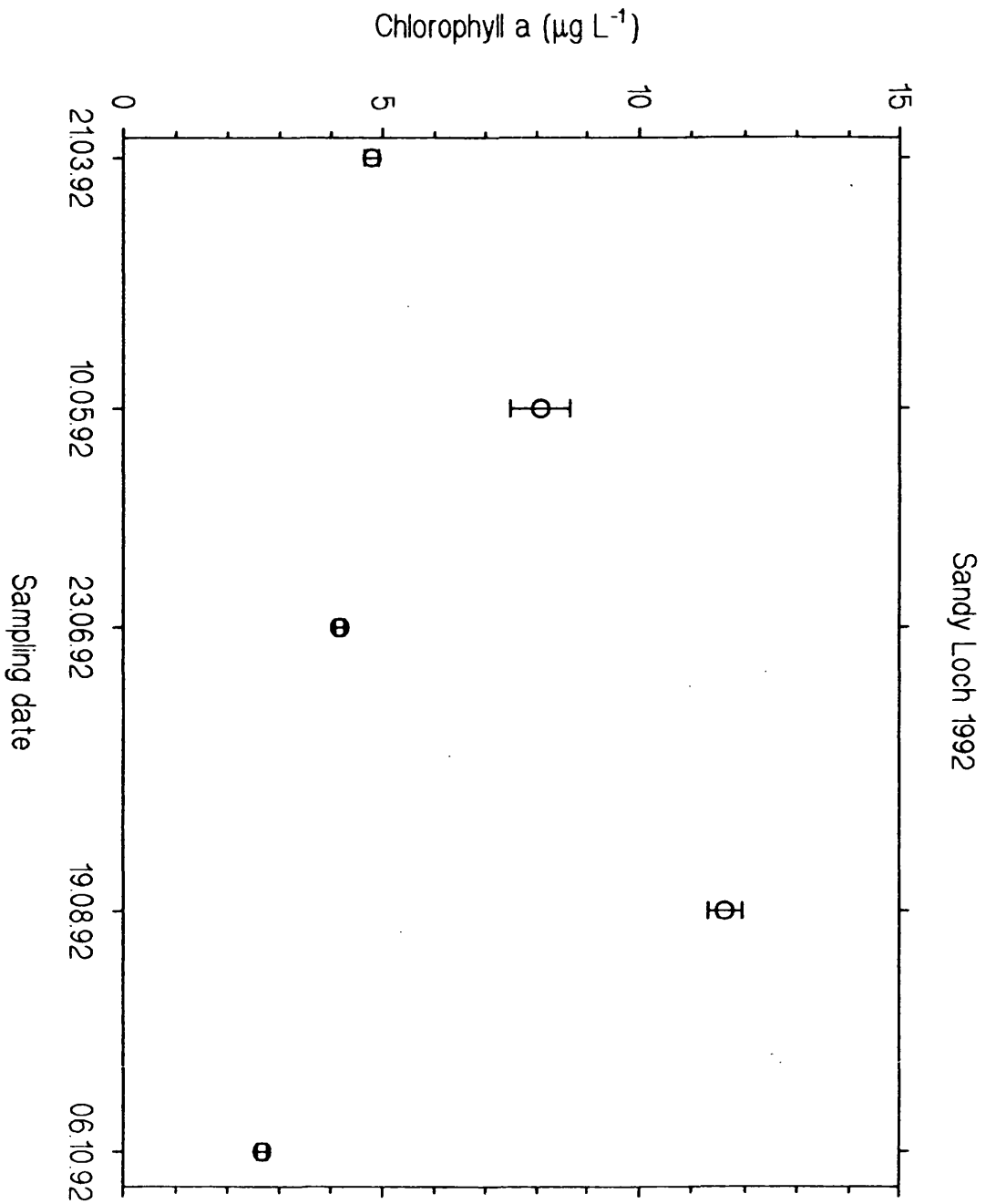


Figure 2.18 Chlorophyll *a* levels in Sandy Loch, 1992 sampling season (n=8)



2.3.2.4.9 Turdale Water

Commencing at 159.0 μg P L^{-1} in March, mean water column TP concentration increased to a maximum of 203.4 μg P L^{-1} in May. TP levels were then depleted to 36.5 μg P L^{-1} in August, before increasing once more to 127.4 μg P L^{-1} in October (Figure 2.19). TDP concentrations followed a similar pattern to TP levels, exhibiting maximum (134.2 μg P L^{-1}) and minimum (23.1 μg P L^{-1}) concentrations in May and August respectively. Mean water column DRP concentration increased from 68.1 μg P L^{-1} in March to 115.4 μg P L^{-1} in May, but was below the limit of detection of 1.0 μg P L^{-1} during June and August. However, DRP returned to a mean level of 46.7 μg P L^{-1} in October (Figure 2.19). Mean chl *a* levels in Turdale Water increased from 12.1 μg P L^{-1} to 284.6 μg P L^{-1} in June. Minimum chl *a* concentration of 5.2 μg chl *a* L^{-1} was observed in August, after which chl *a* increased to 9.7 μg chl *a* L^{-1} in October (Figure 2.20).

2.3.2.4.10 Turdale Water inflow waters (Table 2.13)

Maximum recorded TP concentration in Turdale inflow water was 2.22 mg P L^{-1} in Inflow 1 during May. Lowest TP concentration detected at this time was 172.3 μg P L^{-1} in Inflow 2. In June, Inflow 2 and Inflow 5 exhibited concentrations of 120.3 μg P L^{-1} and 16.2 μg P L^{-1} respectively, the latter being the minimum TP level recorded in a Turdale inflow in 1992. In August TP had decreased to 66.5 μg P L^{-1} in Inflow 2, but increased to 18.0 μg P L^{-1} in Inflow 5. TP content of samples collected in October ranged from 20.9 μg P L^{-1} in Inflow 1 to 1.34 mg P L^{-1} in Inflow 5. TDP concentration in May ranged from 149.9 μg P L^{-1} in Inflow 2 to 1.46 mg P L^{-1} in Inflow 1. The latter TDP concentration was the highest recorded TDP level in Turdale inflow waters during 1992. In samples of Inflow 2 and Inflow 5 collected in June, TDP contents were found to be 97.7 μg P L^{-1} and 9.7 μg P L^{-1} respectively, whilst in August the corresponding values were 51.2 μg P L^{-1} and 13.6 μg P L^{-1}. Greatest TDP concentration in October occurred in the Inflow 3 sample (545.2 μg P L^{-1}), the lowest in the Inflow 1 water (12.9 μg P L^{-1}). In May, DRP content of inflow waters collected ranged from 96.6 μg P L^{-1} in Inflow 2 to 0.97 mg P L^{-1} in Inflow 1. Concentration of DRP was $<$ 1 μg P L^{-1} in Inflow 2 and Inflow 5 during June and August. However, in October, DRP levels measured were between $<$ 1 μg P L^{-1} in Inflow 1 and 503.4 μg P L^{-1} in Inflow 3.

Figure 2.19 Phosphorus levels in Turdale Water, 1992 sampling season (n=3)

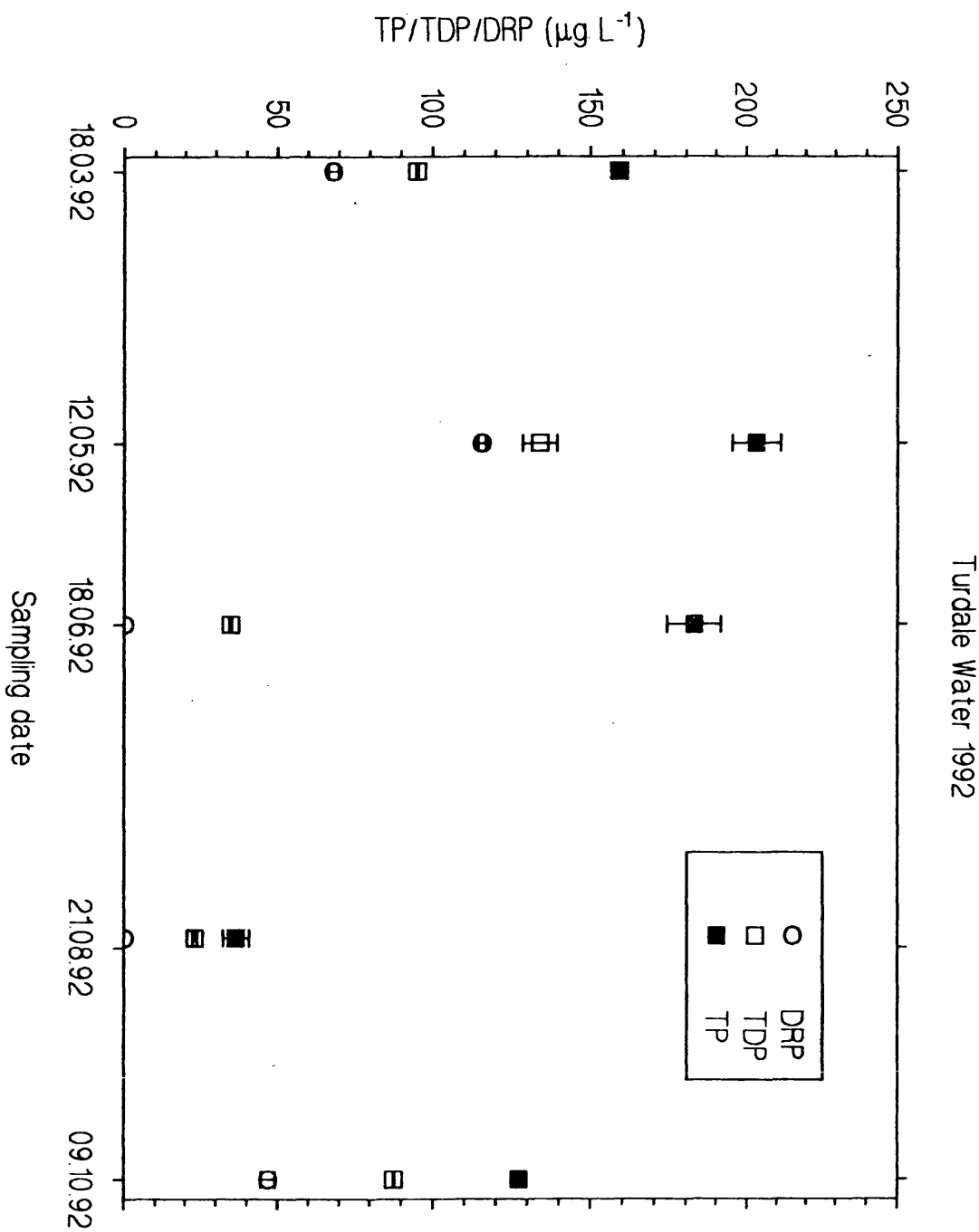
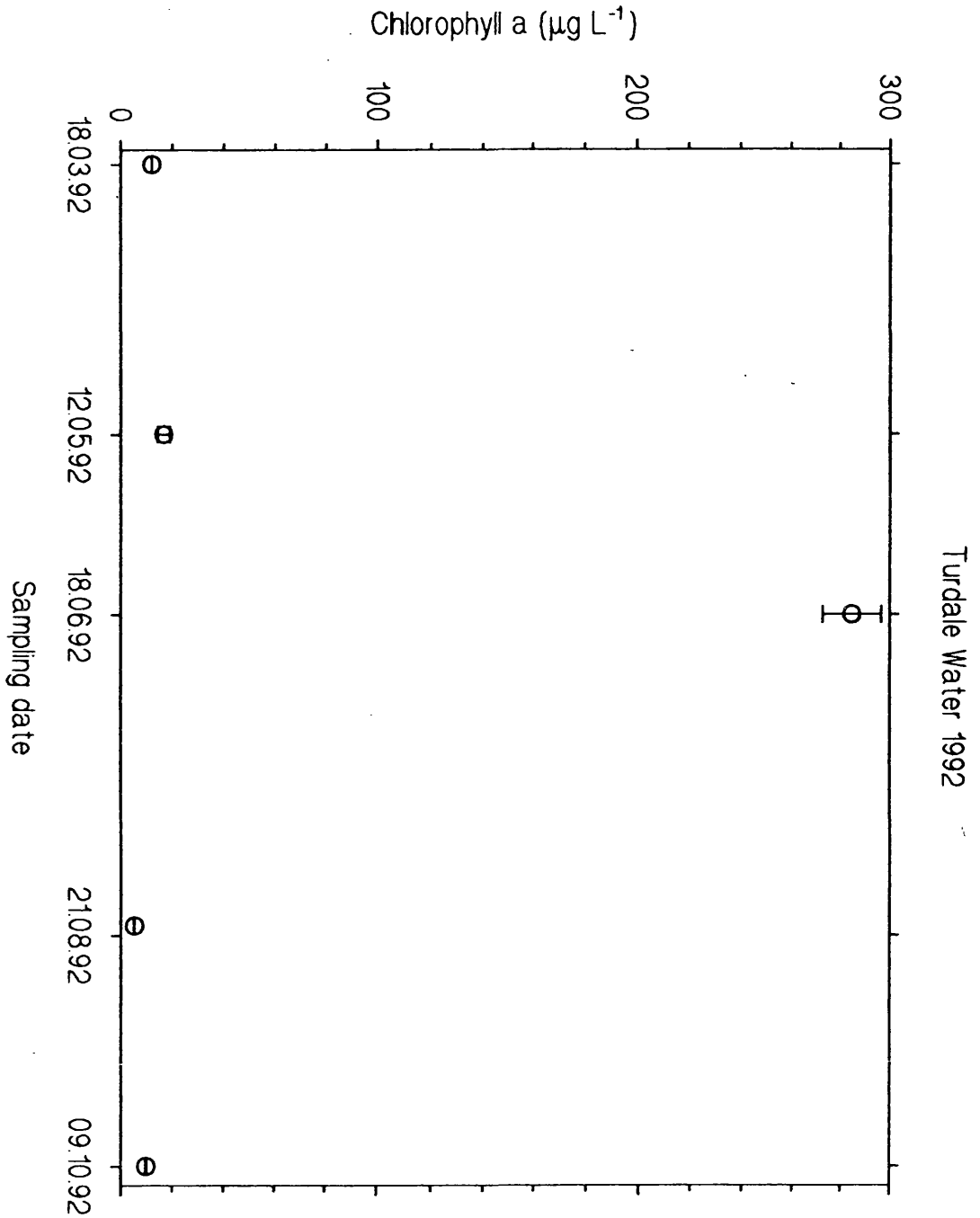


Figure 2.20 Chlorophyll *a* levels in Turdale Water, 1992 sampling season (n=3)



2.3.2.5 pH, conductivity and alkalinity in the five study lochs in 1993 (Table 2.14)

In Loch of Gonfirth, mean water column pH ranged from 6.23 during March to 6.35 in August, pH values in May and October being 6.34 and 6.26 respectively. Average water column conductivity was 185-189 μS cm^{-1}, falling to 177 μS cm^{-1} in August only. Buffering capacity was lowest during August, when mean alkalinity was 0.09 meq L^{-1}. Subsequently, average alkalinity increased to the maximum of 0.15 meq L^{-1} during October.

Average water column pH values for Helliers Water increased from 6.80 during March to 7.01 in August and October. Lowest average water column conductivity of 252 μS cm^{-1} was recorded in May, whilst greatest mean conductivity of 324 μS cm^{-1} occurred in October. An increase in buffering capacity was observed from the minimum mean alkalinity in March of 0.18 meq L^{-1} to 0.61 meq L^{-1} in October.
Mean pH values in Loch of Tingwall increased from 7.50 in March to 7.95 in August, before decreasing to 7.80 in October. In August, the high pH of the waters of the North Basin resulted in the elevated mean water column pH for Loch of Tingwall. The pH in the water column of the North Basin ranged from 8.02 to 8.22, whereas pH 7.66 and pH 7.85 were the extremes noted in the South Basin. Conductivity in the water column decreased from 371 μS cm^{-1} during March to 323 μS cm^{-1} in May, rising to 385 μS cm^{-1} in October. Maximum and minimum average water alkalinity levels were recorded in March (1.43 meq L^{-1}) and May (1.50 meq L^{-1}) respectively.

Average water column pH values in Sandy Loch ranged from 6.89 during August down to 6.48 in October. Lowest average conductivity of 221 μS cm^{-1} occurred in May, greatest of 284 μS cm^{-1} during October. Buffering capacity within the water column increased from 0.29 meq L^{-1} in March to 0.35 meq L^{-1} in August, subsequently decreasing to 0.34 meq L^{-1} in October. In Turdale Water a great change in average water column pH was noted. The pH increased from 6.75 in March to 9.02 in May, exhibiting values of pH 7.60 and 7.50 in August and October respectively. Conductivity decreased from 253 μS cm^{-1} in March to 239 μS cm^{-1} in May, before rising to 375 μS cm^{-1} in October.

Table 2.14 Mean water column pH, conductivity and alkalinity ranges of the five study sites, 1993

Site	pH	Conductivity ($\mu S\ cm^{-1}$)	Alkalinity ($meq\ L^{-1}$)
Loch of Gonfirth	6.23-6.35	177-189	0.09-0.15
Helliers Water	6.80-7.01	252-324	0.18-0.61
Loch of Tingwall (both basins)	7.50-7.95	323-385	1.43-1.50
Sandy Loch	6.48-6.89	221-284	0.29-0.35
Turdale Water	6.75-9.02	239-375	0.24-1.24

A large change also occurred in alkalinity, values of 0.24 meq L^{-1} and 1.24 meq L^{-1} being noted in March and October, respectively.

2.3.2.6 Phosphorus and chlorophyll *a* concentrations of lochs and their inflows in 1993

Changes in TP, TDP, DRP and chl *a* concentrations over time are presented in Figures 2.21-2.30. These figures represent the water column parameter mean ± 2 s.e. for each sampling date.

2.3.2.6.1 Loch of Gonfirth

Maximum average TP concentration was recorded in March, that value being 4.4 μg P L^{-1}. Minimum average TP concentration of 1.9 μg P L^{-1} was found in the May sample. Mean TP concentration rose to 3.8 μg P L^{-1} during July, before decreasing once more to 2.3 μg P L^{-1} in October (Figure 2.21). Concentrations of TDP determined in Loch of Gonfirth water samples followed a similar pattern to those of TP. Maximum average water column TDP concentration of 2.7 μg P L^{-1} was recorded in March, levels dropping to 1 μg P L^{-1} in May, the minimum determined. Water column average TDP concentration then increased to 1.7 μg P L^{-1} in July, before decreasing to 1.4 μg P L^{-1} in October. Of the samples taken, in March, May, July and October, none had detectable levels of DRP *i.e.* concentration was always < 1 μg P L^{-1} (Figure 2.21). Chl *a* concentrations recorded from water samples from Loch of Gonfirth indicated a minimum mean water column value of 0.6 μg chl *a* L^{-1} during March and the maximum level of 2.4 μg chl *a* L^{-1} in May (Figure 2.22). A less pronounced peak of 1.4 μg chl *a* L^{-1} was observed in October, mean chl *a* concentration having risen from 0.9 μg chl *a* L^{-1} in July. Water column concentrations of P and chl *a* exhibited peaks and troughs at different times *i.e.* when TP and TDP concentrations were elevated, chl *a* concentration was at lower levels and *vice versa* (Figures 2.21 and 2.22).

2.3.2.6.2 Loch of Gonfirth inflow waters (Table 2.15)

The range of TP concentrations found in Loch of Gonfirth inflow waters in March was from 2.8 μg P L^{-1} in Inflow 1 to 5.9 μg P L^{-1} in Inflow 4A. In May, Inflow 1 was again observed to have the lowest TP concentration, whilst the highest TP level of 9.3 μg P L^{-1} was recorded in Inflow 3.

Figure 2.21 Phosphorus levels in Loch of Gonfirth, 1993 sampling season (n=6)

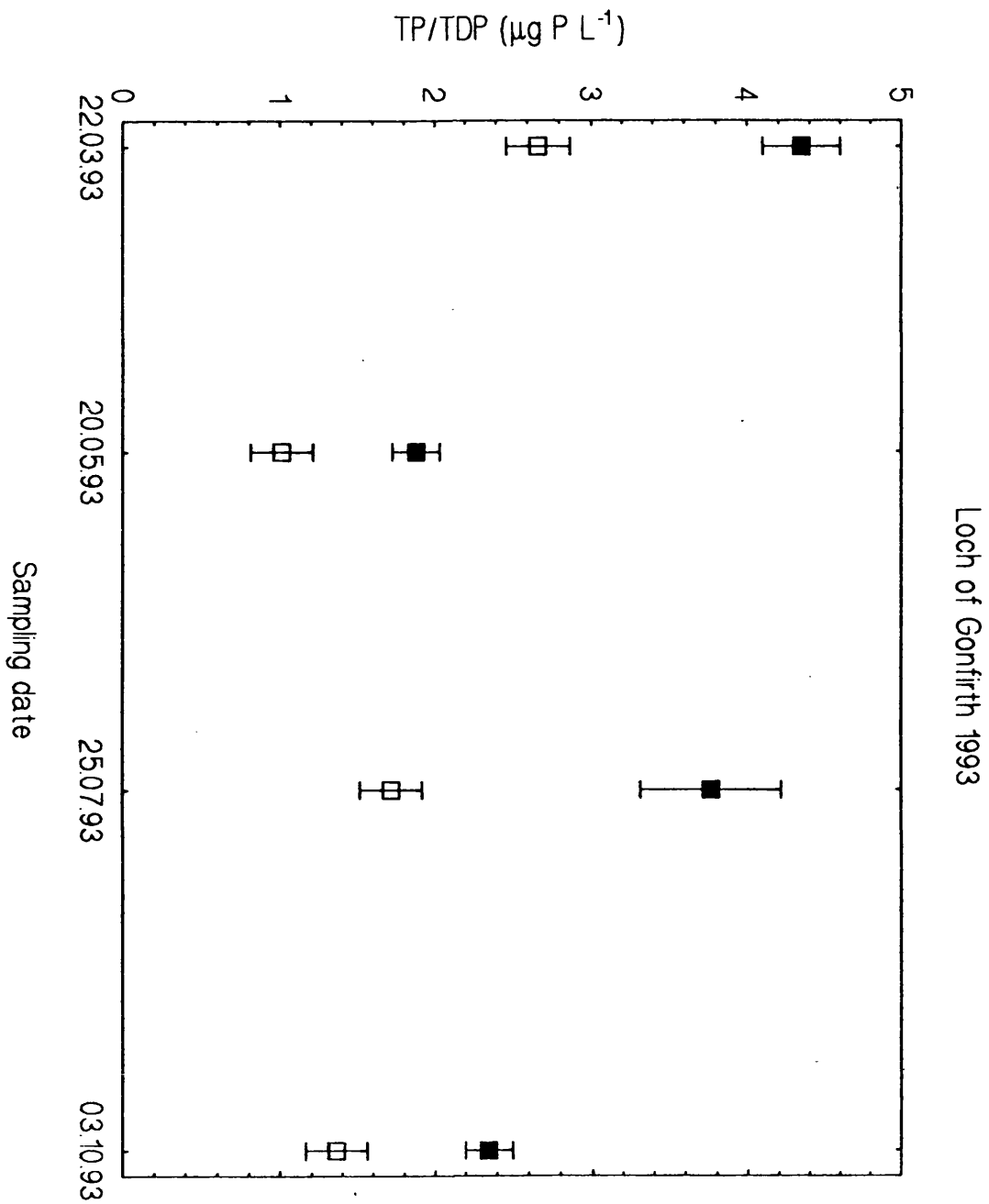


Figure 2.22 Chlorophyll *a* levels in Loch of Gonfirth, 1993 sampling season (n=6)

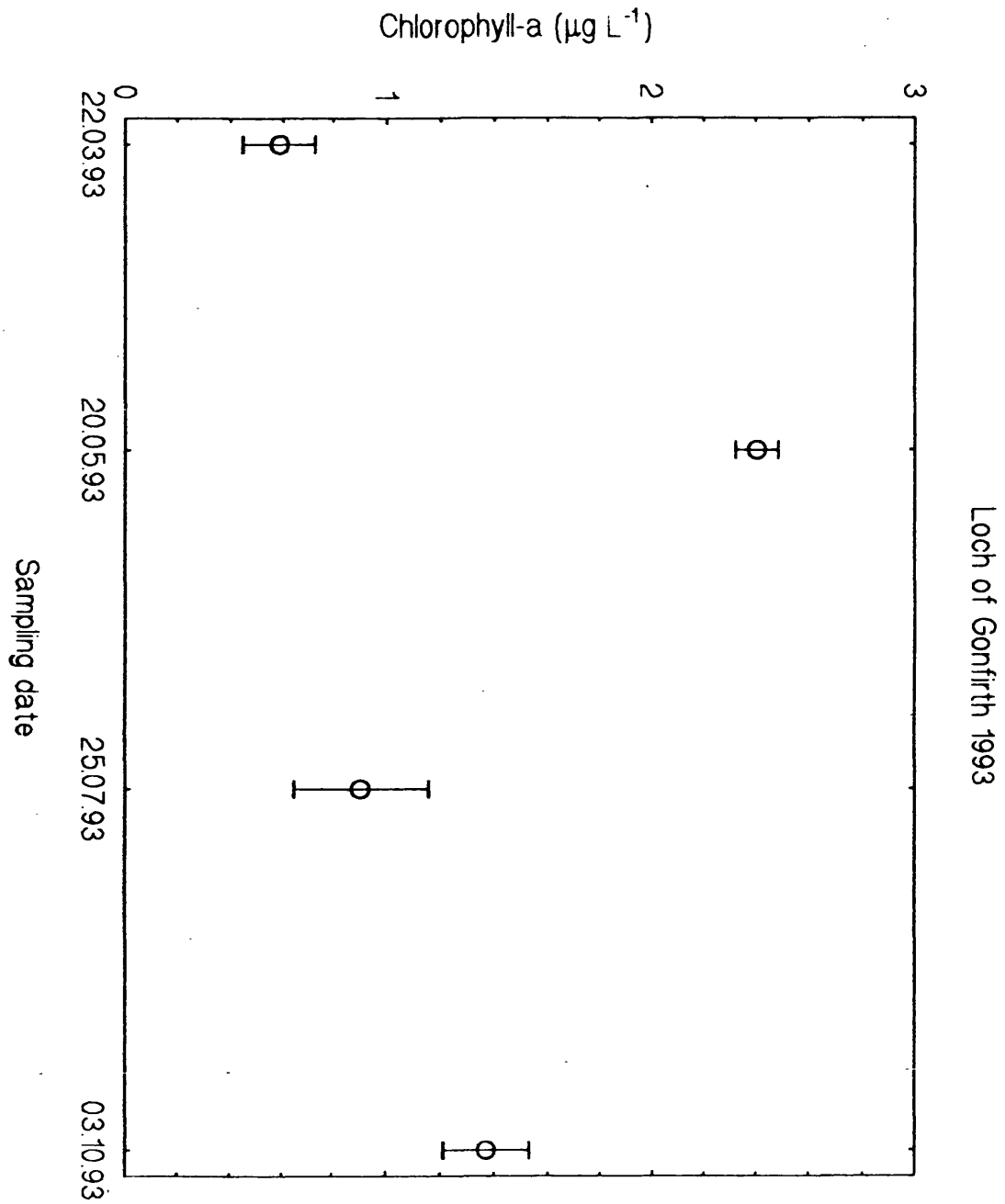


Table 2.15 **Inflow water quality for the five study lochs, 1993** (all data reported in $\mu g\ P\ L^{-1}$)

(site details given on Figure 3.1)

Loch of Gonfirth

	Site	In 1	In 2	In 3	In 4A	In 4B	In 5	In 6
	Date							
	22.03.93							
TP		2.8	4.0	3.4	5.9	4.0	4.0	5.3
TDP		n.s.	4.0	n.d.	4.7	n.d.	2.1	2.8
DRP		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	20.05.93							
TP		2.8	3.4	9.3	4.1	4.1	4.1	8.0
TDP		0.8	0.8	3.4	2.8	2.8	4.1	6.7
DRP		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	25.07.93							
TP		n.s.	n.s.	n.s.	n.s.	n.s.	4.0	6.5
TDP							2.0	4.6
DRP							n.d.	n.d.
	03.10.93							
TP		4.8	5.4	23.8	8.7	8.7	12.0	10.0
TDP		3.4	4.8	14.6	6.7	7.4	11.3	10.0
DRP		n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

Helliers Water

	Site	In 1	In 2	In 3
	Date			
	23.03.93			
TP		2.1	4.7	n.s.
TDP		1.4	2.1	
DRP		n.d.	n.d.	
	23.05.93			
TP		2.1	1.4	n.s.
TDP		1.4	0.8	
DRP		n.d.	n.d.	
	28.07.93			
TP		1.4	3.3	7.2
TDP		1.4	2.0	4.6
DRP		n.d.	n.d.	n.d.
	02.10.93			
TP		3.4	4.1	n.s.
TDP		2.1	2.1	
DRP		n.d	n.d.	

Table 2.15 (cont.)

Sandy Loch

	Site	In 1	In 2	In 3	In 4	In 5	Drain
	Date						
	21.03.93						
TP		48.6	12.8	6.5	15.3	35.4	188.6
TDP		31.6	8.4	6.0	12.2	17.8	181.0
DRP		14.9	n.d.	n.d.	n.d.	n.d.	147.6
	22.05.93						
TP		45.8	n.s.	26.2	n.s.	16.5	98.7
TDP		38.6		12.5		11.2	92.8
DRP		23.4		5.0		n.d.	48.5
	27.07.93						
TP		49.9	35.0	28.6	n.s.	29.2	13.0
TDP		42.2	29.2	18.9		23.4	11.1
DRP		20.2	n.d.	n.d.		n.d.	n.d.
	01.10.93						
TP		90.8	25.1	19.2	n.s.	59.3	73.1
TDP		31.7	9.4	9.4		8.7	38.3
DRP		n.d.	n.d.	n.d.		n.d.	n.d.

Loch of Tingwall

	Site	In 1	In 2	In 3A	In 3B	In 4	In 5	In 6	In 7
	Date								
	24.03.93								
TP		20.3	24.1	21.0	28.5	n.s.	36.0	26.0	36.7
TDP		13.4	16.0	12.8	22.9		10.3	18.5	8.4
DRP		n.d.	n.d.	n.d.	n.d.		1.9	n.d.	n.d.
	21.05.93								
TP		23.0	10.6	n.s.	n.s.	n.s.	16.5	111.7	n.s.
TDP		19.7	7.3				11.9	74.5	
DRP		n.d.	n.d.				n.d.	3.8	
	26.07.93								
TP		n.s.	20.2	n.s.	n.s.	n.s.	n.s.	7416	n.s.
TDP			13.7					n.d.	
DRP			n.d.					4544	
	04.10.93								
TP		64.5	29.7	12.6	n.s.	n.s.	29.1	2430	n.s.
TDP		25.8	17.2	10.0			19.2	2496	
DRP		n.d.	n.d.	n.d.			n.d.	n.d.	

Table 2.15 (cont.)

Turdale Water

Site	In 1	In 2	In 3	In 4	In 5
Date					
24.03.93					
TP	703.2	167.2	318.5	470.4	75.9
TDP	700.1	146.5	305.3	413.3	67.4
DRP	n.s.	120.5	240.2	348.1	42.0
22.05.93					
TP	n.s.	32.8	n.s.	n.s.	21.0
TDP		28.2			11.2
DRP		10.0			n.d.
29.07.93					
TP	n.s.	16.3	n.s.	n.s.	13.0
TDP		12.4			9.1
DRP		n.d.			n.d.
05.10.93					
TP	1254	285	1169	719	167
TDP	1166	259	1077	624	122
DRP	n.s.	n.s.	n.s.	n.s.	n.s.

In all inflows on the west side of the catchment (Inflows 4A, 4B and 5), TP concentrations were 4.1 μg P L^{-1}. In July, only two inflows were of sufficient depth to allow water samples to be taken. Inflow 5 had a concentration of 4 μg P L^{-1}, whilst that of Inflow 6 was 6.5 μg P L^{-1}. Maximum recorded TP concentrations occurred in the October samples. Concentration of TP determined in Inflow 3 water was relatively high at 23.8 μg P L^{-1}. As in March and May, lowest TP concentration of 4.8 μg P L^{-1} was measured in the sample of Inflow 1. As with TP, all inflows exhibited maximum TDP concentrations in the October samples. TDP concentration ranged from 3.4 μg P L^{-1} in Inflow 1 to 14.6 μg P L^{-1} in Inflow 3. In July, TDP levels in the two inflows sampled were 2 μg P L^{-1} and 4.6 μg P L^{-1} for Inflow 5 and Inflow 6 respectively. In samples taken during May, a range of 0.8 μg P L^{-1} (Inflows 1 and 2) to 6.7 μg P L^{-1} (Inflow 6) was observed. The maximum TDP concentration in March, which occurred in Inflow 4A, was 4.7 μg P L^{-1}, although TDP concentrations in Inflows 4B and 1 were the lowest determined, at 2.0 μg P L^{-1}.

2.3.2.6.3 Helliers Water

Average water column TP concentration ranged from 4.9 μg P L^{-1} in the March sample to 8.1 μg P L^{-1} in July. Mean values observed for TP in May and October were similar, concentrations being 6.4 μg P L^{-1} and 6.9 μg P L^{-1} respectively (Figure 2.23). Water column TDP levels did not follow TP concentrations, minimum TDP concentration occurring in May (1.2 μg P L^{-1}), maximum in October (3.4 μg P L^{-1}). Concentrations in March and July were 2.0 μg P L^{-1} and 2.9 μg P L^{-1} respectively. In all samples collected, DRP concentration was $<$ 1 μg P L^{-1} (Figure 2.23). In March, lowest mean water column chl *a* concentration of 2.0 μg chl *a* L^{-1} was detected. Subsequently chl *a* content rose to 3.2 μg chl *a* L^{-1} in May (Figure 2.24). Greatest mean chl *a* concentration of 5.4 μg chl *a* L^{-1} was recorded in the October sample, levels having risen since July, when water collected was found to contain, on average, 2.6 μg chl *a* L^{-1}. Maximum mean concentrations of TP and chl *a* did not coincide, although minimum values did, and maximum TDP concentration was concurrent with that of chl *a*.

Figure 2.23 Phosphorus levels in Helliers Water, 1993 sampling season (n=3)

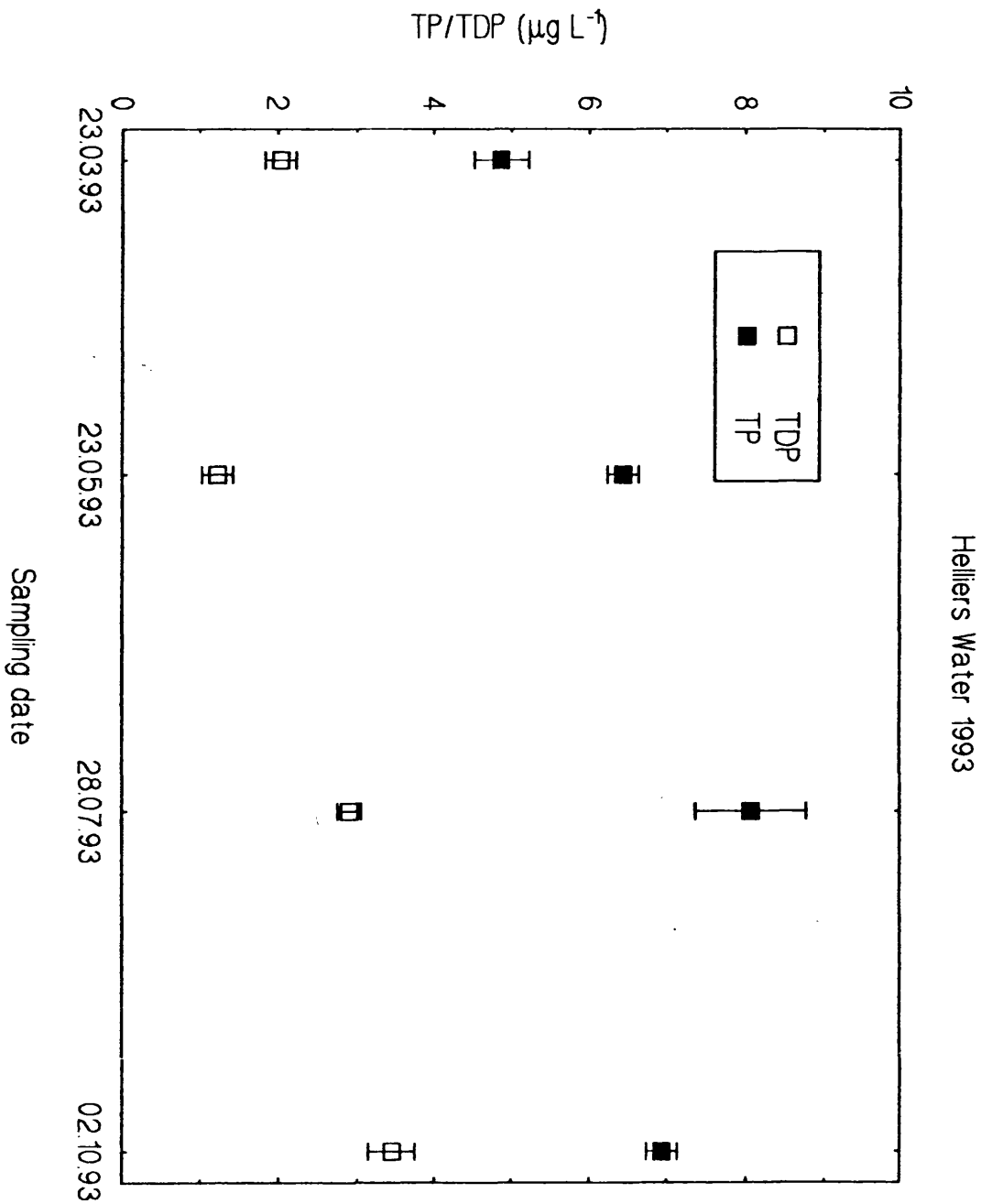
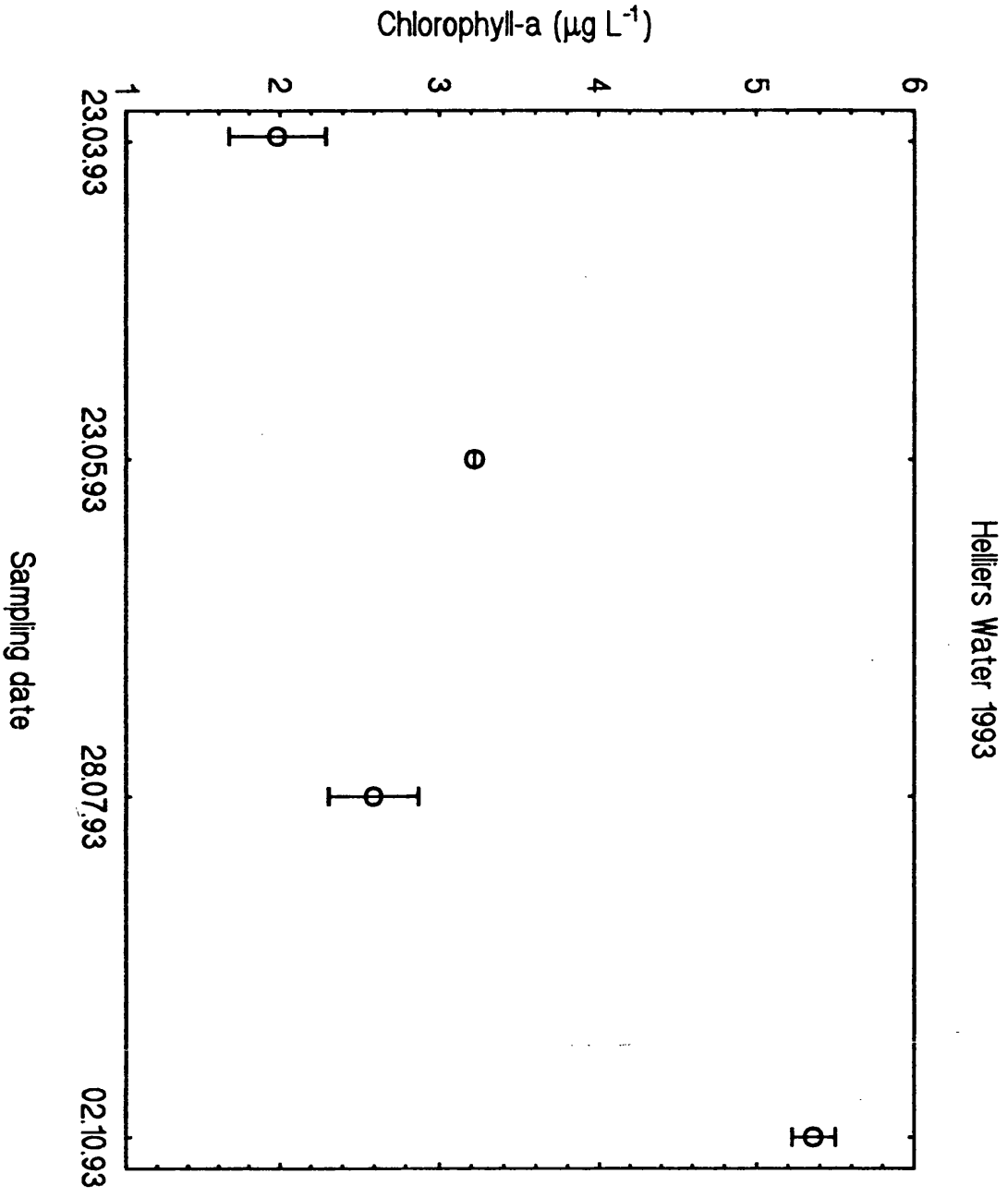


Figure 2.24 **Chlorophyll *a* levels in Helliers Water, 1993 sampling season (n=3)**



2.3.2.6.4 Helliers Water inflow samples (Table 2.15)

Maximum concentrations of both TP and TDP were found in water from Inflow 3 *i.e.* from Loch of Watlee during July. Levels of P determined were 7.2 μg TP L^{-1} and 4.6 μg TDP L^{-1}. Lowest recorded TP concentration was 1.4 μg P L^{-1} in samples from Inflow 1 and Inflow 2 in July and May respectively. Minimum TDP concentration (< 1.0 μg P L^{-1}) was also detected in Inflow 2 in May. Peak TP and TDP levels were determined for Inflows 1 and 2 in water collected in October. Analyses found DRP to be < 1 μg P L^{-1} in all inflow water samples.

2.3.2.6.5 Loch of Tingwall

TP concentration in Loch of Tingwall was greatest during March, with a mean water column concentration for both basins combined of 13.3 μg P L^{-1}. Average TP in the South basin decreased from 12.3 μg P L^{-1} in March to 8.8 μg P L^{-1} in October, whilst that of the North basin exhibited a maximum of 14.6 μg P L^{-1} in March and a minimum of 9.6 μg P L^{-1} in May. Mean water column TP concentration then showed a secondary peak in the North basin of 13.5 μg P L^{-1} in July, before falling to 10.5 μg P L^{-1} in October (Figure 2.25). Average TDP concentration for both basins combined was greatest in March at 6.9 μg P L^{-1} and lowest in May at 4.4 μg P L^{-1}. In the North basin, TDP maximum concentration (8.0 μg P L^{-1}) occurred in July, having risen from the minimum (4.2 μg P L^{-1}) in May. In the South basin, TDP ranged from 6.9 μg P L^{-1} in March down to 5.4 μg P L^{-1} in May. All determinations of water column DRP concentration were < 1 μg P L^{-1} (Figure 2.25). Mean chl *a* concentration for both basins combined ranged from 11.2 μg chl *a* L^{-1} in March down to 2.6 μg chl *a* L^{-1} during October (Figure 2.26). Considering the basins separately, average water column chl *a* concentration in the North basin decreased from 10.7 μg chl *a* L^{-1} in March to 3.6 μg chl *a* L^{-1} in October. That of the South basin decreased from 11.6 μg chl *a* L^{-1} in March to 3.5 μg chl *a* L^{-1} in May. A small peak of 5.3 μg chl *a* L^{-1} occurred in July, before levels declined to the minimum of 2.0 μg chl *a* L^{-1}.

2.3.2.6.6 Loch of Tingwall inflow waters (Table 2.15)

Water collected from Inflow 6 had the highest concentration of TP, TDP and DRP from May onwards. Maximum concentration of TP recorded for a sample of a Loch of Tingwall inflow was 7.42 mg P L^{-1}. This was determined in water collected from Inflow 6 in July.

Figure 2.25 Phosphorus levels in Loch of Tingwall, 1993 sampling season (n=10)

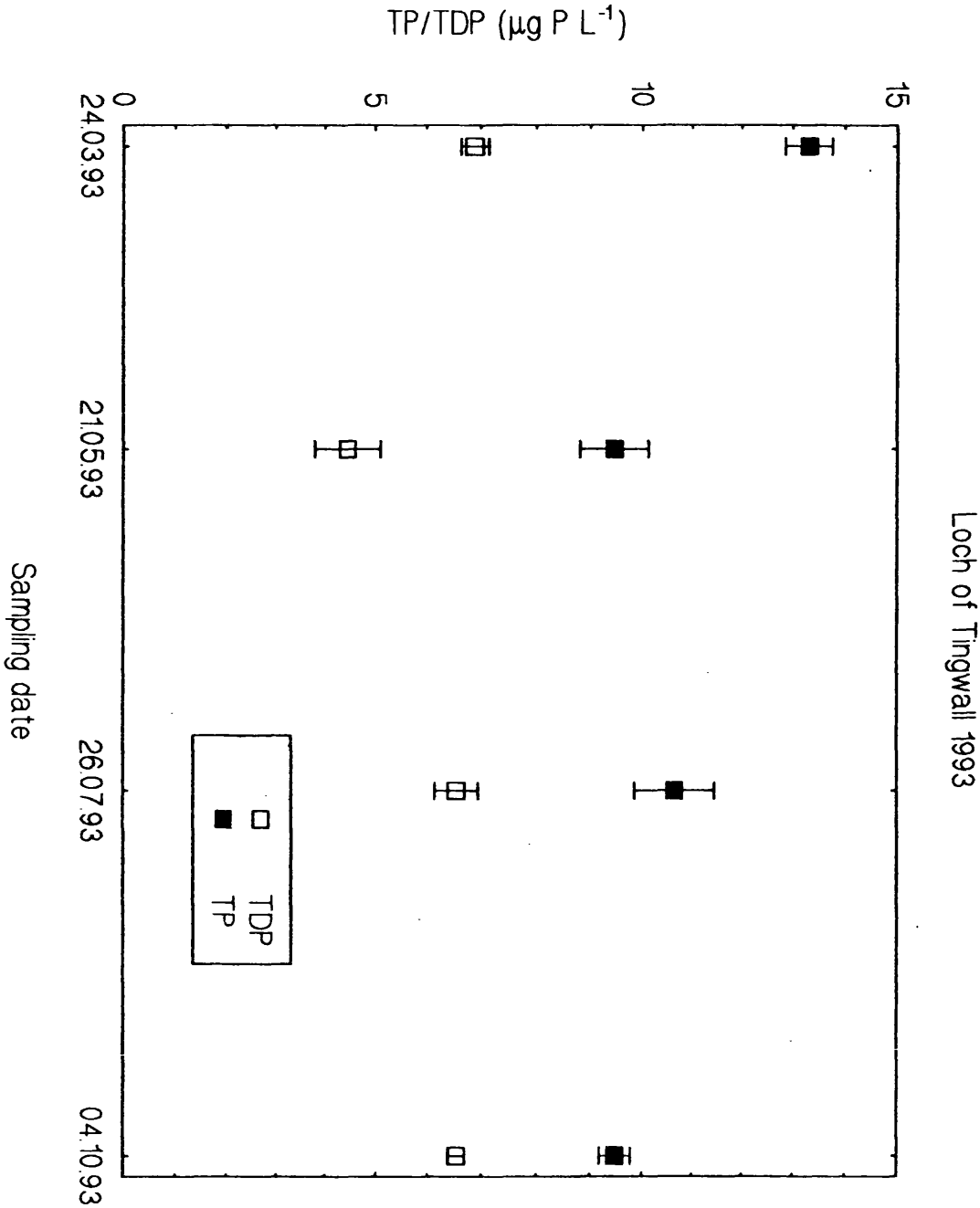
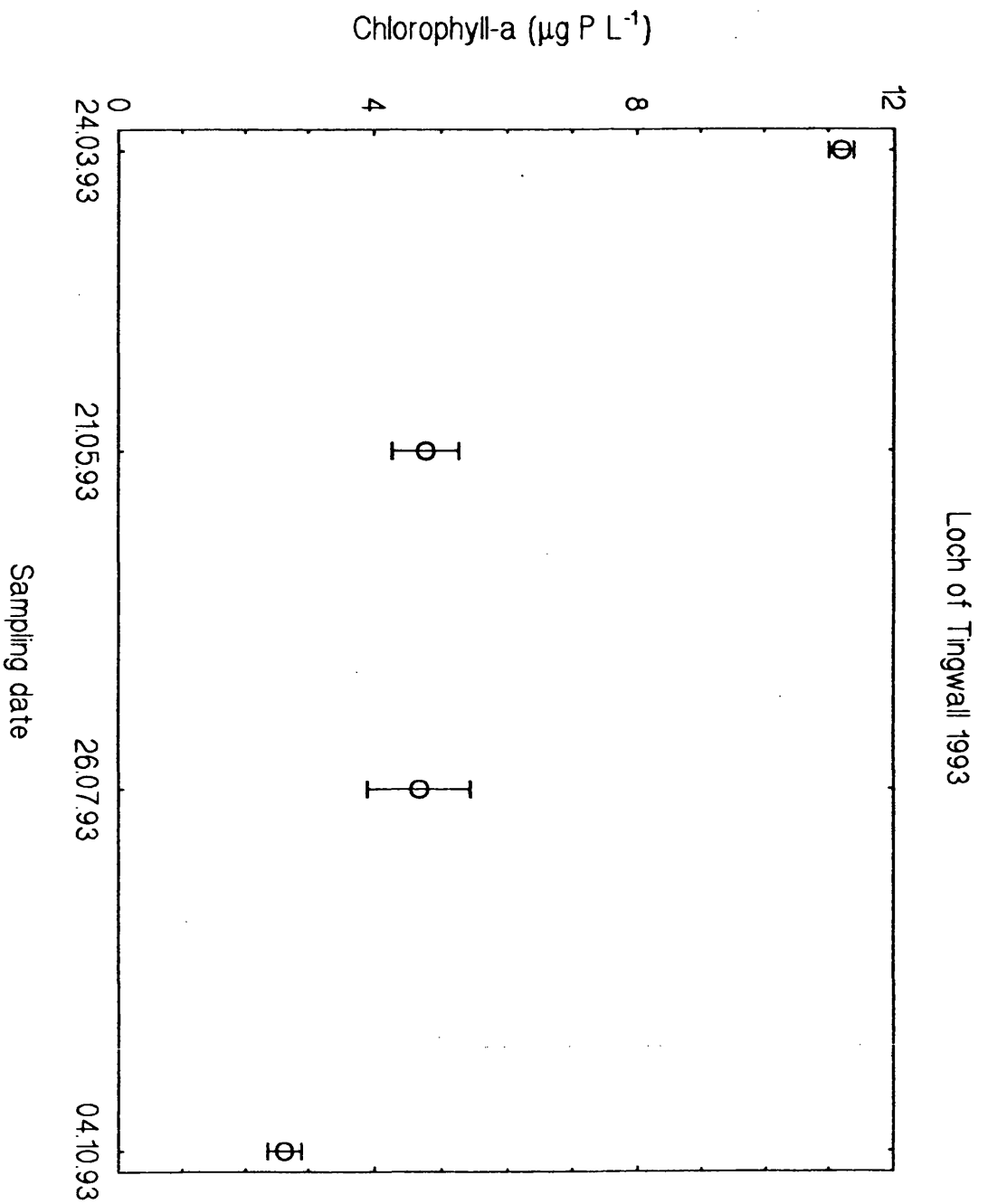


Figure 2.26 Chlorophyll *a* levels in Loch of Tingwall, 1993 sampling season (n=10)



Greatest TDP and DRP concentrations were also measured in this sample, accounting for 6.97 mg P L^{-1} and 4.54 mg P L^{-1} respectively. The lowest concentration of TP, 10.6 μg P L^{-1}, was found in the Inflow 2 sample taken in May. Minimum TDP concentration of 7.3 μg P L^{-1} was also found in this sample. DRP concentration was found to range from $<$ 1 μg P L^{-1} in all samples except those of Inflow 5 (24/03/93) and Inflow 6 (21/05/93, 26/07/93, 04/10/93).

2.3.2.6.7 Sandy Loch

The range of mean water column TP concentrations determined in Sandy Loch was from 33.7 μg P L^{-1} in March down to 21.0 μg P L^{-1} in May. Average water column TP levels then increased to 24.2 μg P L^{-1} in July and 27.7 μg P L^{-1} in October (Figure 2.27). In contrast, greatest TDP concentrations were found in the samples from July and October, levels reaching 20.6 μg P L^{-1} and 20.3 μg P L^{-1} respectively. From a mean water column TDP concentration of 17 μg P L^{-1} in March, TDP decreased to the minimum recorded level of 14.5 μg P L^{-1}. DRP concentration in all samples collected were $<$ 1 μg P L^{-1} (Figure 2.27). Minimum average water column chl *a* concentration was found in March, 4.9 μg chl *a* L^{-1} being measurable in the water analysed. Chl *a* levels then increased to 7.6 μg chl *a* L^{-1} in May. Highest recorded mean chl *a* concentration was 8.7 μg chl *a* L^{-1} during July, decreasing little to 8.4 μg chl *a* L^{-1} in October (Figure 2.28).

2.3.2.6.8 Sandy Loch inflow waters (Table 2.15)

During each sampling date, concentrations of TP, TDP and DRP were greatest in water from Inflow 1, with the exception of DRP in October, as it was $<$ 1 μg P L^{-1} in all inflows. DRP was detectable in Inflow 1 only, greatest recorded concentration being 23.4 μg P L^{-1} in May. Maximum TP concentration of 90.8 μg P L^{-1} was recorded in October, the lowest inflow concentration occurring in March, when 6.5 μg P L^{-1} was present in Inflow 3. In contrast, highest TDP concentration (42.2 μg P L^{-1}) was found in July in Inflow 1, though the lowest concentration (6.0 μg P L^{-1}) coincided with that of TP in Inflow 3. Water in a drain to Inflow 1 from the land in the north east of the catchment area exhibited levels of TP ranging from 13.0 to 188.6 μg P L^{-1}. A high proportion of the TP concentration was in the dissolved fraction, the levels of which ranged from 11.1 to 181.0 μg P L^{-1}.

Figure 2.27 Phosphorus levels in Sandy Loch, 1993 sampling season (n=3)

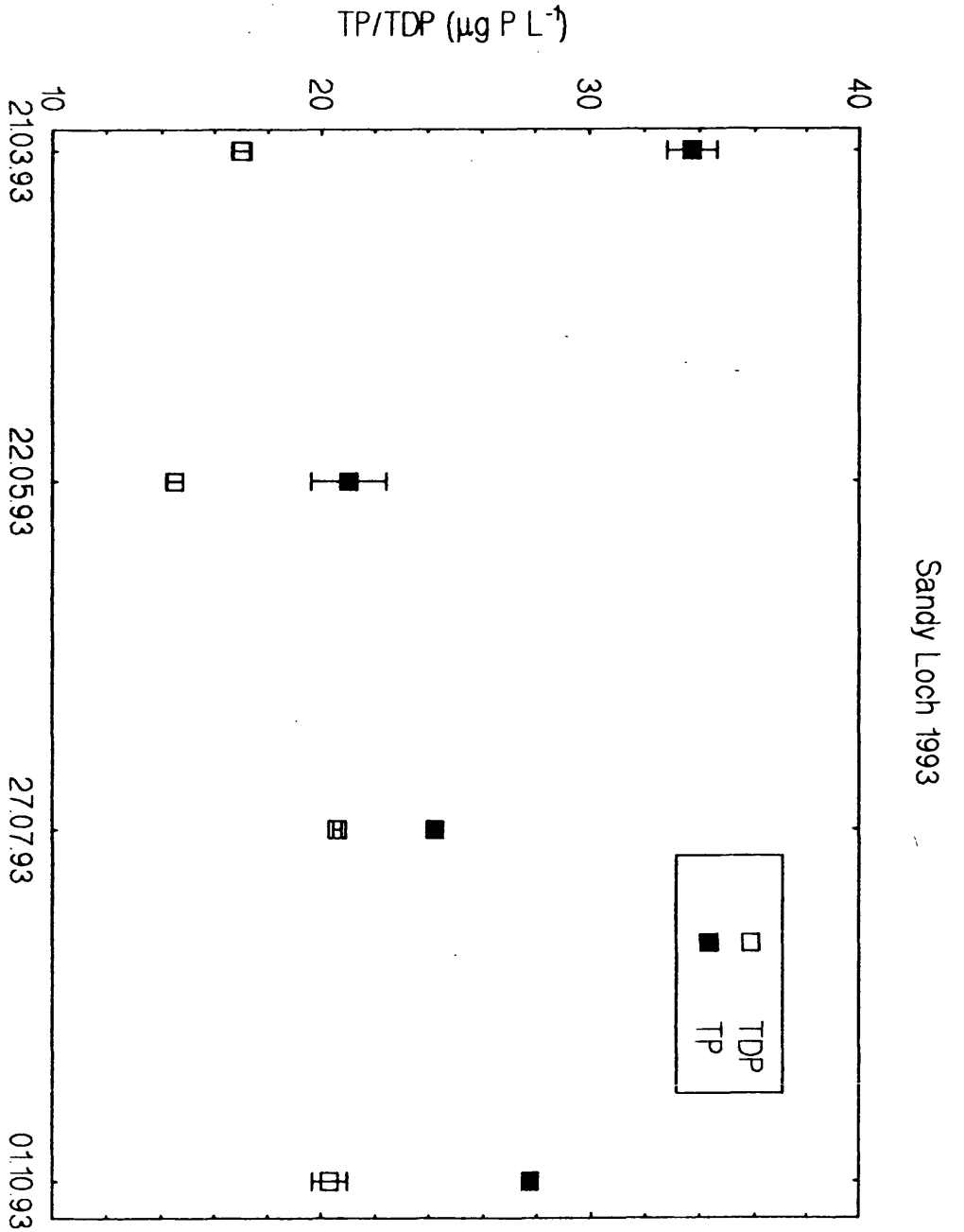
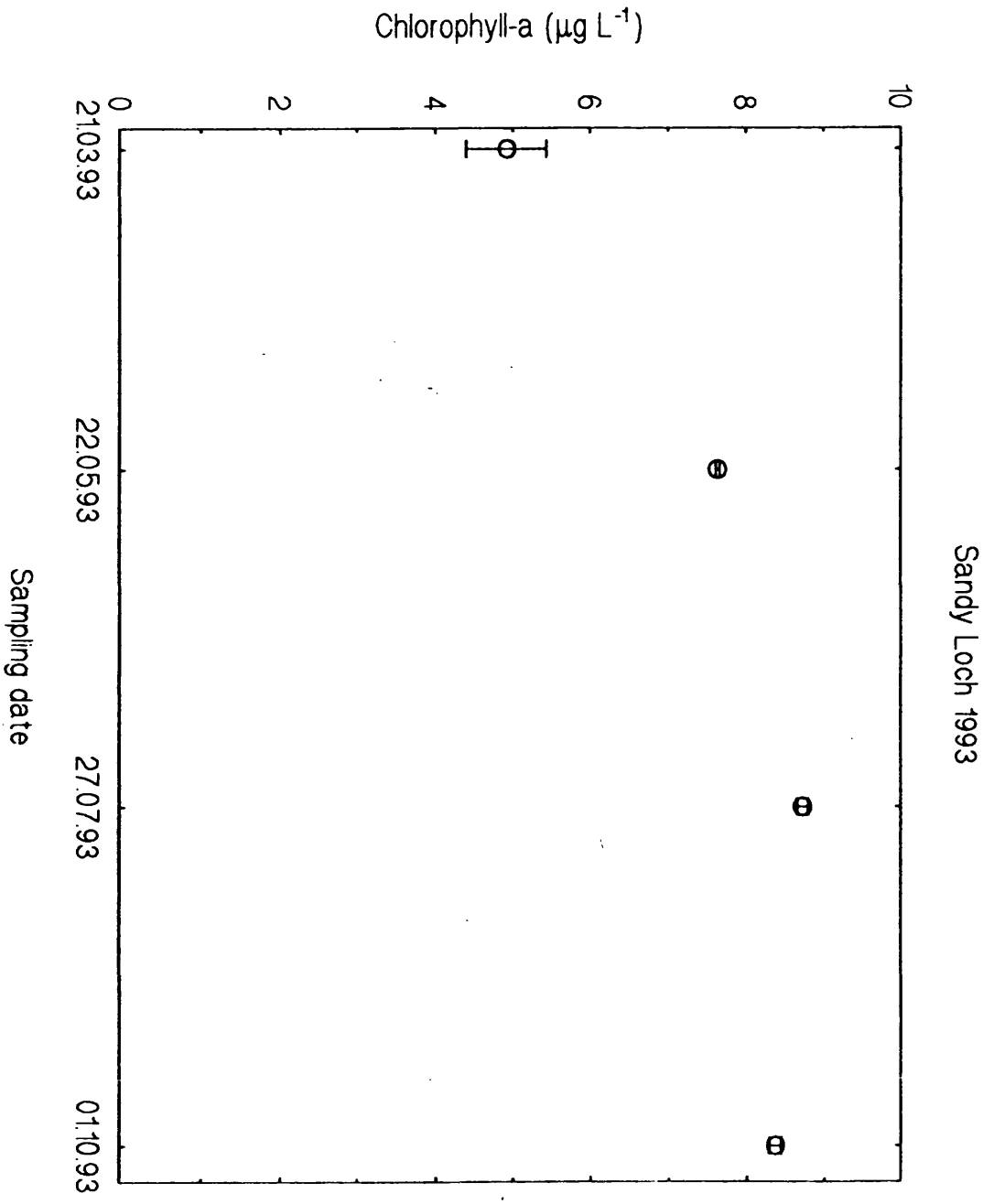


Figure 2.28 Chlorophyll *a* levels in Sandy Loch, 1993 sampling season (n=3)



2.3.2.6.9 Turdale Water

Mean water column TP concentration was at its maximum of 250.5 μg P L^{-1} during March. Thereafter it decreased to 124.1 μg P L^{-1} in May and 34.6 μg P L^{-1} in July, before rising to 43.7 μg P L^{-1} in October (Figure 2.29). TDP followed a similar pattern to TP, maximum mean water column concentration of 88.8 μg P L^{-1} occurring in March, falling to 25.8 μg P L^{-1} during May. TDP remained at similar concentrations of 23.4 μg P L^{-1} and 23.8 μg P L^{-1} in July and October respectively. Like TP and TDP, greatest average DRP concentration was detected in the water column in March. During May and October, DRP levels decreased to < 1 μg P L^{-1}, but a second peak occurred during July, when DRP was present at 4.5 μg P L^{-1} (Figure 2.29). Mean water column chl *a* concentration in March samples was 24.4 μg chl *a* L^{-1}. This increased to 100 μg chl *a* L^{-1} in May, decreasing thereafter to 6.9 μg chl *a* L^{-1} in July. Levels were slightly increased in the October samples, mean chl *a* concentration accounting for 8.7 μg chl *a* L^{-1} (Figure 2.30).

2.3.2.6.10 Turdale Water inflow waters (Table 2.15)

Greatest TP and TDP concentrations were determined as 1.25 mg P L^{-1} and 1.17 mg P L^{-1} respectively in Inflow 1 during October. Minimum concentrations of TP (13 μg P L^{-1}) and TDP (9.1 μg P L^{-1}) were measured in the sample taken from Inflow 5 in July. DRP concentrations ranged from < 1 μg P L^{-1} (Inflow 2, 29/07/93; Inflow 5, 22/05/93; Inflow 5, 29/07/93) to 669.4 μg P L^{-1} (Inflow 1, 24/03/93).

2.4 DISCUSSION

2.4.1 The suitability of the techniques used in water analysis

2.4.1.1 Filtration of water samples

A sample volume of up to 2 L was filtered to ensure that at least 1 μg chl *a* was retained on the filter paper (Stirling, 1985), in order to achieve meaningful estimates of phytoplankton biomass (Stockner *et al.*, 1990). Samples were filtered within 24 hours of collection in order to minimise degradation processes in suspended matter, including phytoplankton, and consequent release of dissolved nutrients to the water sample. Storage of algae overnight at ≤ 5°C can result in significant release of orthophosphate (Fitzgerald and Faust, 1967).

Figure 2.29 Phosphorus levels in Turdale Water, 1993 sampling season (n=3)

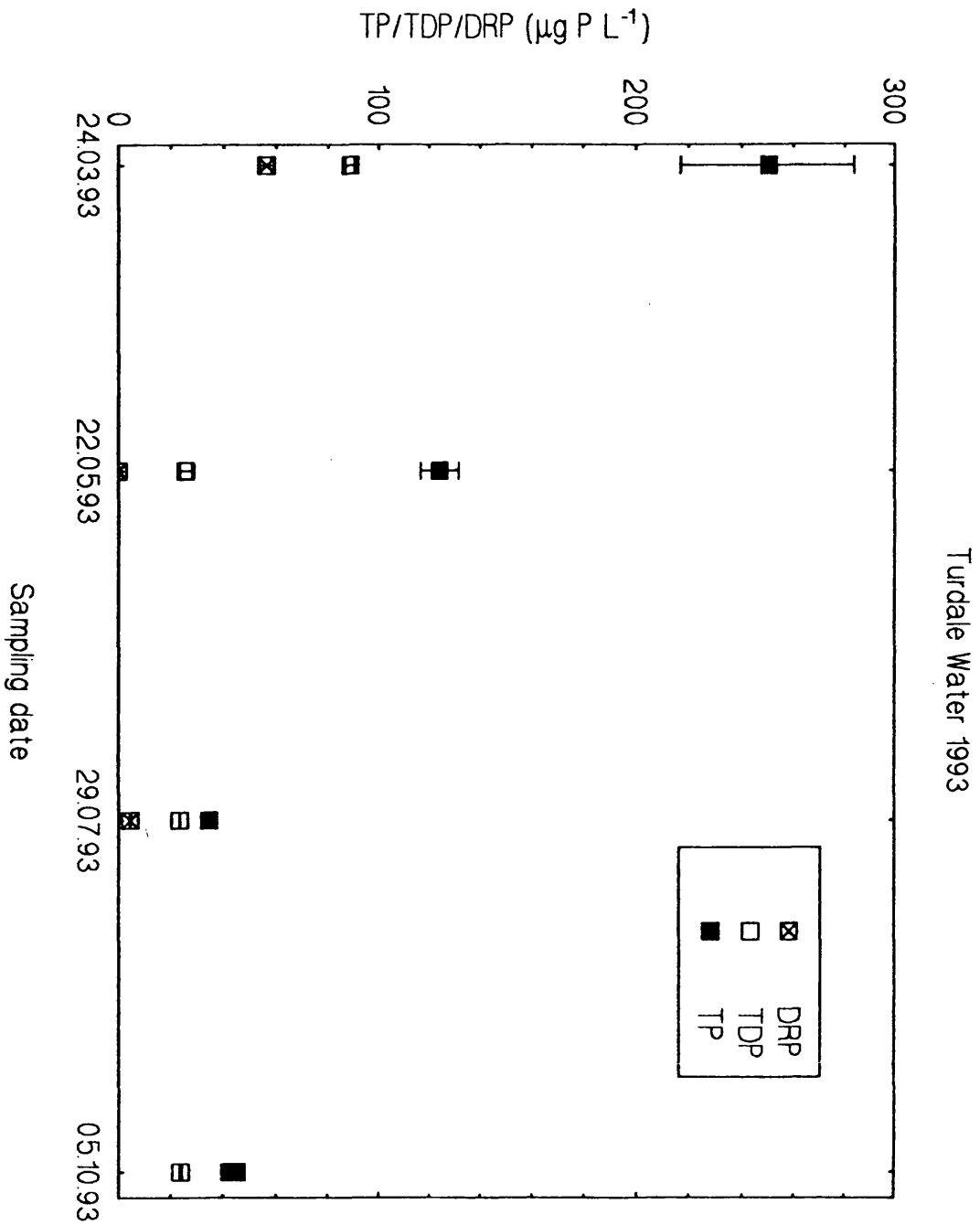
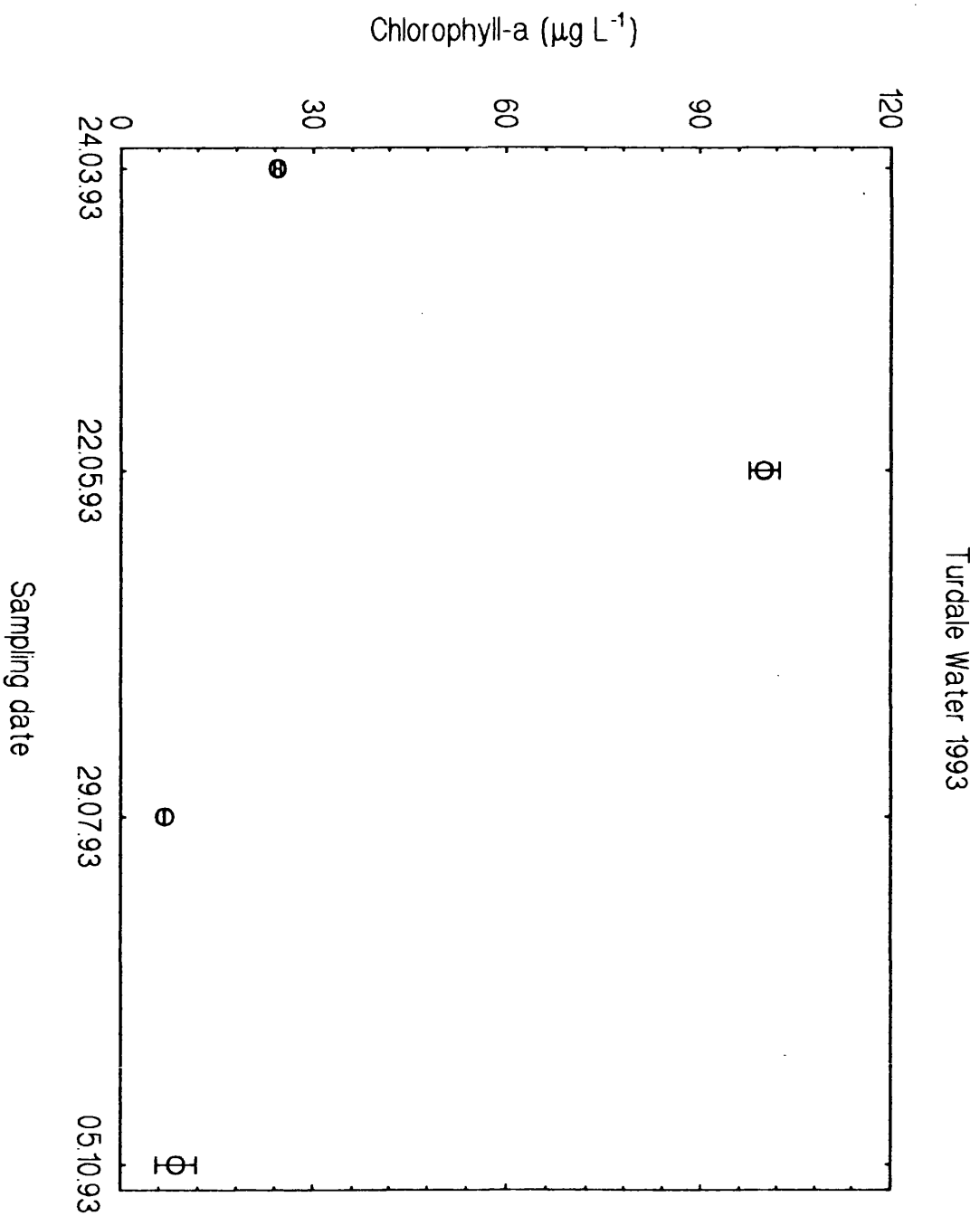


Figure 2.30 Chlorophyll *a* levels in Turdale Water, 1993 sampling season (n=3)



Choice of filter paper is extremely important as it defines what is measurable in the filtrate. Of particular importance are the filter aperture size, the speed at which water can pass through the filter and a lack of contamination effects. In the 1991 field season, use of 0.45 μm cellulose nitrate filters was recommended (Pulford and Flowers, University of Glasgow, *pers. comm.*). However, for a number of reasons detailed below, GF/C 1.2 μm papers were used thereafter. Filter papers may 'leak', as aperture size is rarely constant and may be larger than the pore size stated, in glass fibre, cellulose nitrate and cellulose acetate varieties (Stockner *et al.*, 1990). Initial leakage from GF/C 1.2 μm papers is reduced as holes clog, whereas filtering with 0.45 μm filters is not practical for large volumes of water as pores block completely. The 1.2 μm papers filter water at a faster rate and recover the same amount of chl as 0.45 μm membrane filters from a variety of waters (Holm-Hansen and Riemann 1978). Vacuum pressure used during filtration is an important determinant of size of particle retained on a filter paper. Low pressure filtration minimises "drag through" or lysis of cells. Cell damage during filtration can cause elevated levels of dissolved nutrients in the filtrate (Rigler, 1968). There is therefore an error involved in employment of vacuum filtration apparatus, when using GF/C or 0.45 μm membrane filters.

Cellulose nitrate filters have been shown to exhibit significant leaching of DRP and to increase TDP concentration in filtrate, despite prewashing of the filters with 250 mL distilled water. Cellulose acetate papers are reported to generate almost no leaching, whilst GF/C papers demonstrate only a small leaching effect within the error range of the P analysis (Bloesch and Gavrielli, 1984). Cellulose nitrate papers should not be used if determinations of dissolved nitrogen compounds are intended, as they may cause contact contamination (HMSO, 1982b). In addition to these problems, membrane filters dissolve in alcohol, producing turbidity in chl extracts and consequent difficulties in determination.

It is recognised that filter pore sizes in normal use (> 0.4 μm) are inadequate in their separation of particulate and dissolved fractions in natural waters, especially those of high colloidal content such as bog, forest, or estuarine waters (Danielsson, 1982). It was concluded that although both 0.45 μm and 1.2 μm filters are likely to undertrap particulate matter, operational disadvantages associated with the membrane filters

made them unsuitable for this investigation. Ease of filtration with GF/C papers is extremely important when time available for field work is restricted. The same filter papers should obviously be used for chl *a* retention as for obtaining filtrate for determination of dissolved parameters, so allowing direct comparison of the different variables measured.

2.4.1.2 Storage of water samples

Deterioration of water samples stored frozen occurs as a result of two main processes **(a)** exchanges of determinands to and from container walls and **(b)** transport of elements from ice to the air cavity within each bottle. P and N are affected primarily by these processes (APHA, 1989) respectively. No reliable method of preservation of water samples for N analysis is known (HMSO, 1982b), therefore it is possible for N compounds measured to be different to actual concentrations. However, freezing should minimise processes of conversions between different N compounds such as TAN and TON (denitrification and nitrification). Samples were retained in a freezer separate from those containing sediment, soil, plant matter or animal remains in order to minimise possibility of N uptake through the ice surface. Owing to the relatively low levels of inorganic nitrogen compounds present in the samples and the rapidity of freezing after filtration, any changes in concentrations of TON and TAN were likely to have been small (Avanzino and Kennedy, 1993).

Ideally, glassware should be used for transport and storage of water samples for TP analysis. However, cost and distance travelled made this option impractical during field work. By treating the polyethylene bottles used for P samples with iodine, the problem of phosphorus exchange with container walls was considerably reduced (HMSO, 1981). Dissolved samples for DRP and TDP analyses were stored frozen in polyethylene bottles. In waters low in P, significant changes in P concentration may occur after only a few weeks (Phillips, 1985a). However, freezing has been shown to be an effective short-term means of preserving samples for P analyses (Avanzino and Kennedy, 1993) and samples were analysed promptly on return to the laboratory.

Interference with sample Na and K concentrations was minimised by storage in polythene bottles. Small containers such as the 50 mL bottles used minimise the area available for pick up of metals on container walls. It is also useful to retain water

samples for Na analysis in plastic bottles, as it is possible for contamination to occur under alkaline or low Na conditions because of leaching from glassware. Shaking the bottle promotes solution of Na and K attached to the container walls (APHA, 1985), in addition to ensuring the sample is well mixed before analysis.

2.4.1.3 Measurement of pH and DO

Owing to the processes of plant respiration and photosynthesis, in productive waters, both pH values and dissolved oxygen levels may change significantly within any twenty four hour period. In darkness, pH and dissolved oxygen concentrations would tend to be lower than during daylight. Therefore, the pH and dissolved oxygen results recorded in the present study may not have been representative of the range of values which occurred during each day of sampling. In contrast, in unproductive waters, there is likely to have been relatively little variation in pH and dissolved oxygen levels throughout the day.

2.4.1.4 Measurement of conductivity

Conductivity is related to the total ionic concentration of a water sample and is a measure of the ability of a solution to conduct an electric current (Mackereth, 1963). However, when making comparisons of conductivity between different water bodies, it is important to consider that the relationship between conductivity and ionic content is dependent on the types and relative amounts of the dominant ions present.

2.4.1.5 Determination of alkalinity

Alkalinity is a measure of the buffering capacity of the water *i.e.* its ability to withstand pH changes. It represents the combined concentrations of anions of weak acids, principally bicarbonate and carbonate in natural freshwaters. The 0.01 M HCl used in titration contained 0.01 meq acid per mL as 0.01 M HCl equals *N*/100. Therefore each mL of standard acid used in titration corresponds to 0.01 meq HCO_3^- per 100 mL sample. Alkalinity is therefore an important indicator of the free CO_2 status of a water body, along with pH. However, extrapolation of free CO_2 from alkalinity and pH measurements is not precise in waters in which free mineral or organic acids are present (Mackereth, 1963). A buffer solution of sodium acetate and acetic acid for the purpose of colour standardisation (Mackereth, 1963) was not used in the present study, as water from each loch had a different initial colour which

would affect the end point hue. Results were expressed in terms of HCO_3^- rather than $CaCO_3$ as the latter "has no basis in reality" (Mackereth, 1963). Results were also represented in chemical equivalents as asserting alkalinity in terms of molarity or mass concentration is inappropriate owing to its variable molecular basis (Stirling, 1985).

2.4.1.6 Techniques of measurement of TON and TAN concentrations

"By far the best method for analysis of nitrate nitrogen in water is to reduce the nitrate in alkaline-buffered solution to nitrite by passing the sample through a column of copperized cadmium metal filings" (Wood *et al.*, 1967, in: Wetzel and Likens, 1990). The cadmium-copper column method gives precise and quantitative results (Phillips, 1985a) and the method is suitable for freshwater and waters of higher salt content (Table 2.16). Two methods are generally used in the spectrophotometric determination of TAN; one is based on phenol chemistry, the other on salicylate reactions. When undertaking ammonia analyses using the phenol-hypochlorite method, the hypochlorite stock solution may not be reliable throughout the period of analysis. In contrast, the salicylate method used in the present study allows generation of hypochlorite *in situ*. HMSO (1982a) define the salicylate method as the preferred technique (except in the analysis of saline waters) owing to the greater reagent stability and efficacy of analysis using less hazardous chemicals. When considering safety regulations (COSHH), there is also an obligation to use the cadmium method as risk assessment reveals hydrazine to be potentially more harmful, being more toxic and carcinogenic.

2.4.1.7 Phosphorus determination

Methods involving formation of yellow vanadomolybdophosphoric acid are less sensitive than those relying on reduction of molybdophosphoric acid to a molybdenum blue complex (Allen *et al.*, 1974). In addition, it is advantageous to use ascorbic acid as a reducing agent for P determination as the resultant blue colour is more stable than that obtained using stannous chloride (Murphy and Riley, 1962) and precision is improved using the former (Strickland and Parsons, 1972). The accuracy of the technique is enhanced by using 4 cm cells rather than 1 cm cells owing to the applicability of spectrophotometric principles of the Beer-Lambert Laws.

Table 2.16 Reported methods and ranges of detection for two nitrate determination methods

Hydrazine method	Cadmium method	Source
Concentration range ($\mu g\ L^{-1}$)		
10-10,000		APHA (1985)
50-260	≥ 1.3	HMSO (1981)
≥ 14		Hilton and Rigg (1983)
	≥ 1.5	Nakashima *et al.* (1984)
	2-100	Gaugush and Heath (1984)

Throughout this study, absorbance was read at 690 nm, the secondary absorbance peak of this method, as antimony in the colour development reagent may absorb light at 882 nm (Murphy and Riley, 1962).

Over estimation of DRP may occur using the molybdenum blue complex technique of determination, possibly because of acid breakdown of easily hydrolysable organic P compounds (Rigler, 1968). The extent of this error will depend on the characteristics of each water sample. DRP determination using this method is therefore actually molybdate reactive P and should not be referred to as orthophosphate (Broberg and Pettersson, 1988).

A method similar to that of this study (APHA, 1985) shows no interference up to 50 mg Fe^{3+} L^{-1}, 10 mg SiO_2 L^{-1} and 10 mg Cu L^{-1} over the analytical range 0.001-10 mg P L^{-1}. Avoidance of positive interference from silicate in P recovery occurs when the acid:molybdate ratio is 4:1 (Murphy and Riley, 1962). Although good recoveries of P are possible from some inorganic salts or sugar phosphate compounds using only an acid digest, in order to estimate total P in a water sample, it is necessary to incorporate persulphate as an oxidising agent (Broberg and Pettersson, 1988). The quantity of persulphate added to each sample is optimized to ensure complete oxidation of the sample, but a minimum residual (Gales *et al.*, 1966).

2.4.1.8 Choice of methods for chlorophyll *a* determination

Absorption characteristics of chl *a* in methanol are not well known and chl *a* is less stable in methanol than in acetone (HMSO, 1983). Chl *a* determinations made with acetone are reproducible *i.e.* precision is good. However, methanol is the more efficient solvent and therefore provides more accurate estimates of actual chl *a* concentrations. Although grinding and maceration of sample is required when using acetone, these procedures are unecessary if methanol is the solvent used (Marker, 1972). Extraction efficiency of methanol may be improved further by heating it to near its boiling point of 64°C (HMSO, 1983). An efficient solvent is particularly important when samples include members of the Chlorophyceae and Cyanophyceae, which are especially resilient to extraction procedures (Bailey-Watts, 1978).

Acidification of chl *a* causes break down to phaeophytin, therefore magnesium

carbonate was added to the methanol, in order to neutralise it before use. Breakdown products of chl *a* have visible absorption spectra similar to those of chl *a* and therefore constitute a possible source of error (Moss, 1967). A correction for phaeophytin interference was used in this work. In large lake systems, phaeophytin levels in the water column are negligible (Bailey-Watts, 1978). However, the lochs of Shetland are shallow and decay products could easily be resuspended from sediments by wind mixing. Phaeophytin concentrations may also be elevated if an algal bloom is in decline (Nusch, 1980). As phaeophytin absorbs light at 665 nm, the sample is acidified to convert chl *a* to phaeophytin, so that by subtraction, the initial concentration of phaeophytin can be calculated. However, neutralisation is necessary to prevent further degradation to *e.g.* chlorophyllide and phaeophorbide (HMSO, 1983). Neutralisation of 100% methanol with $MgCO_3$ after acidification is impractical. An organic base solution was used for the Shetland work because other degradation products such as chlorophyllide and phaeophorbide become absorbed when using $MgCO_3$ (HMSO, 1983).

Extraction with alcohol, followed by spectrophotometric determination of chl *a* concentration, can only be an estimate of actual levels in the water column. When chlorophyllase is present in decomposing cells, both chlorophyllide and phaeophorbide will be present in addition to phaeophytin. It is probable that spectrophotometric investigations cannot distinguish these products from each other (Marker, 1972). Routinely used fluorometric and spectrophotometric techniques are unable to partition chl *a* from its break down products (Jacobsen *et al.*, 1988). Although fluorometric analysis is more sensitive than spectrophotometric measurement, there are still problems concerned with distinguishing between different pigments and detection performance is related to excitation energy combined with the optics of each particular instrument (Jacobsen *et al.*, 1988). Limit of detection is determined by the characteristics of the spectrophotometer used and commonly approximates to 1 μg chl *a* L^{-1} (Nusch, 1980).

2.4.2 Comparison of water chemistry of Shetland lochs with those of other studies

2.4.2.1 pH

The range of pH values in Shetland lochs exhibits higher extremes than those in the

literature (Table 2.17). Lowest mean summer pH was pH 5.49 in Gorda Water, the minimum individual reading of pH 5.09 occurring in this loch. In contrast, several surveys of lochs in mainland Scotland have shown water bodies to have pH < 5. Waters in Tayside (Maitland and Morris, 1981), Sutherland (Bell, 1991), the Inner Hebrides (Maitland and Holden, 1983) and Scottish lochs generally (Phillips, 1985b; Harriman and Pugh, 1994) all included such acid water bodies (Table 2.17). The minimum pH value observed in 643 freshwater lochs in Scotland was 4.09 (Harriman and Pugh, 1994). Lochs studied in the Outer Hebrides had a minimum pH of 5, this being most similar to the lowest values in the Shetland study. Possibly this similarity exists owing to the more exposed nature of the Outer Hebrides in comparison to other sites studied in the literature. Exposure of the Shetland Islands probably results in deposition of wind blown basic elements of marine origin in its water bodies, resulting in higher pH readings than would otherwise be expected. Alternatively, the higher minimum pH values could be due to an lack of small, highly coloured water bodies located exclusively on acid bedrock and blanket peat in the present study, rather than their absence from the Shetland landscape. During a previous study of freshwaters in Shetland, lochs were noted as having a range from pH 4.00 to pH 10.0; furthermore highly acidic waters were generally peaty pools, often of high water colour (Carter and Bailey-Watts, 1981).

Maximum recorded mean summer pH value for a loch in the present study was pH 9.38, in Loch of Brow. The pH values in Shetland lochs therefore tend to be high compared to those quoted in the literature for studies elsewhere in northern Britain, the greatest recorded in the literature reviewed being pH 9.19 in the survey of 643 Scottish freshwaters (Harriman and Pugh, 1994). However, mean summer pH in Loch of Brow was found to be well in excess of pH in the other lochs studied. Loch of Huesbreck ranked second with pH 7.81 in summer 1991. Fourteen lochs were between pH 7.00 and pH 8.00, twelve between pH 6.00 and pH 7.00. The vast majority of lochs in the present study therefore fell within the ranges of pH determinations in the literature, with twelve being of comparable pH to the five largest lochs of Scotland (Bailey-Watts and Duncan, 1981b), Loch Lurgainn and Loch Bad o' Ghaill (Spence and Allen, 1979) lochs in Northern Ireland (Rippey and Gibson, 1984) and Ennerdale Water (Fryer, 1991) (Table 2.17).

Table 2.17 **pH, conductivity and alkalinity values determined in lakes in northern U.K.**

Water body	pH	conductivity ($\mu S\ cm^{-1}$)	alkalinity (meq L^{-1})	Reference
Loch Shiel	6.14	29	0.042	1
Loch Ness	6.70	30	0.09	
Loch Lomond	6.78	34	0.127	
Loch Morar	6.63	35	0.065	
Loch Awe	6.90	41	0.179	
Loch of the Lowes	7.90	64	0.46	2
Balgavies Loch	8.30	213	21.0	
Forfar Loch	8.30	439	2.90	
Coldingham Loch		272-424		3
Loch Borralie	8.50	363	2.28	4
Loch Calladail			2.70	
Loch Croispol			2.89	
546 lochs in Sutherland	4.20-9.00	27-390	0-3.4	5
Scottish lochs (n=8)	4.69-8.78	43-359	0.001-0.011	9
Inner Hebrides (n=17)	6.3-8.4		0.112-2.48	10
Inner Hebrides (n=4)	4.08-4.23	103-116	0	
Outer Hebrides (n=59)	5-7		< 0.2	11
Outer Hebrides (n=10)	7.2-8.3		0.5-2.12	
Tayside lochs (n=74)	4.3-8.5	24-5100	0.01-3.3	12
Scottish lochs (n=643)	4.09-9.19	11-1094 (μmhos)	0.069-4.004	13
Loch Urigill	7.90	121	0.71	6
Loch Borallan	7.75	113	0.52	
Cam Loch	7.70	105	0.46	
Loch Lurgainn	6.60	70	0.04	
Loch Bad o' Ghaill	6.75	79		
Loch Owskeich	7.00	81	0.195	
Loch Raa	7.15	142	0.09	
Loch Battachan	7.40	151		
Loch na Dalach	7.20	80	0.07	
Loch Buine Mhor	7.30	125		
Loch an Arbhair	7.50	162	0.29	
Loch na Doire Daraich	7.50	167		
Loch Maol a' Choire	8.20	240	1.76	

Table 2.17 (cont.)

Water body	pH	conductivity (μS cm^{-1})	alkalinity (meq L^{-1})	Reference
30 lakes in N. Ireland	6.60-8.20	70-240	0.04-1.76	7
Ennerdale Water	6.5		0.042	8
Lake Windermere N	7.0		0.204	
Lake Windermere S	7.1		0.236	
Esthwaite Water	7.1		0.386	
Easedale Tarn	5.6		0.006	
Urswick Tarn	8.0		4.357	

KEY:

1 Bailey-Watts and Duncan (1981b)
2 Harper and Stewart (1987)
3 Bailey-Watts *et al* (1987b)
4 Spence *et al* (1984)
5 Bell (1991)
6 Spence and Allen (1979)
7 Rippey and Gibson (1984)
8 Fryer (1991)
9 Phillips (1985b)
10 Maitland and Holden (1983)
11 Waterston *et al* (1979)
12 Maitland and Morris (1981)
13 Harriman and Pugh (1994)

In terms of pH, fourteen lochs were comparable with Loch of the Lowes (Harper and Stewart, 1987), the majority of studied lochs of the Ullapool area (Spence and Allen, 1979), the range quoted for the thirty lakes examined in Northern Ireland (Rippey and Gibson, 1984) and selected lakes of the English Lake District (Fryer, 1991) (Table 2.17). Many lochs in Shetland are probably slightly alkaline in nature owing to at least some basic rather than acidic geology in catchment areas (Table 2.18). This is also the case in several lochs of the Ullapool area *e.g.* Cam Loch and Loch Borrallan which are in drainage areas which consist partly of limestone (Spence and Allen, 1979). In contrast, Loch Borralie which exhibited a value of pH 8.5 is located entirely on limestone (Spence *et al.*, 1984). More alkaline waters may also occur owing to primary production within the water column. Forfar Loch and Balgavies Loch are examples of eutrophic systems where plant biomass probably accounts at least in part for high pH values of pH 8.30 in each water body. It is possible that this process has not occurred to such an extent in Shetland, all mean summer pH values being pH $<$ 8.00, with the exception of Loch of Brow.

2.4.2.2 Conductivity

As with pH values, determinations of mean summer conductivity in Shetland lochs exhibited values which were greater than those noted in the literature (Table 2.17). The lowest conductivity results were 175 μS cm^{-1}, 188 μS cm^{-1} and 199 μS cm^{-1} corresponding to Roer Water, Whitelaw Loch and Eela Water respectively. These are high in comparison to minimum levels found in the literature, conductivity of Shetland lochs contrasting with that of the deep, dilute waters of the five largest Scottish lochs and the standing waters exhibiting low conductivities in the study of Harriman and Pugh, 1994) (Table 2.17). This phenomenon was also noted by Carter and Bailey-Watts (1981). Of the survey ranges examined, the most similar minimum conductivity was found in the data for the Inner Hebrides (Table 2.17). It is likely that conductivity in freshwater lochs of the Shetland Islands is higher than expected owing to the wind blown salts in this exposed island group. This would explain the similarity of results from the Hebridean Islands. Conductivity results for the Outer Hebrides which might have been more analogous to those of the Shetland lochs were not available for comparison. Excluding Strand Loch, which had a saline influence, greatest mean summer conductivity of 594 μS cm^{-1} was observed for Loch of Spiggie, followed by 449 μS cm^{-1} for Loch of Brow and 438 μS cm^{-1} for Gorda Water.

Table 2.18 Solid and drift geology of the 31 loch catchments of the 1991 survey

Water body	Drift geology	Solid geology
Arthurs Loch	bedrock near surface	felsite and unclassified acid rocks: mostly conglomerate (breccia)
Bu Water	till and morainic drift, bedrock near surface	gneissose quartzite and schist
Loch of Brindister	peat, some boulder clay, bedrock near surface	micaceous psammite, some calc-silicate and limestone: some sandstone, siltstone and basal breccia
Loch of Brough (Bressay)	peat, boulder clay bedrock near surface	flaggy sandstone and siltstone
Loch of Brough (Yell)	peat	mica-plagioclase-gneiss
Loch of Brow	boulder clay, alluvium, peat	sandstone, some siltstone
Loch of Cliff	undifferentiated drift, peat, metamorphosed sedimentary and volcanic rocks, little alluvium	siliceous and quartzo-feldspathic flags with phyllite; schist, granitic material, serpentinite, granulite, mica schist, quartzo-feldspathic-granulite
Eela Water	mostly peat, some undifferentiated drift	granite, granophyre, diorite, gabbro
Loch of Gonfirth	till and morainic drift, peat, bedrock near surface	quartzite, schist, granite, granophyre, diorite, hornblende
Gorda Water	undifferentiated glacial drift, boulder clay	rhyolite, ignimbrite, some basalt
Gossa Water	peat	granite, diorite, some limestone
Helliers Water	older intrusive igneous, acid to ultrabasic	greenstone, metagabbro
Loch of Huesbreck	blown sand	sandstone
Loch of Huxter	till, morainic drift bedrock near surface	gneissose quartzite, schist, granitic gneiss, micaceous schist and gneiss
Loch of Kettlester	boulder clay, peat	mica-plagioclase-gneiss, some granulitic-hornblende-gneiss
Lunga Water	peat, bedrock near surface	
Mill Pond	bedrock near surface	micaceous psammite, some calc-silicate rock and limestone, gneissose rocks
Papil Water	undifferentiated drift blown sand, alluvium	green beds, granulite, schist, wid quartzo-feldspathic-granulite, phyllitic, slaty rocks
Punds Water	peat, some undifferentiated drift	diorite, some granite and granophyre

Table 2.18 (cont.)

Water body	Drift geology	Solid geology
Roer Water	peat, undifferentiated drift	granite, granophyre, diorite, some gabbro
Sand Water	moraines, peat	limestone, some hornblende-schist, granulite with schist, hornblende-schist and calcareous rocks
Sandy Loch	peat	conglomerate, sandstone
Skutes Water	undifferentiated drift, some metamorphosed sedimentary and volcanic rocks	antigoritite, phyllitic and slaty, some graphitic phyllite and schist, green beds and unclassified serpentinite
Loch of Spiggie	boulder clay, peat, blown sand, bedrock near surface	porphyritic adamellite, grandiorite, monzonite, some quartzite and schistose grit, sandstone
Strand Loch	till and morainic drift, alluvium, peat	limestone with hornblende-schist
Loch of Tingwall	boulder clay, peat, undifferentiated drift bedrock near surface	limestone, micaceous psammite, calcareous and siliceous rocks, phyllite with quartzite and schistose grit, some epidiorite, hornblende-schist, granite
Turdale Water	peat	limestone
Loch of Ustaness	peat, bedrock near surface	migmatitic gneiss, psammitic rock, granite
Loch of Watlee	peat, undifferentiated drift older intrusive igneous (acid to ultrabasic)	granulite, schist, quartzo-drift, feldspathic granulite, mica schist, granulitic hornblende gneiss, phyllite with garnet kyanite, chloritoid andalusite
Whitelaw Loch	hill peat, serpentinite erratic	hornblende-biotite-diorite, gneissose, psammitic, granulite

Although the highest conductivity in the data of Harriman and Pugh (1994) was 1094 μS cm^{-1}, the mean of the 642 lochs was as low as 106 μS cm^{-1}. The greatest value recorded in the remainder of the literature consulted was 439 μS cm^{-1}, in Forfar Loch, a eutrophic system (Table 2.18). Again, the likely causes of elevated conductivity in Shetland lochs are wind blown ions and geology of catchment, rather than anthropogenic enrichment.

2.4.2.3 Alkalinity

It is possible only to compare alkalinity results from 1992 and 1993 in five lochs of the present study with those found in the literature (Table 2.17). In a previous study of Shetland waters (Carter and Bailey-Watts, 1981), minimum alkalinity of waters was < 0 meq L^{-1} *i.e.* positive acidity was observed. This was found to occur in small, acid, peaty pools, none of which were included in the present study. Lowest mean water column alkalinity determined was 0.086 meq L^{-1} for Loch of Gonfirth, whilst highest alkalinity was 1.757 meq L^{-1} for Loch of Tingwall South Basin. The buffering capacity in Loch of Gonfirth is therefore considerably lower than the mean alkalinity value of 0.310 meq L^{-1} in the survey of 643 Scottish freshwater lochs (Harriman and Pugh, 1994). Alkalinity in Loch of Gonfirth is comparable with that of Loch Ness and low alkalinity lochs of the Inner Hebrides, but relatively high compared to water bodies at the lower extremities of alkalinity in the studies of Bailey-Watts and Duncan (1981b), Phillips (1985b), Bell (1991), Rippey and Gibson (1984), Fryer (1991) and Maitland and Morris (1981) (Table 2.17). Although Loch of Tingwall has a high buffering capacity in comparison with the other four Shetland lochs studied, it is not as high in alkalinity as Lochs Borralie, Croispol and Calladail, Forfar Loch, Urswick Tarn, nor the lochs of greatest buffering capacity in the studies of the Inner and Outer Hebrides and the 643 Scottish water bodies (4.00 meq L^{-1}) (Harriman and Pugh, 1994). It is comparable with Loch Maol a' Choire and the maximum alkalinity recorded in the survey of lakes in Northern Ireland (Table 2.17). Like that of Loch Maol a' Choire, the catchment of Loch of Tingwall is not situated entirely on limestone (Table 2.18) and is also influenced by peaty soil within its drainage area. Neither is it eutrophic as is Forfar Loch.

2.4.2.4 Cation concentrations

Minimum K concentrations were found in Loch of Gonfirth and Roer Water, mean

summer levels being 0.9 mg K L^{-1} in each water body. This is high compared to the low K lakes in the studies of Bailey-Watts and Duncan (1981b), Bell (1991), Rippey and Gibson (1984) and Fryer (1991). However, when comparing the maximum K concentration of the Shetland study (3.2 mg K L^{-1} in Loch of Spiggie) with the extent of the surveys in Table 2.19, the value falls within the range of maximum K concentrations. However, in comparison with the literature, Na levels in Shetland waters were found to be high, varying from 23.8 mg Na L^{-1} in Sand Water to 52.8 mg Na L^{-1} in Loch of Spiggie. Lakes exhibiting Na concentrations of similar magnitude were Forfar Loch (23 mg Na L^{-1}) and Coldingham Loch (32 mg Na L^{-1}) (Table 2.19). Certainly, there is likely to be a marine influence on the latter, as it is situated near the sea and is relatively exposed. Ca concentration was lowest in Roer Water (1.3 mg Ca L^{-1}), followed by Loch of Ustaness (2.6 mg Ca L^{-1}) and Whitelaw Loch (2.6 mg Ca L^{-1}). Maximum Ca concentration of 196.8 mg Ca L^{-1} in Strand Loch was followed by 68.5 mg Ca L^{-1} in Loch of Huesbreck and 33.7 mg Ca L^{-1} in Loch of Tingwall. The concentration in Strand Loch is well in excess of any of the published figures, though Ca levels in Loch of Huesbreck are comparable with those of Urswick Tarn (Fryer, 1991) and standing waters in Tayside (Maitland and Morris, 1981) (Table 2.19). A high Ca concentration would be expected in Loch of Huesbreck owing to its location on sandstone (Table 2.18). The remaining Shetland figures lie within the range of values in Table 2.19. Lowest water Mg concentrations were 3.1 mg Mg L^{-1} and 3.6 mg Mg L^{-1} in Loch of Gonfirth and Roer Water respectively, whilst greatest values were 177.3 mg Mg L^{-1} in Strand Loch and 20.3 mg Mg L^{-1} in Loch of Watlee. Though Strand Loch exhibited greater Mg levels than any quoted in Table 2.19, Loch of Watlee mean Mg concentration was within the expected range. At the other extreme, Mg levels found for the Shetland lochs studied were all greater than minimum values reported elsewhere. Loch of Watlee and other water bodies of Unst and Fetlar were relatively high in Mg in the context of lochs in the present study, reflecting the Mg rich nature of the geology of the Northern Isles (Table 2.18).

Table 2.19 **Major cation concentrations (mg L^{-1}) in water bodies of northern U.K. surveyed in the literature**

Location	K	Na	Ca	Mg	Ref
Loch Shiel	0.25	4.24	0.98	0.75	1
Loch Ness	0.27	3.84	1.99	0.81	
Loch Lomond	0.33	3.45	3.00	1.00	
Loch Morar	0.34	3.34	1.23	0.88	
Loch Awe	0.27	4.47	4.01	0.99	
Loch of the Lowes	0.78	5.06	10.02	2.4	2
Balgavies Loch	1.56	11.96	44.09	8.0	
Forfar Loch	5.47	23.0	56.11	9.7	
Coldingham Loch	2.2-2.4	12-32	26-29	15	3
Loch Borralie			33.47	12.16	4
Sutherland (n=546)	0.23-31.0		0.39-43.0	0.4-90	5
Loch Urigill			15.63		6
Loch Borallan			11.42		
Loch Lurgainn			3.21		
Loch Owskeich			7.41		
Loch Raa			6.41		
N. Ireland (n=30)	0.5-4.3	7.0-19.6	1.8-39.1	1.1-11.3	7
Ennerdale Water	0.39	4.30	2.00	0.88	8
Lake Windermere N	0.55	4.65	6.29	0.98	
Lake Windermere S	0.66	5.04	8.53	1.12	
Esthwaite Water	0.98	5.73	12.65	1.50	
Easedale Tarn	0.27	3.52	1.94	0.45	
Urswick Tarn	2.54	12.31	76.7	13.34	
Inner Hebrides (n=17)			1.4-44.8	1.2-9.7	9
Inner Hebrides (n=4)			1.0-1.1	1.6-2.1	
Outer Hebrides					
Outer Hebrides (n=59)			1-5	1-3	10
Outer Hebrides (n=10)			8-42		
Tayside (n=74)			0.4-66.5	0.2-134	11

KEY:

1 Bailey-Watts and Duncan (1981b)
2 Harper and Stewart (1987)
3 Bailey-Watts *et al* (1987b)
4 Spence *et al* (1984)
5 Bell (1991)
6 Spence and Allen (1979)
7 Rippey and Gibson (1984)
8 Fryer (1991)
9 Maitland and Holden (1983)
10 Waterston *et al* (1979)
11 Maitland and Morris (1981)

In summary, the tendency is that many of the Shetland lochs examined have higher than expected pH, conductivity, alkalinity and cation concentrations. In water bodies of infertile geology, predominantly wind blown salts probably account for elevated levels of conductivity and cations, whereas in waters of rich geology, the effect may not be as important as that of underlying bedrock. Although pH and alkalinity are also affected by these factors, the absence of small, acid, peaty pools from this study must also result in higher minimum pH and alkalinity results than might occur in a completely random number of water bodies.

2.4.2.5 Phosphorus

Although there are lochs in the Shetland study which have low TP concentrations, the lowest mean summer TP level recorded in 1991 was 5.0 μg P L^{-1} for Loch of Ustaness. This is slightly higher than low values reported elsewhere, as TP has been found to be < 5 μg P L^{-1} in *e.g.* several water bodies of the English Lake District (Fryer, 1991) and in Sutherland (Bell, 1991) (Table 2.20). However, several ranges of values in the literature exceed the mean summer TP concentration of 83.2 μg P L^{-1} for Turdale Water (the maximum for the present study), certain water bodies exhibiting levels well in excess of this *e.g.* lochs in Sutherland (Bell, 1991), Tayside (Maitland and Morris, 1981) and Coldingham Loch (Bailey-Watts *et al.*, 1987b) (Table 2.20). Concentrations of DRP in the Shetland lochs studied were low, only Turdale Water having significant levels. Generally DRP concentrations were < 1 μg P L^{-1}. When compared to DRP concentrations in lakes in other areas of northern Britain, levels in Shetland lochs are low, but it is likely that when DRP concentration has been noted as < 10 μg P L^{-1} or < 5 μg P L^{-1}, this is the level of detection and the actual concentration may be < 1 μg P L^{-1}, as in the present work. When considering mean summer DRP concentration of 32.6 μg P L^{-1} in Turdale Water, this loch is similar to Loch of the Lowes, though if maximum value of 90.8 μg P L^{-1} is observed, Turdale Water is more analogous to the P enriched systems of the Sutherland lochs examined. Turdale Water is within the range of values observed previously in lakes in northern Britain (Table 2.20).

2.4.2.6 Nitrogen

The range of TON figures for Shetland lochs was within the extent of reported values of TON in Table 2.20.

Table 2.20 Nutrient chemistry of standing freshwaters in northern U.K. studied in the literature

Water body	TP	DRP	TON	TAN	Ref
Loch Shiel		<10	<50-<150	<100^	1
Loch Ness		<10	>50-<150	<100	
Loch Lomond		<10	>150-<250	<100	
Loch Morar		<10	>50-<150	<100	
Loch Awe		<10	<50-<200	<100^	
Coldingham Loch	55-300	5-225	50-1500		2
Loch Borralie	50	<5	8	0	3
Sutherland lochs (n=546)	<5-310	<5-110	<10-190	<10-1100	4
Scottish lochs (n=8)		1-24	1-400•	5-135	
			1-20+		7
Tayside lochs (n=74)			5-5500 sum of TAN+TON		8
Loch of the Lowes		32	194		5
Balgavies Loch		77	2690		
Forfar Loch		2460	5870		
Wastwater	<5				6
Ennerdale Water	<5				
Buttermere	<5				
Crummock Water	<5				
Thirlmere	<5				
Coniston Water	<5				
Ullswater	5-10				
Derwentwater	5-10				
Loweswater	5-10				
Lake Windermere North	10-15				
Bassenthwaite	10-15				
Rydal Water	10-15				
Lake Windermere South	15-20				
Esthwaite Water	15-20				
Grasmere	20-25				
Blelham Tarn	20-25				

KEY:

^ one determination of >100 μg TAN L^{-1}; • NO_3-N; + NO_2-N

1 Bailey-Watts and Duncan (1981b)
2 Bailey-Watts *et al* (1987b)
3 Spence *et al* (1984)
4 Bell (1991)
5 Harper and Stewart (1987)
6 Fryer (1991)
7 Phillips (1985b)
8 Maitland and Morris (1981)

With the exception of Loch of Gonfirth which had a mean summer concentration of 254 μg N L^{-1}, all values were < 150 μg N L^{-1}. Shetland values were therefore similar to those of Sutherland (Bell, 1991) and the largest lochs of Scotland (Bailey-Watts and Duncan, 1981b). Ranging from 16 μg N L^{-1} to 103 μg N L^{-1}, TAN concentrations in Shetland lochs were also broadly comparable with available information on other lakes in Scotland. Maximum concentration found in the Sutherland survey was however much greater than the highest level found in Shetland lochs (Table 2.20).

2.4.3 Water quality of Shetland lochs in comparison with existing standards

2.4.3.1 Dissolved oxygen levels in Shetland waters

Three main physical factors affect the solubility of oxygen in water *i.e.* temperature, salinity and atmospheric pressure. As temperature rises, water holds less oxygen. Less oxygen is also present at higher salinities, or higher altitudes owing to the decrease in atmospheric pressure. Shetland lochs are at low altitude, therefore temperature is the most important of these parameters influencing DO. Owing to the saline input to Strand Loch, expected DO saturation values will vary. However, DO concentration never decreased below 10 mg O_2 L^{-1}. Generally, decreases in concentration of DO in Shetland lochs were concurrent with increases in temperature, therefore DO concentration tended to be lower during July and August. Other factors which influence DO concentration in water are organic loadings (*e.g.* from septic tank waste), phytoplankton blooms and aquatic vertebrates and invertebrates. Bacterial oxidation of organic matter exerts an oxygen demand, as does respiration by phytoplankton and other aquatic life. Death of phytoplankton blooms may result in a decrease in DO in the same way as other organic substrates. Despite the oxygen demands of respiration and decomposition and the increased water column temperature during summer, DO concentrations in the Shetland lochs studied remained at concentrations which would not be harmful to aquatic life. For example, when considering standards recommended for waters supporting salmonid fish, which tend to have limited tolerance ranges for many environmental parameters, at > 6.0 mg O_2 L^{-1} these organisms grow and reproduce normally. Levels > 7.0 mg O_2 L^{-1} are recommended for efficient development of the eggs, owing to their high DO requirement (Alabaster and Lloyd, 1980). However, though DO levels of between 6.0

and 7.0 O_2 L^{-1} were recorded, measurements were made from May to September, *i.e.* before spawning was expected.

2.4.3.2 pH

Prescribed Concentration Values (PCVs) of pH from the Water Supply (Water Quality)(Scotland) Regulations (1990) are pH 5.5 to pH 9.5. In terms of water supply, Gorda Water in its untreated form, failed this standard in July and August, pH 5.09 and pH 5.06 being recorded respectively. The pH value for Loch of Brow during August (pH 9.80) was in excess of the PCV for drinking water. However, Loch of Brow is not a potable supply reservoir. Values of pH > 9.0 and < 5.0 cause sublethal effects in fish. Between pH 5.0 and 6.0, fish productivity is poor. Therefore the optimum pH range for most freshwater fish is pH 6.0 to pH 9.0. Loch of Brow at pH 9.8 (August) may have resulted in stress to aquatic life. This was, however, the only water body which became more alkaline than pH 9.0, although Loch of Ustaness, Roer and Gorda Water were consistently at pH < 6.0.

2.4.3.3 Inorganic nitrogen compounds

The following equilibrium exists in water:

$$NH_3 + H_20 \rightleftarrows NH_4^+ + OH^-$$

TAN measured in the present study is comprised of NH_3 (unionised ammonia in the gaseous form) and NH_4^+ (ionised ammonia *i.e.* the ammonium ion). The unionised form is the more toxic. The PCV for ammonia from the water supply (Water Quality)(Scotland) Regulations 1990, is 500 μg NH_4 L^{-1}, presumably referring to total ammonia, rather than NH_3. Concentration of the latter in the water column is dependent upon pH and temperature. As each of these parameters increases, percentage of NH_3 increases. For example, at pH 7.0 and 20°C, percentage NH_3 is 0.4%; at pH 9.6 and 20°C, percentage NH_3 is 61.3%. Temperatures recorded in the present study did not exceed 19.1°C, whilst there was a tendency for TAN concentrations to be low during times when temperatures were greatest.

Although pH was found to be as high as pH 9.80 in Loch of Brow during August, TAN concentration was 33 μg N L^{-1} and temperature only 15.2°C. When considering the amenity value of waters in terms of supporting freshwater fish, salmonids require water containing < 20 μg NH_3 L^{-1}. With respect to the pH, temperature and TAN

results and consequent proportion of NH_3 recorded in all the water bodies studied, it is evident that ammonia concentration at no time exceeded the limits specified above. It was at no time at concentrations which could be harmful to aquatic life or with respect to human consumption.

PCVs of nitrate and nitrite are 50 mg NO_3 L^{-1} and 100 μg NO_2 L^{-1} respectively. Nitrate is not toxic to fish except at concentrations > 400 mg NO_3 L^{-1}. Therefore both reservoir waters and those requiring an EQS for support of freshwater fish were in compliance with required nitrate levels as maximum recorded TON concentration was 258 μg N L^{-1}. Nitrite levels in Scottish freshwaters are generally very low, often being < 3.0 μg N L^{-1}. It is unlikely that nitrite concentrations were in exceedence of the standard, as high nitrite values are associated with low DO concentrations and organic pollution.

2.4.4 The trophic status of Shetland's standing freshwaters, as defined by TP and chlorophyll *a* concentrations

The Organisation for Economic Cooperation and Development (OECD) produced guidelines on monitoring assessment and control of freshwater lakes, covering a wide range of geographical and limnological situations (OECD, 1982). Research was carried out into a number of different water bodies, including Alpine waters, North American lakes, reservoirs and shallow lakes. The data generated from this work were used to produce a tentative classification of lochs by trophic status, based on water column concentrations of P and chl *a* (Table 2.21). Although natural systems form a continuum and other factors may be involved in limitation of primary production, such as insufficient light, or grazing pressure, it is useful for water management purposes to categorise freshwater bodies in such a manner, as a means to form a risk assessment of likelihood of increasing primary production.

Comparing mean summer concentrations of TP and chl *a* in the lochs of the 1991 Shetland survey with those of the OECD (1982) categories resulted in the classification of Shetland lochs as seen in Table 2.22. Only six could be categorised as oligotrophic and therefore unlikely to have problems with excessive phytoplankton growth, assuming that no increase in catchment nutrient input occurred.

Table 2.21 Classification of standing freshwaters (OECD, 1982)

Trophic state	mean TP	mean Chl*a*	max Chl*a*
Ultraoligotrophic	≤4	≤1.0	≤2.5
Oligotrophic	≤10	≤2.5	≤8.0
Mesotrophic	10-35	2.5-8	8-25
Eutrophic	35-100	8-25	25-75
Hypertrophic	≥100	≥25	≥75

mean TP	mean summer TP concentration
mean Chl*a*	mean summer chlorophyll *a* concentration
max Chl*a*	maximum summer chlorophyll *a* concentration

Table 2.22 Trophic classification of Shetland lochs with mean summer concentrations of TP and chlorophyll *a* according to OECD (1982)

Water body	Mean summer water column concentration	
	Total phosphorus	chlorophyll *a*
Arthurs Loch	oligotrophic	oligotrophic
Loch of Gonfirth	oligotrophic	oligotrophic
Roer Water	oligotrophic	oligotrophic
Helliers Water	oligotrophic	oligotrophic
Loch of Ustaness	oligotrophic	oligotrophic
Lunga Water	oligotrophic	oligotrophic
Whitelaw Loch	mesotrophic	oligotrophic
Loch of Kettlester	mesotrophic	oligotrophic
Skutes Water	mesotrophic	oligotrophic
Loch of Brindister	oligotrophic	mesotrophic
Eela Water	oligotrophic	mesotrophic
Loch of Tingwall	oligotrophic	mesotrophic
Loch of Huesbreck	oligotrophic	mesotrophic
Loch of Brough (Bressay)	mesotrophic	mesotrophic
Gorda Water	mesotrophic	mesotrophic
Gossa Water	mesotrophic	mesotrophic
Loch of Huxter	mesotrophic	mesotrophic
Sand Water	mesotrophic	mesotrophic
Loch of Snarravoe	mesotrophic	mesotrophic
Sandy Loch	mesotrophic	mesotrophic
Strand Loch	mesotrophic	mesotrophic
Loch of Watlee	mesotrophic	mesotrophic
Papil Water	mesotrophic	mesotrophic
Punds Water	mesotrophic	mesotrophic
Loch of Spiggie	mesotrophic	mesotrophic
Loch of Cliff	mesotrophic	eutrophic
Loch of Brow	mesotrophic	eutrophic
Bu Water	eutrophic	mesotrophic
Loch of Brough (Yell)	eutrophic	eutrophic
Turdale Water	eutrophic	eutrophic
Mill Pond	eutrophic	eutrophic

Of twenty one water supply lochs, fifteen are at risk of having such problems, as once mesotrophic levels of P are reached, it is possible for a bloom to occur. Seven lochs were found to be borderline oligo/mesotrophic, with four possessing oligotrophic P concentrations, but mesotrophic chl *a* levels, possibly indicating that a maximum limit for TP of 10 μg P L^{-1} is in excess of that required to ensure low algal productivity. The lowest mean TP concentration associated with mesotrophic mean summer chl *a* concentrations (6.5 μg chl *a* L^{-1}) was 7.1 μg P L^{-1} for Loch of Huesbreck. Bloom problems have been found to occur at P concentrations as low as this in the literature. However, it was previously reported in sites deeper than those in the 1991 study.

Twelve lochs in this study fell into the mesotrophic group, three into mesoeutrophic, whilst only three were found to correspond to eutrophic conditions. Of the borderline mesoeutrophic lochs, Bu Water was observed to have a mesotrophic mean chl *a* level, but eutrophic TP concentration. The opposite was true of Loch of Cliff and Loch of Brow. If trophic status of more humic lochs is considered, they range from oligo/mesotrophic to eutrophic, the most eutrophic lochs in the study being highly coloured. A classification of Shetland lochs by geology of catchment alone (Britton, 1974) showed the vast majority of waters to be either oligotrophic or dystrophic, with the assumption that dystrophic was synonymous with nutrient poor, rather than a brown water loch of variable nutrient concentrations. If water bodies involved in the 1991 study are representative of Shetland lochs, it is possible that a deterioration has occurred in water quality of standing freshwaters in Shetland since only six of those studied were oligotrophic. This situation may have arisen through catchment management practices or natural eutrophication processes. Of the Shetland lochs with higher water colour, *i.e.* Lochs of Brough (Yell) and Kettlester, Bu, Turdale and Sand Water, Strand and Sandy Lochs and Mill Pond, all were of mesotrophic to eutrophic status (four being the most enriched systems of the lochs studied). In addition, the lochs which exhibited blooms or scums were all of high water colour (although the water colour of Punds Water is not known).

2.4.5 Further study of five Shetland lochs of different trophic status

2.4.5.1 Oxygen and temperature profiles of the five lochs in 1992 and 1993

In the five lochs studied in detail during 1992 and 1993, stratification was either

absent or weak and intermittent, with DO levels never becoming low, *e.g.* at 20 m depth, at Site 2, in Loch of Gonfirth, in June 1992, DO saturation was 80.6%; at 20 m depth, at Site 2, in Loch of Tingwall, in July 1993, DO saturation was 71.0%. In Loch of Gonfirth and Loch of Tingwall, stratification occurred approximately at the depth at which the depression within the loch basin (at Site 2 in each loch) became deeper than the rest of the basin (at approximately 15 m depth), the loch morphometry restricting mixing and water circulation. Stratification has been found to be a feature of other lochs in Scotland, notably the largest lochs, Loch Shiel, Loch Lomond, Loch Awe, Loch Morar and Loch Ness. These lochs are all well mixed from late autumn to spring and stratification develops from May to autumn (Smith *et al.*, 1981). Stratification in smaller, shallower lochs in Scotland has been found to be discontinuous over the summer period. Included in this category are Coldingham Loch (Bailey-Watts *et al.*, 1987b), Loch of the Lowes, Balgavies Loch, Forfar Loch (Harper and Stewart, 1987) and Loch Borralie (Spence *et al.*, 1984). The latter was noted to be mixed entirely for most of the year and stratification to be only intermittent. These water bodies, which do not form stable thermoclines or oxyclines, are more comparable with Lochs of Tingwall and Gonfirth where interruption to the mixing process is infrequent. In lakes which are particularly shallow, stratification is unlikely. For example, Loch Leven (Kinross) has a mean depth of 4 m and is non-stratifying (Bailey-Watts, 1978). Turdale Water, Helliers Water and Sandy Loch did not stratify as they are extremely shallow. High wind exposure conditions are prevalent in Shetland, wind speeds being greater than those experienced on mainland Scotland. For example, from May to August, 1990, maximum wind gust in Shetland ranged from 33-45 knots (SIC, 1991). Under such conditions, a water body of similar volume to Loch of Tingwall or Loch of Gonfirth, but with a more uniform basin shape, probably would not stratify.

2.4.5.2 Concentrations of phosphorus and chlorophyll *a*

In Loch of Gonfirth TP concentrations were lower in 1992 and 1993 than in 1991, possibly due in part to an increase in rainfall to the catchment, thereby causing a dilution of the Loch water. With TP < 5 μg P L^{-1}, this water body became ultraoligotrophic. Chl *a* concentrations confirmed that this Loch remained nutrient poor in nature. Although there was little variation in TP concentration from March to October, higher values tended to occur earlier in the year. Owing to a number of

factors, maximum TP concentration in temperate lake systems is expected during early spring or late winter. Weather conditions early in the year mean that lake systems are extremely well mixed. P in dissolved and particulate form can be brought into the water column from disturbance of sediment. Heavy rainfall may allow increased erosion and leaching of P from the catchment to inflow waters. However, temperature and light levels remain low. Primary production is not encouraged, so leaving nutrients in the water column. Assuming TP in rainwater to be between 6.7 and 10 μg P L^{-1} (Chapter 7), inflow waters were generally as expected in a catchment with no external nutrient source. However, Inflows 3 and 5 both exhibited levels in excess of 10 μg P L^{-1} during May, 1992. These elevated levels were associated with particulate P, therefore are likely to be due to transport of plant or soil material in the drainage system. The elevated levels of TP in these inflows coincided with the greatest concentration in the water column, thereby suggesting that at that time inflow sources were maintaining the Loch at a P concentration in excess of 4.5 μg P L^{-1}. In 1993, no inflow exhibited TP concentrations > 10 μg P L^{-1} until October. Chl *a* concentration was greatest in May in both 1992 and 1993, phytoplankton biomass being stimulated by increased temperature and light levels in addition to the elevated nutrient levels. In 1992, chl *a* increases and decreases were concurrent with those of TP levels, although TDP decreased from March to October. This may have occurred as whilst phytoplankton incorporate P in a particulate form, a decrease in the soluble P means a decreasing nutrient supply, partly through algal uptake, but also through processes such as loss through sediment adsorption and outflow which is not replenished through leaching processes in the catchment area.

TP concentrations in Helliers Water were relatively variable for an oligotrophic water body, ranging from 4.8-9.8 μg P L^{-1} during the period from July 1991 to October 1993. Elevated TP concentrations in inflow waters were concurrent with increased concentrations in the water column. The highest TP concentrations occurred in May during 1992 and in July during 1993, rather than in winter, early spring or autumn. At these times, water was being pumped from Loch of Watlee into Helliers Water. TP and TDP levels in this inflow were in excess of those of the other inflows. It is, therefore, likely that transfer of water from Loch of Watlee to Helliers Water, was increasing the nutrient status of Helliers Water. Chl *a* levels followed the same general pattern of increases and decreases as TP concentrations, with the exceptions

of the results for May 1992 and July 1993. During these times, chl *a* concentration was lower than expected from the increase in TP levels. Nutrients from the Loch of Watlee inflow were possibly not utilised immediately in increased phytoplankton production, but elevated chl *a* concentrations were observed during the subsequent monitoring visit in each case.

In Loch of Tingwall, during both 1992 and 1993, TP concentrations were highest in March, as would be expected. However, fluctuations in chl *a* levels were not particularly similar to those of the TP concentrations. Although this may have occurred due to presence of varying amounts of inorganic particulate matter and differences between algal types and cell condition, it is also likely that P from inflow waters was affecting the TP-chl *a* relationship.
Within-loch TP concentrations ranged from 8.5-16.4 μg P L^{-1}. Results of 1992 and 1993 surveys suggested that Loch of Tingwall was more mesotrophic than originally surmised from 1991 data, stressing the importance of spring sampling. The trophic status of this water body is as expected if it is considered that TP concentrations in all inflows monitored were at least mesotrophic in nature. It is likely that elevated TP levels in the inflow waters were as a result of human habitation and agricultural land use within the catchment area.

As in Loch of Tingwall, the highest TP concentrations measured in 1992 and in 1993 in Sandy Loch both occurred in March, as would be expected in a temperate freshwater lake. Over the three year study period, TP concentrations ranged from 21.0-38.2 μg P L^{-1}. With the exception of the latter value, all results confirmed Sandy Loch as being moderately productive. Inflow 1 consistently exhibited TP concentrations considerably higher than those of either the Loch or the other inflow waters. Although a covered, disused tip was partly within the catchment area for Inflow 1, this Inflow also received drainage water from fertilised land areas; further evidence that fertiliser treatment resulted in a loss of nutrients to the drainage system. In addition, a high proportion of the TP was in the DRP fraction. Fluctuations in chl *a* and TP concentrations in Sandy Loch did not correspond especially well. This may have been related to high TP concentrations, but low phytoplankton numbers, in inflow waters, causing immediate TP addition to the water column, but a delay occurring before nutrients were utilised in increased phytoplankton productivity.

Instances of decreasing TDP and increasing chl *a* were observed, this perhaps occurring because of uptake of the bioavailable fraction of TDP by the phytoplankton.

Turdale Water continued to be a highly productive water body throughout the study period. Inflow waters of this loch had extremely high TP concentrations. As most inflows consisted of drainage water from reseeded areas and no other land use, it is suggested that the excessive TP concentrations occurred as a direct result of land fertilisation. Similarly, it is probable that eutrophication of Turdale Water has arisen because of high losses of P from fertilised land. The considerably lower TP concentrations observed in the Turdale Water water column during summer may have been a result of Inflows 1,3 and 4 drying up and TP levels in Inflows 2 and 5 being much reduced. It is assumed that TP levels in inflows were higher in spring and autumn because of increased rainfall resulting in greater nutrient leaching. In addition, P uptake by plants decreases in autumn and vegetation dies back, so releasing decay products such as P to the system. Although much of the TP input was as particulate matter, concentrations of TDP and DRP were also high. It is likely that TP concentrations in Turdale Water change rapidly. Consequently, an obvious relationship between TP and chl *a* throughout the period of study would not necessarly be expected. However, low chl *a* concentrations during summer in 1992 and 1993 were probably due to the decrease in input of readily available P at those times.

2.5 CONCLUSIONS

(1) A variety of loch types, incorporating a range of physical and chemical characteristics was observed within the thirty one water bodies surveyed. Values for pH, alkalinity, conductivity and water cation concentrations were slightly elevated in comparison with lochs elsewhere in Britain, but water chemistry was as would be expected in shallow, lowland waters, with influences from fertile geology and maritime salts.

(2) Water quality in Shetland waters was generally good, fulfilling the criteria necessary for potable water supplies and for waters supporting freshwater fish populations.

(3) A range of trophic states was observed, from oligotrophic to eutrophic. Only six water bodies were classified as oligotrophic and therefore unlikely to

exhibit excessive phytoplankton production.

(4) A degree of variation in TP concentrations is to be expected in loch and inflow waters and in chl *a* levels of these standing freshwaters, even in situations where there is no anthropogenic nutrient input, other than in the form of airborne substances.

(5) Data collected suggested that inflow waters were likely to be a source of loch nutrient enrichment in catchment areas incorporating improved grassland, cattle and septic tanks.

CHAPTER 3: SHETLAND LOCH SEDIMENTS AS A STORE AND SOURCE OF PHOSPHORUS

3.1 INTRODUCTION

3.1.1 Sediment as a nutrient sink and store

P retention in lakes is dependent on availability and sedimentation characteristics of possible P binding sites, organic or inorganic. P content of lake bottom deposits therefore depends on a dynamic balance between the sediment P retention capacity and the external P loading. The difference between quantity of naturally bound P and potential immobilisation capacity may be small. However, if sediment P is loosely bound, the internal P loading which this can exert may be significant in the overall lake system (Boström, 1988). In the later stages of eutrophication, water column P concentration may be expected to increase relatively rapidly in the lake waters, although during the early stages of nutrient enrichment, P concentration may rise only slowly (Golterman, 1982a). This is a result of P binding capacity in sediment of oligotrophic lakes typically being high, so that effects of P enrichment through increased external P loads on the P concentration in the water column may not be immediately obvious. Lake sediments generally immobilise more P than is released from them on an annual basis (Marsden, 1989). In more enriched lakes, P adsorption sites in the sediment may already be occupied, so decreasing the capacity of the lake to immobilise excess P. Effects on primary production within the water column may therefore occur more rapidly.

Shallow lakes have a low water volume:sediment surface area ratio. The potential for immobilisation of P from external sources may, therefore, be relatively large. Consequently, shallow lakes can exhibit relatively high P concentrations before changes occur in the biology of the lake (Berge, 1990). However, there is also the possibility that resuspension and rerelease of P from the sediments could have a considerable impact on the water column P concentration in shallow lochs. As Shetland lochs tend to be shallower than most Scottish mainland lochs (Table 1.5; George and Maitland, 1984) they are exposed to mechanical stirring of sediments *via* wind-driven wave action. Through disturbance of the sediment, cycling of P from sediments may assume importance in the loch nutrient cycle. Wind conditions in Shetland ensure that lochs seldom stratify (Chapter 2). Contrary to classical temperate large lake mechanics which involve temperature/chemical stratification in summer,

possibly resulting in an anoxic hypolimnion and consequent P release from sediments, anoxia is not necessarily a prerequisite for P release from sediments, and an oxygenated overlying water column does not always prevent it (Andersen, 1974; 1982). It is, therefore, possible that many Shetland lochs will exhibit higher P levels than expected, due to internal, mechanical processes.

3.1.1.1 Forms of P present in sediment

Several inorganic P compounds have been defined in freshwater sediments (Table 3.1). However, P may also be stored in organic forms within the sediment. The sediment-water interface is the major site of detrital decomposition within standing freshwaters. Doremus and Clesceri (1982) found that in terms of microbial activity, 1 cm of surface sediment was approximately twice as productive as 18 m of water column in soft water oligotrophic Lake George, New York. Dividing sediment into humic and Fe/Ca-bound fractions of P, it was shown that four times more P was incorporated into humic compounds than was combined with Fe/Ca complexes. Inorganic P sorption by humic substances results in temporary P storage in an organic form. Both microbial activity and presence of organic matter are therefore important in P immobilisation, but separation of the effects of these parameters would be difficult because of rapidity of turn over between living and dead components of the biodetritus (Doremus and Clesceri, 1982).

Algal bioassay analyses (using *Scenedesmus quadricauda*) of sediment from four lakes in the Netherlands, including clay, sand/peat and peat composition revealed that algal extractable P was positively correlated with TP, total Fe and clay content, though negatively correlated with organic matter (Klapwijk *et al.*, 1982). Percentage extractable P varies from lake to lake, depending upon sediment type. A significant proportion of organic P in sediments has been found to incorporated in phytic acid and similar compounds. Sequestration prevents chemical binding of ions without removing them from solution. Phytic acid has been found to form complexes with Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+} and Fe^{3+} (de Groot and Golterman, 1993). Golterman *et al.* (1993) have found P adsorption efficiency to be related to pH but also to presence of salts such as NaCl, $MgCl_2$ and $CaCl_2$, which may cause an effect through the electric double layer of Fe(OOH). Conversely, S^{2-} inactivates Fe(OOH) with regard to its P binding capacity.

Table 3.1 **Phosphorus compounds in freshwater sediments (Pettersson *et al.*, 1988)**

Compound	Chemical formula
Apatite	$Ca_{10}(F,OH)(PO_4)_6$
Brushite	$CaHPO_4$, $2H_4O$
octoCalciumphosphate	$(Ca_4H(PO_4)_3$, $3H_2O)_2$
Anapaite	$Ca_3Fe(PO_4)_3$, $4H_2O$
Strengite	$FePO_4$, $2H_2O$
Vivianite	$Fe_3(PO_4)_2$, $8H_2O$
Lipscombite	$Fe_3(PO_4)_2(OH)_2$
Phosphoferrite	$(Mn,Fe)_3(PO_4)_2$, $3H_2O$
Ludlamite	$(Fe,Mn,Mg)_3(PO_4)_2$, $4H_2O$
Variscite	$AlPO_4$, $2H_2O$
Wavellite	$Al_3(OH)_3(PO_4)_2$

3.1.2 Release of nutrients within lake sediments

The gradient in P concentrations between sediment interstitial water and water column is an important mechanism of sediment P release to the overlying water. Under anoxic conditions, sediment P release is linearly dependent upon the concentration gradient across the sediment surface (Kamp-Nielsen, 1974). The magnitude of P release within the sediments is therefore important in terms of its effect on the likelihood of subsequent release of P to the water column. Mineralisation processes affect the concentration gradient and diffusion to the water column is influenced by the redox potential (Eh) and pH (Ryding, 1985).

3.1.2.1 Redox potential (Eh)

Oxidation is defined as a loss of electrons, whilst reduction is a gain of electrons, these electron transfer reactions being reversible. "The Eh of a system is a quantitative expression of its oxidising or reducing intensity. Redox potential may be defined as the electron escaping tendency of a reversible oxidation-reduction system, and is thus an intensity factor" (ZoBell, 1946b). The Eh in oxygenated water is generally approximately +500 mV, but reducing conditions become dominant below the sediment surface (Boström *et al.*, 1982). Eh values of < +500 mV indicate that conditions are no longer fully aerated (NCC, 1990). When dissolved oxygen concentration in the water overlying the sediment is > 1-2 mg L^{-1}, Eh at the oxidised surface layer of sediment is generally in the region of +300 to +400 mV (Moss, 1980). In principle, this layer has a high P sorption capacity and limits release of P from deeper sediment (Marsden, 1989).

The rapidity with which Eh decreases below sediment surface is dependent upon a combination of processes within the sediment (Marsden, 1989). Sediment bacterial action accounts for an oxygen demand resulting from utilisation of organic matter as an energy source. Oxygen in surface sediment is replaced through diffusion from or mixing with the water column. However, below the oxidised microlayer, oxygen supply cannot meet demand. Anaerobic conditions are characterised by Eh values of < +200 mV, which approximates to 0.01 mg DO L^{-1} (NCC, 1990). Reduction of the following chemicals takes place within the sediment as Eh decreases: NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-} and CO_2.

Several types of bacteria, including *Pseudomonas*, *Achromobacter* and *Escherichia* are involved in denitrification *i.e.* successive reduction of NO_3^- to NO_2^- to NO and subsequently N_2. A fall in Eh allows Mn^{4+} to be reduced to Mn^{2+}, releasing Mn-bound P into solution (Davison and Woof, 1984). With a further decrease in Eh, Fe^{3+} is reduced to Fe^{2+}. Therefore, both Fe and P are released into the water column from the sediment (Mortimer, 1941; 1942). Sulphate reducing bacteria include *Desulphovibrio desulphuricans*, which produces H_2S. Anaerobic bacterial utilisation of proteins can result in sulphide production and microbes such as *Beggiatoa* and *Thiothrix* are capable of conversion of sulphide to sulphur (Moss, 1980).

In extreme anaerobic conditions, CO_2 may be utilised by methanogens to produce CH_4 as a by-product (Moss, 1980). Many microbial species are required in the breakdown of carbon compounds in organic matter. The first group break down cellulose and chitin to produce fatty acids and H_2 through hydrolysis and fermentation. The second group utilise these end products to produce CO_2 and CH_4, whilst a third group convert fatty acids and alcohols to forms which can be used as substrates by H_2/CO_2 fermenting methanogenic bacteria (Cappenberg, 1979). The rate limiting step of methanogenesis is the breakdown of algal cell walls to produce mainly acetate, the major precursor of methanogenesis, which has a relatively high turnover rate to CO_2 and CH_4 (Cappenberg *et al.*, 1982).

Consequently, in anaerobic sediment, accumulation of inorganic decomposition products may occur within the interstitial water. TAN and P may come into solution in sediment interstitial water in significant amounts, due to the chemical and bacterial reactions resulting from oxygen demand exceeding supply. Decrease of Eh to -100 mV or less, may result in precipitation of Fe with sulphide produced by the sulphate reducing bacteria. When Fe is thus bound, Fe-P precipitation is no longer possible and P may become available to phytoplankton within the water column (Moss, 1980).

3.1.2.2 pH effects

The Eh at which different chemical species are present is related to the sediment pH. From pH 7.5 to 8.0, Mn^{4+} is stable above +400, Mn^{2+} below +400. Above and below Eh +100, Fe^{3+} and Fe^{2+} respectively are stable, and SO_4^{2-} is stable above -220. However, as pH increases, Eh becomes lower as do the Eh values at which

chemical species are stable (Meadows and Campbell, 1988).

Breakdown of organic matter through bacterial fermentation in sediment results in interstitial water becoming more acid (Marsden, 1989). Consequently, Si may be released because of an increase in the dissolution rate from siliceous structures of phytoplankton. Acidic breakdown of Ca- and Mg-bound P compounds may result in release of these three elements to the sediment interstitial water.

3.1.3 Release of sediment P to the water column

Studies of P release from laboratory batch experiments with sediment from eight different lakes were carried out by Böstrom and Pettersson (1982). Sediments could be divided into three categories from behaviour of P in control, acetate (10 mg C L^{-1}) or NO_3-N (mg N L^{-1}) treatments:

(1) No P release. Mostly these were characterised by low adsorption, high desorption, water extractable P, 1-2%, non-apatite inorganic P, 5% and apatite P, 40% of TP. Sediment from one lake had 10% apatite P and 20% non apatite inorganic P. These lakes were shallow and large areas of agricultural cultivation in the catchment, little on low sewage input.

(2) High P release following acetate addition which stimulated bacterial oxygen demand, but no release after addition of NO_3-N which stabilized Eh conditions. Adsorption capacity was high, desorption low, water extractable P 3-7% and non-apatite inorganic P constituted 10% of TP. Lower percentage of cultivated land in drainage area and have periods of stratification.

(3) P release to a constant level regardless of acetate or NO_3-N additions. These lakes were shallow, had received substantial inputs of wastewater, had a high organic P content and were apparently P saturated. Water extractable P was 10% of TP. Sediment produced P loading in summer despite oxygenated water column.

This example illustrates that sediment P release is dependent upon several factors and also that, in certain conditions, presence of NO_3 may suppress sediment P release.

3.1.3.1 Factors influencing P release to an oxygenated water column

Most aerobic P release has been associated with eutrophic, shallow lakes which have

been receiving large nutrient inputs from industrial or domestic waste water (Bőstrom and Pettersson, 1982). P released from Fe and Mn under reducing conditions in the deeper sediments often does not become available in the water column, as the released P encounters oxygenated surface sediment and is usually reprecipitated. However, it is still possible for P release to occur, as the oxidised surface zone of sediment is shallow and may become saturated with respect to P. When this occurs, release of P to the water column is feasible. Oxygen demand within the sediment increases with increasing temperature, resulting in a thinner oxidised surface zone and higher concentration of P within the interstitial water. P release may, therefore, become independent of water column oxygen content when temperature rises above 17°C (Kamp-Nielsen, 1974).

If P binding capacity of surface sediment is low due to, for example, low Fe concentrations, this may allow passage of P from sediments to the lake water column. Since P adsorption capacity of peaty soil is poor, as a consequence of low Fe content, it follows that effective P immobilisation may not occur in peaty sediments. In addition, sorbed P may be released from aerobic organic sediment when surrounding water is of a low P concentration, as occurs in soil chemistry, with P being released from its adsorption sites (Chapter 6).

P release to an aerobic water column may also occur when high pH reduces ability of Fe^{3+} to bind with P, so that in waters where primary production had raised pH, rather than there being naturally occurring alkaline, hard water, P could become available in the water column. In Ca rich waters there may be a relatively low Fe pool, so that if acid conditions occur in the sediment, P could be mobilized. It is likely that on reaching the overlying water this P would become Ca-bound.

A potential route of P release to aerobic conditions occurs when the major site of decomposition is within an organic layer resulting from sedimentation of high algal biomass *i.e.* at the sediment surface rather than deep in the mud. It is possible that aerobic decomposition could mobilize P to the water column (Marsden, 1989).

3.1.3.1.1 Effect of nitrate on sediment DRP release

Jensen and Andersen (1990) examined impact of nitrate on P cycling. Experimental

tests were carried out with sediment cores from two shallow eutrophic lakes. At 5°C, in January, sediment P release was greater at 0.1 mg NO_3-N L^{-1} than at 2 mg NO_3-N L^{-1}. However, in May, at a temperature of 15°C no significant difference was observed in DRP release between the two NO_3-N concentrations. During September, at a temperature of 15°C, raised NO_3-N concentrations had a positive influence on DRP release from the sediment. Both lakes were found to have significant internal P loading during summer. With few exceptions, the greatest net internal P loadings occurred during increasing blue-green algae biomass and depletion of inorganic N (IN) in the water column. Net P loading is a result of gross sediment DRP release and sedimentation of PP. Because net internal P loading exceeded gross release of DRP, it was concluded that increased PP occurred in the water column due to buoyancy of *Microcystis* and *Aphanizomenon*, thereby increasing summer TP concentrations in the lakes.

High NO_3^- concentration in the water column may result in decreased gross internal P loading to a water body. In dimictic eutrophic lakes, P release from anoxic sediments is suppressed because of the delay in Fe^{3+} reduction influencing P sorption capacity of the sediment (Boström and Pettersson, 1982). NO_3^- can postpone or prevent release of Fe-P by maintaining Eh at a high level (Ryding, 1985), because NO_3^- may act as an alternative electron acceptor to O_2 and be reduced through denitrification, so allowing increased mineralisation rates of organic matter (Ryding, 1985).

3.1.3.1.2 Effects of Fe:P ratio on P release

In the Norfolk Broads, high rates of P release occurred when the Fe:P ratio in interstitial water was $<1.8:1$. In this situation external nutrient control measures alone are unlikely to allow recovery of the water body (Phillips and Jackson, 1990). Jensen *et al.* (1992) found in a study of 116 lakes, that water column TP decreased as Fe:P ratio increased. In those with Fe:P ratios $>15:1$, there was a smaller increase in lake water TP concentration from winter to summer than in the other waterbodies studied. The greatest difference between winter and summer TP concentrations in lake water occurred when Fe:P ratios were between 10:1 and 15:1. In lakes with a Fe:P ratio of $<10:1$, no correlation was demonstrated between Fe:P ratio and DRP release rate, although there were significant correlations with all

sediment P fractions, thus suggesting that perhaps organic P sources are controlling sediment P loss in lakes where sediment Fe content is low. It is suggested that Fe:P ratio shows an estimate of the available sites for orthophosphate sorption by Fe in aerobic sediment.

3.1.3.1.3 Biological influences on sediment P dynamics

Nutrient requirements of bacterial decomposers on the sediment surface may be satisfied either through diffusion of nutrients from deeper sediment or sedimentation of material in the water column. Sediment microorganisms have the ability to uptake and release DRP. The processes are dependent on Eh. Significant bacterial DRP fixation has been found to occur after oxygenation of anoxic sediment, whilst laboratory sterilization experiments have resulted in decreased DRP sorption in aerobic sediment (Gächter *et al.*, 1988). Since anoxic release of Fe and DRP have been found to be partly uncoupled, bacterial fixation and release of DRP may be controlled partly by redox-dependent changes in microbial physiology as well as through production and decomposition of microbial biomass (Gächter *et al.*, 1988). In addition to effects caused by bacteria, algal cells also influence sediment P dynamics. TP concentration may increase in the water column as a result of recruitment of phytoplankton cells from the sediment. Similarly, TP content of the surface sediment may increase as a consequence of death and sedimentation of the water column algal population.

Refractory organic matter is unavailable to aquatic animals because they are unable to digest it. However they have the ability to digest microbial cells. Death and excretion products of animals may then be reutilised by bacteria (Moss, 1980). Protozoan detritivores increase P turnover through excretion of inorganic P and increase P retention time within the biodetritus (Barsdate *et al.*, 1974). Invertebrates feeding on biodetritus influence sediment-water P flux through excretion and irrigation of the sediment by burrowing (Doremus and Clesceri, 1982). Vertical burrowing increases sediment mixing (Ryding, 1985). Benthic invertebrate activity within sediments might therefore be expected to have an effect on lake P cycling, although it may be minor only (Kamp-Nielsen *et al.*, 1982).

A significant relationship was found ($p < 0.002$) between P release rate and number

of fourth instar *Chironomus plumosus* larvae in the Norfolk Broads. However, no relationship was observed between P release and numbers of any other small chironomids or tubificid worms (Phillips and Jackson, 1990).

During previous studies of aerobic and anaerobic sediment and fourth instar *Chironomus plumosus* larvae, silica release was increased 2-3 times after addition of larvae to sediment cores. In aerobic core tubes TP release rate was at least doubled after introduction of larvae. Fe and Mn release also increased in these tubes. Effects on TON and NH_4-N were variable. TP release from anaerobic cores was already elevated compared with the aerobic sediment. Average TP release rate increased by 1.26-1.57 mg P m^{-2} d^{-1} in cores from two of the lakes studied and decreased by an average of 0.12 mg P m^{-2} d^{-1} in anaerobic cores from the third. NH_4-N release also increased from these cores, but decreased from sediment in the other two. No change was noted in TON release after addition of the animals to anaerobic cores, but both Fe and Mn release decreased.

Changes associated with the oxygen status of the core tubes were much more important in terms of release rates than those resulting from chironomid action. It is postulated that effects of burrowing are physical only, greater exchange of water column, interstitial water and high concentrations of inorganic nutrients becoming possible (Granéli, 1979). However some further oxygenation of deeper sediment might occur in close proximity to the burrows. Downward movement of surface deposits might result in increased P immobilisation, whereas upward transport of material could cause increased release of P from the sediment (Kamp-Nielsen *et al.*, 1982). Effects of invertebrates are obviously complex, depending on the particular conditions of individual sediments, size, species and numbers of animals. N release, being closely linked to bacterial activity may be little affected by invertebrate activity.

3.1.4 Availability of P released from lake sediments

When sediment resuspension or P release to the water column occurs, the P does not necessarily become available to the phytoplankton. Resuspended organic P may settle again in particulate form, whilst DRP may become chemically bound within the water column. Precipitation of P with metal ions is dependent upon the concentration of metals available for binding and on the water column pH. In hard water lakes, for

example, Ca^{2+} is as important as Fe^{3+} in regulation of P availability. When higher pH occurs in interstitial water than in the water column, Fe controls P availability in the lake. However, pH increases associated with algal growth in nutrient enriched lakes can result in Ca^{2+} concentration controlling P solubility (Golterman, 1982a). It has been suggested that the availability of Ca-bound and Fe-bound P compounds to phytoplankton is different (Golterman, 1982b). P which has been recently combined with calcite ($CaCO_3$) is in equilibrium with water DRP. Consequently desorption may occur if water DRP concentrations decrease (Marsden, 1989).

In addition to chemical immobilisation, availability of P released from sediments may also be limited by the distance travelled upward through the water column. Cycling of nutrients in lake systems may be limited to the deepest water. For example, Mn flux upward through soluble diffusion from sediment in Lac Léman, Switzerland, has been found to be approximately equal to downward flux through settlement of *Metallogenium*, all within the deepest hypolimnetic waters (Jaquet *et al.*, 1982).

3.1.5 Aims

P binding and release by lake sediments are dependent upon many factors, such as sediment temperature, pH, Eh, oxygen, TON, Fe, Al and Ca content. From review of published literature on sediment P dynamics, it is evident that lake sediments may act either as a P sink, or as a source of P to the overlying water column. There was no information available on P in loch sediments in Shetland, but clearly, sediment P binding or release, could have a significant effect on water column P concentrations, particularly as the water bodies are shallow and of low volume. The aims of the present study were as follows.

(a) Determine background characteristics of bulk densities, redox potentials and %C, %N and %LOI contents of sediment in the five study lochs.

(b) Measure the quantity of P assimilated by each sediment, *i.e.* the mass of P stored, as a percentage of sediment mass.

(c) estimate the quantity of P which could be released as DRP from sediment in each of the five study lochs, under current conditions.

(d) Depending upon present nutrient status of a water body, assess the sediment P uptake capacity, should the trophic status of a water column be raised to mesotrophic and or eutrophic conditions.

3.2 MATERIALS AND METHODS

3.2.1 Determination of sediment characteristics

Sediment sampling positions were determined from depth and area data, in conjunction with a depth limit set by the SCUBA diver. Sediment cores were taken by SCUBA diver from bottom deposits in Gonfirth (29/08/92), Helliers (21/08/92), Tingwall (26/08/92) and Turdale (26/08/92). Plastic core tubes were of 7.5 cm internal diameter and 0.3 cm wall thickness. At each sediment sampling site, six of these were driven into bottom deposits. A rubber bung placed in the top of each sediment core tube allowed extraction of the intact core from the loch bottom. A second rubber bung was inserted at the bottom of each core to ensure it remained in place. Sediment was transported in an upright position to the shore, where three cores were extruded and sectioned and three were used to obtain redox readings. It proved impossible to obtain cores from Sandy Loch owing to lack of light and the impenetrable nature of the basin bottom, which is composed largely of peat deposits. An Ekman grab was therefore used to collect three samples of surface sediment in this instance (29/08/92). As a result of the sampling technique used at Sandy Loch, no bulk density measurements were possible for this sediment. Locations of sediment sampling sites are illustrated in Figure 3.1.

3.2.1.1 Measurement of redox potential (Eh)

Using a Jenway Model 3070 pH/temperature/millivolt (mV) meter, the electrochemical potential developed by a platinum redox indicator electrode was determined by comparison with the stable potential of the 4MKCl silver-silver chloride reference electrode. Prior to mV measurement in each core, a mV determination in ZoBell's solution (a standard redox system) was recorded to verify the performance of the redox indicator system. This ensured that the indicator electrode had not been damaged or poisoned. The mV readings (± 1 mV) were then taken from surface to 10 cm sediment depth. The redox indicator probe was lowered at 1 cm intervals through each core. At each depth, 1 minute was allowed for stabilisation of the mV reading. As redox potential is expressed as an Eh value (ZoBell, 1946a&b; Riley and Chester, 1971; Andersen, 1982; Meadows and Campbell, 1988), the potential of the reference electrode on the hydrogen scale (+198) was then added to each mV reading recorded, in order to calculate the final redox (Eh) potential. Eh is "the electromotive force of an oxidation-reduction system

referred to a standard hydrogen half-cell" (ZoBell, 1946b).

3.2.1.2 Bulk density and organic content

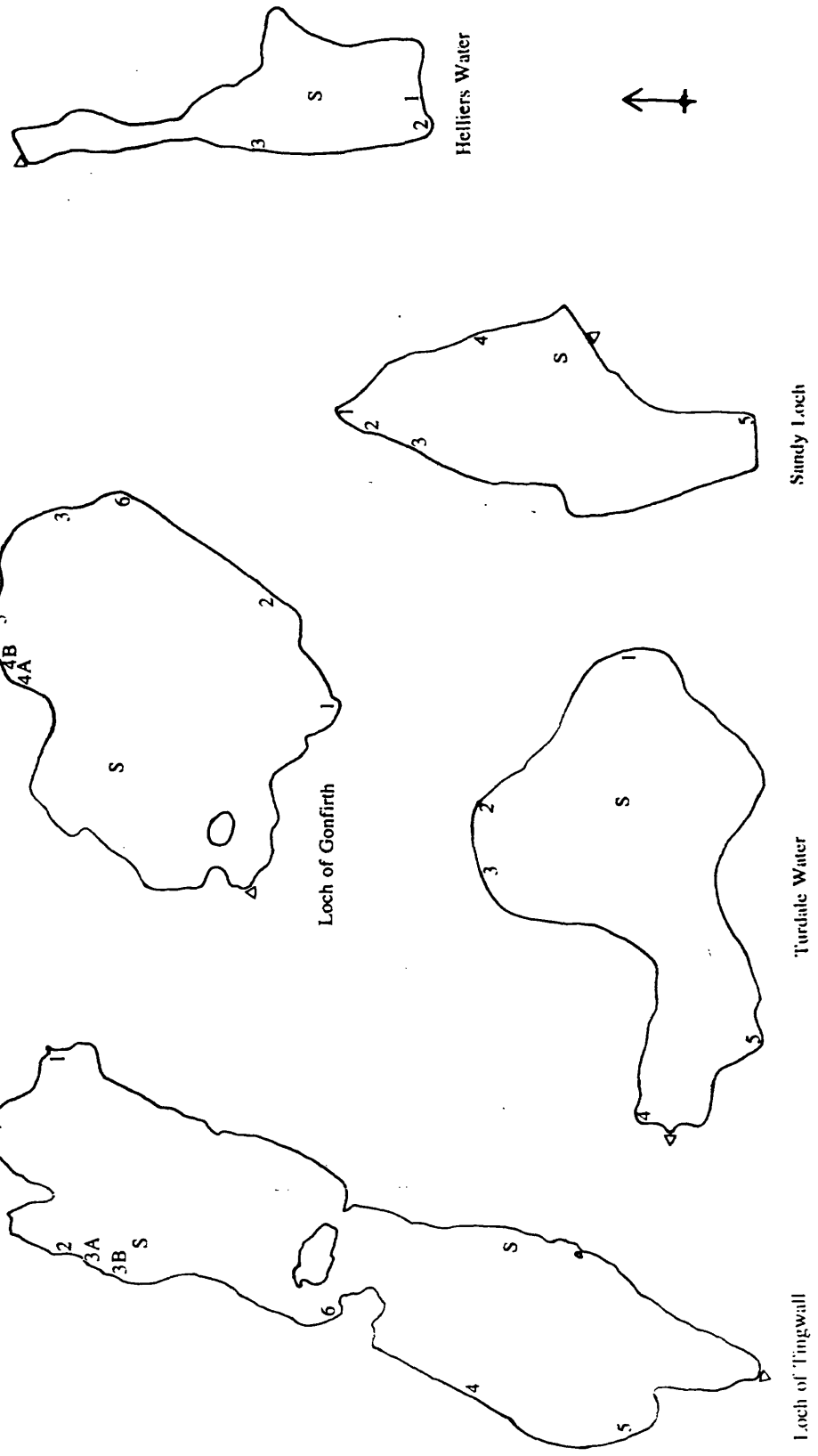
Each of the three cores was cut into slices of 7.5 cm (±0.1 cm) diameter and 1 cm (±0.1 cm) thickness from 0-6 cm depth, then 2 x 1.5 cm (±0.1 cm) sections from 6-9 cm depth. Each fraction was then stored frozen in a polyethylene bag until laboratory procedures could be carried out. Sediment was oven dried at 105°C. All sediment in each slice was weighed (±0.1 mg) for calculation of bulk density (BD) as follows: dry weight of slice ÷ volume of slice. A subsample of dried sediment from each core slice was weighed (±0.1 mg), ignited at 550°C for 6 hours, and reweighed (±0.1 mg), in order to calculate percentage loss on ignition (%LOI) as an estimate of sediment organic matter content.

3.2.1.3 Analysis of sediment %P, %N and %C content

For determination of the quantity of P present in each sediment depth section, composite samples were created from the three cores. Approximately 40 mg of each sample of oven dry sediment was weighed accurately (±0.1 mg) into a Pyrex flask and digested with an acid mixture of nitric acid, 70% perchloric acid and sulphuric acid, in the ratio 5:1:1. Flask contents were boiled almost dry. After cooling, distilled water was added, followed by ammonium solution as described by Strickland and Parsons (1972). Each of these solutions was boiled off before subsequent additions. Acidified water (0.2% concentrated hydrochloric acid) was then introduced to each flask to dissolve solids, before total volume was made up to 40 mL with distilled water. This digest solution was filtered through Whatman Nº1 papers before spectrophotometric determination of molybdate reactive P, as described in Chapter 2, using a 1 cm path length. Standards and blanks were treated as samples and sample digests were adjusted to the pH of standards and blanks prior to analysis. Analysis of each sample was carried out in triplicate. %P was calculated by dividing results in mg P g^{-1} dry weight soil by 10.

The %C (±0.3%) and %N (±0.3%) contents in each individual core segment were determined using 15-20 mg oven dried sediment in a Carlo Erba Model 1106 CHN analyser.

Figure 3.1 **Locations of sediment sampling sites in the five study lochs** (marked with an "s"; inflows marked by number (Chapter 2) and outflow by arrow)



3.2.1.4 Data analysis

Parameters of BD (g cm^{-3}), %LOI, Eh, %C, %N and %P content were plotted against depth of core. Statistical comparisons of each variable (with the exception of Eh) were made between cores from the five different study sites, using the Sign (paired) test (n = 16 or 14, two tailed probability of equalling or exceeding Z percentage value)

3.2.2 P adsorption capacity of sediments in study lochs

Sediment sampling sites of the 1993 survey are illustrated in Figure 3.1. In August 1993, Perspex sediment tubes of 3.9 cm internal diameter were used to retrieve intact, undisturbed sediment cores from Lochs of Gonfirth (31/07/93) and Tingwall (04/08/93), Helliers (02/08/93) and Turdale Water (04/08/93). Coring was not possible in Sandy Loch, owing to the impenetrable nature of the bottom of the Loch. The first 5 cm of each core was sectioned into a glass conical flask on site. On return to the laboratory, three treatments were administered to these mud samples in loch water taken from depth. 50 mL water was added to each flask after spiking with 0, 10 or 50 μg P L^{-1}, with P being present as KH_2PO_4. Five replicates of each treatment were created.

Sediment from the four different loch sites did not receive the same treatments. Loch water alone was added to sediment from all four water bodies, to assess the potential DRP release in 24 hours, under present water column conditions. Loch water spiked with 10 and 50 μg P L^{-1} was added to Loch of Gonfirth and Helliers Water sediment, in order to simulate conditions, should nutrient enrichment result in a mesotrophic or eutrophic water column in these lochs. As Loch of Tingwall already has a mesotrophic water column TP concentration in spring, cores from this loch were not treated with loch water with 10 μg P L^{-1} added, but did receive the 50 μg P L^{-1} spiked water treatment. Similarly, as Turdale Water exhibits eutrophic water column TP levels, cores from this loch were not treated with water which had been further enriched.

Sediment-water mixtures were stirred with a glass rod, then stored in darkness at 16.5 $\pm$0.5°C for 24 hours. A second stir was administered after 20 hours. Flasks were arranged randomly in a 5 x 3 formation. After 24 hours water from each flask was

filtered through a Whatman Nº1 filter paper previously washed in double distilled water. Filtrates were stored frozen in polyethylene bottles until analysis. Analysis was carried out as for DRP in routine water samples (Chapter 2). Colour correction for each sediment filtrate was enabled by addition of DRP colour reagent without reducing agent. Filter papers and sediment contained therein, were dried at 90°C for 48 hours, cooled and weighed for calculation of sediment bulk density. Organic content of each sediment was then determined after ignition at 550°C for 6 hours.

3.3 RESULTS

3.3.1 Characteristics of the sediments from the five study lochs

BD, %LOI, Eh, %C, %N (means of three cores) and %P (composites of three cores) for sediment from each loch except Sandy Loch are plotted in Figures 3.2-3.7. Organic content, %C, %N and %P for Sandy Loch sediment are presented in Table 3.2. Outcomes of statistical comparisons of cores from different sites in terms of BD, %LOI, %C, %N and %P content are presented in Table 3.3.

3.3.1.1 Loch of Gonfirth

BD was found to be in a range from 1.55 g cm^{-3} at 3.0-4.0 cm to 3.2 g cm^{-3} at 7.5-9.0 cm depth (the latter being the highest recorded in this survey) in sediment from Loch of Gonfirth. This sediment was found to be more compacted than bottom deposits from each of the remaining sites (Figure 3.2). Gonfirth sediment was most different from that of Helliers Water ($p < 0.001$), although also significantly different from Tingwall North, Tingwall South and Turdale Water sediments ($p < 0.01$) (Table 3.3). In terms of %LOI, Loch of Gonfirth sediment was also significantly different from the other samples ($p < 0.001$). Organic matter content was found to account for a smaller proportion of Gonfirth sediment than any other, the range of %LOI being 3.1% at 1.0-2.0 cm to 7% at 7.5-9.0 cm depth (Figure 3.3).

Plot of %C content was similar to that for %LOI (Figure 3.4). Loch of Gonfirth sediment was significantly poorer in %C content than the other sediments ($p < 0.001$). Maximum %C content of 3.06% was recorded in sediment at 7.5-9 cm whilst the lowest percentage was 0.94% at 4-5 cm. The proportion of C increased from this depth to surface sediment.

Figure 3.2 **Bulk density profiles of sediments from the five loch coring sites of 1992 (mean values, n=3)**

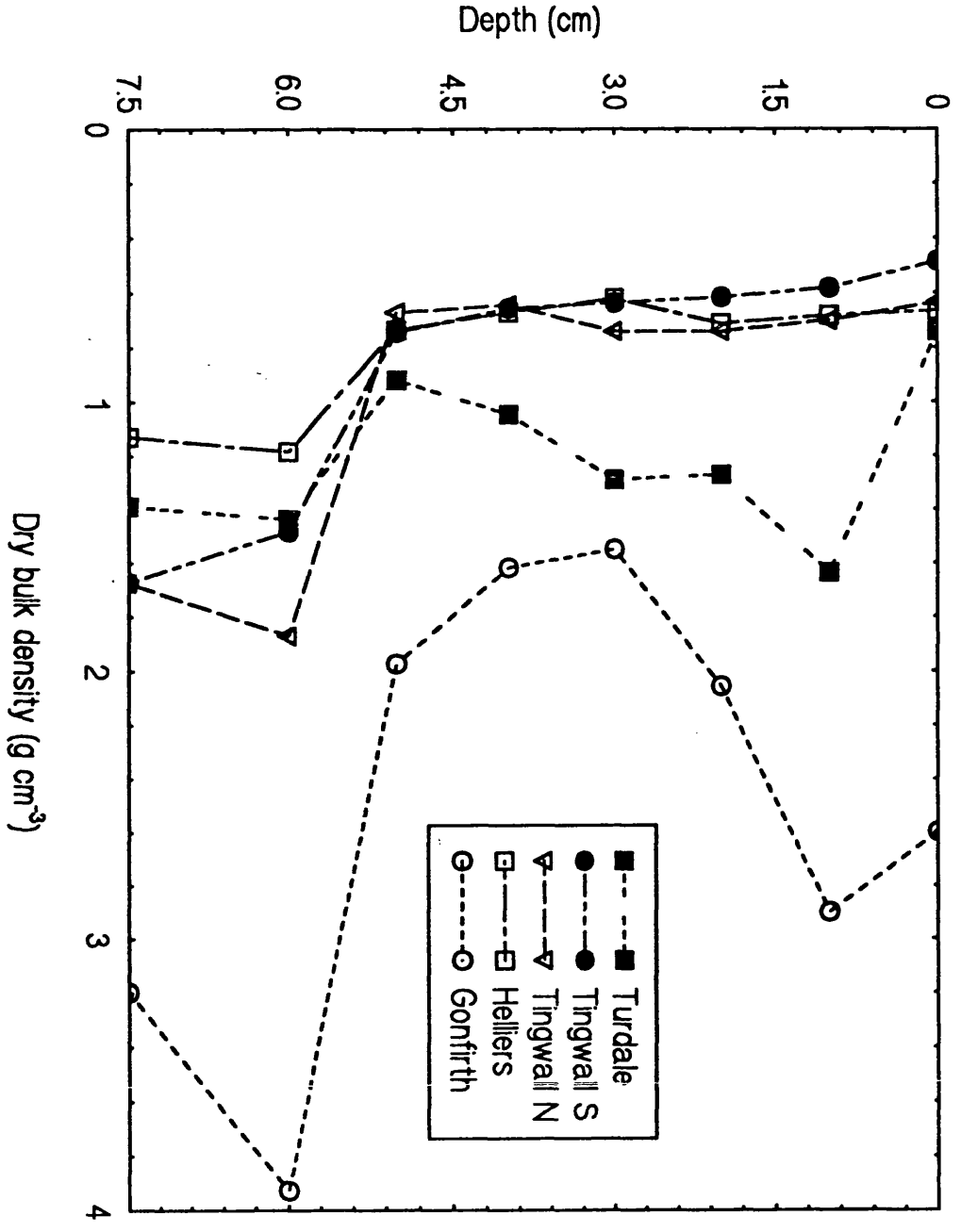


Figure 3.3 **Percentage loss on ignition profiles of sediments from the five loch coring sites of 1992 (mean values, n=3)**

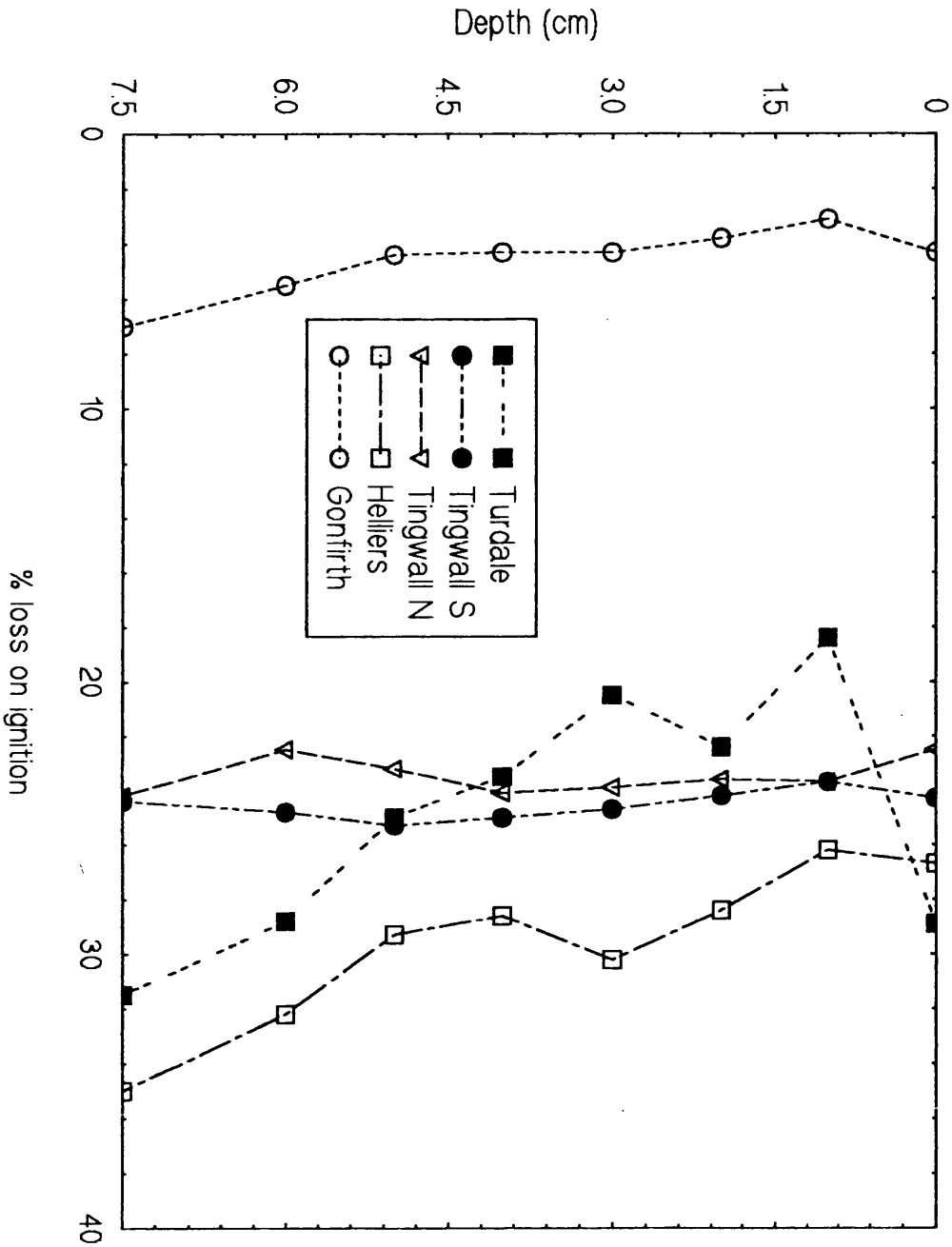


Figure 3.4 **Percentage carbon content profiles of sediments from the five loch coring sites of 1992 (mean values, n=3)**

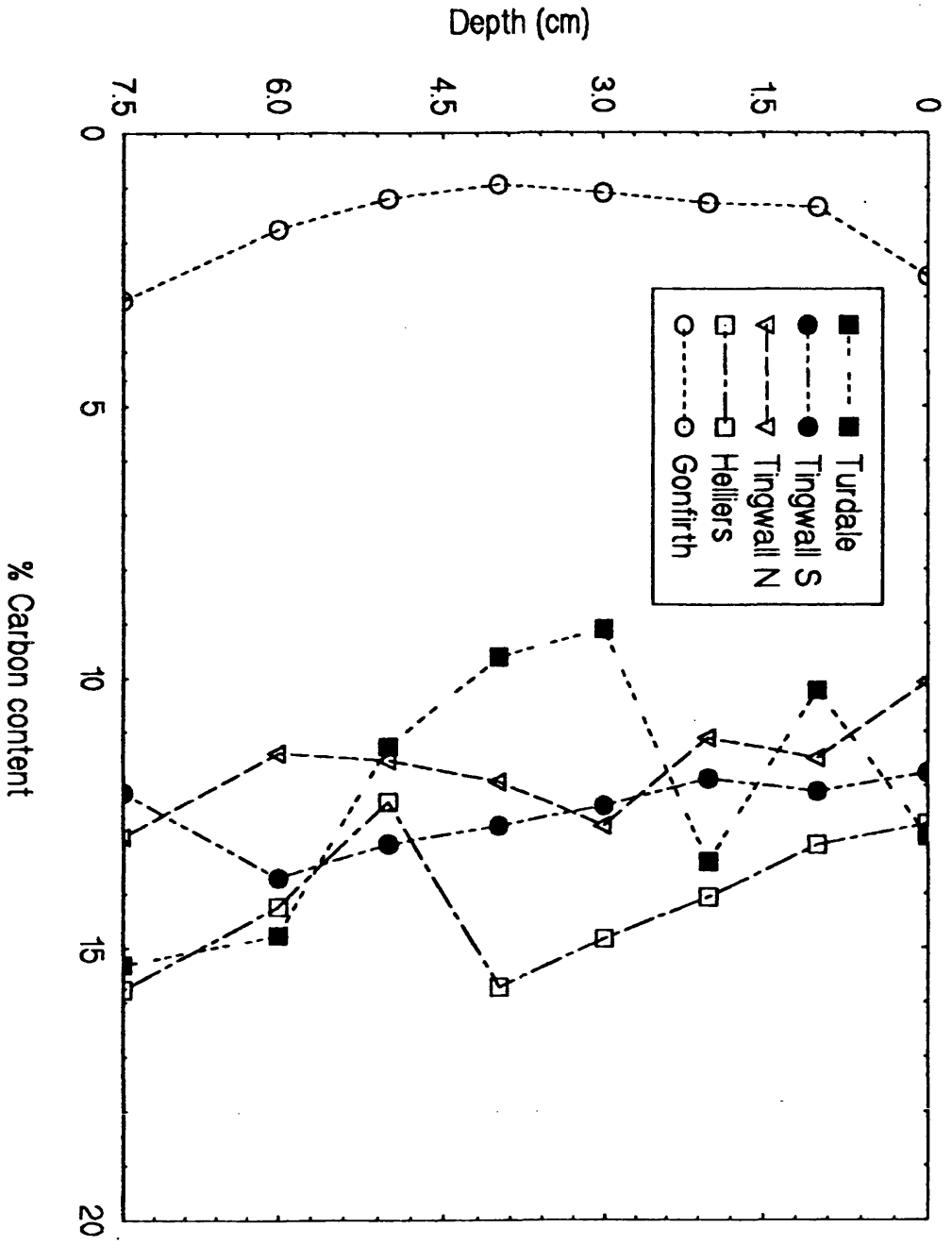


Figure 3.5 **Percentage nitrogen content profiles of sediments from the five loch coring sites of 1992 (mean values, n=3)**

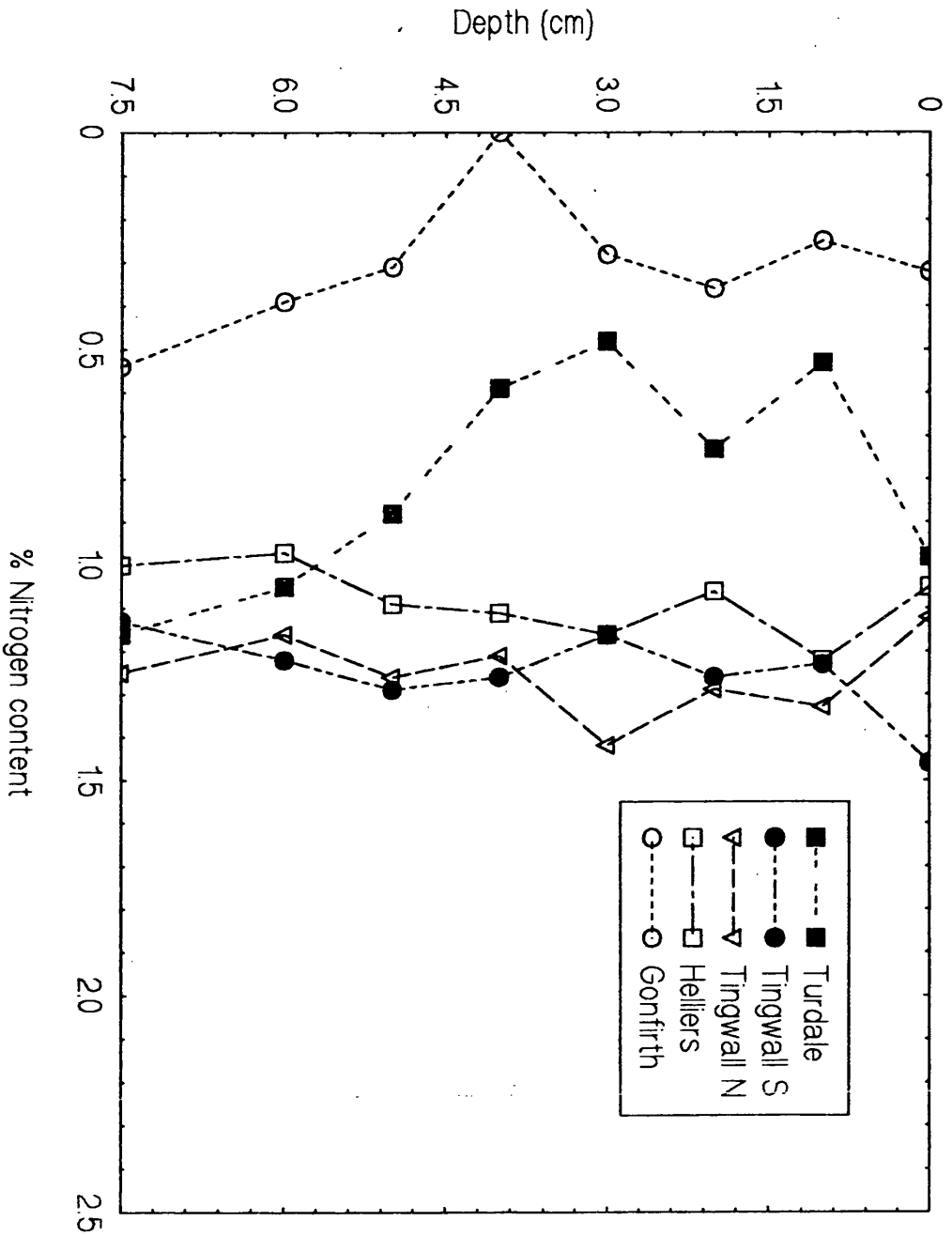


Figure 3.6 **Percentage phosphorus content profiles of sediments from the five loch coring sites of 1992 (composit values, n=3)**

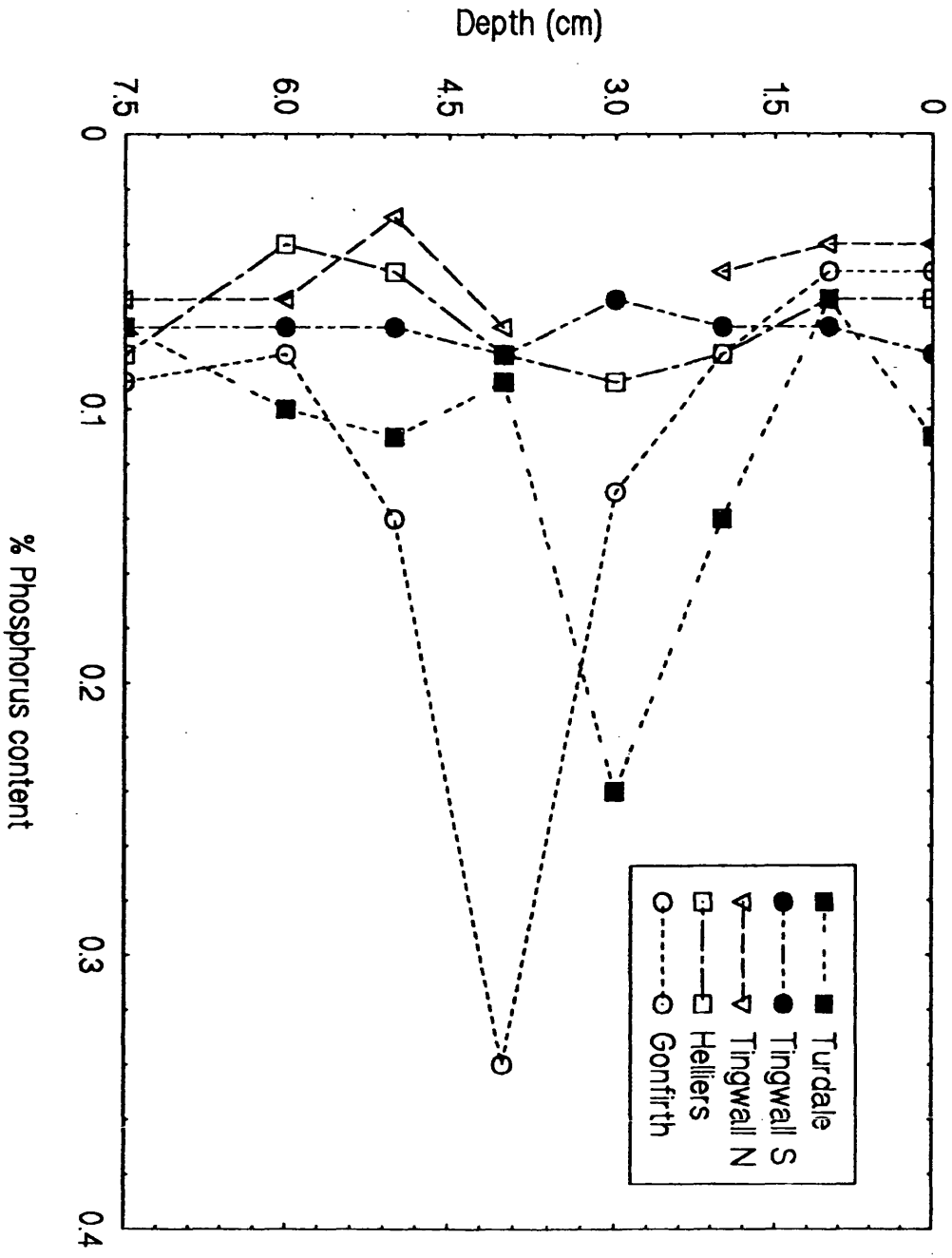


Figure 3.7 **Redox potential profiles of sediments from the five loch coring sites of 1992 (mean values, n=3)**

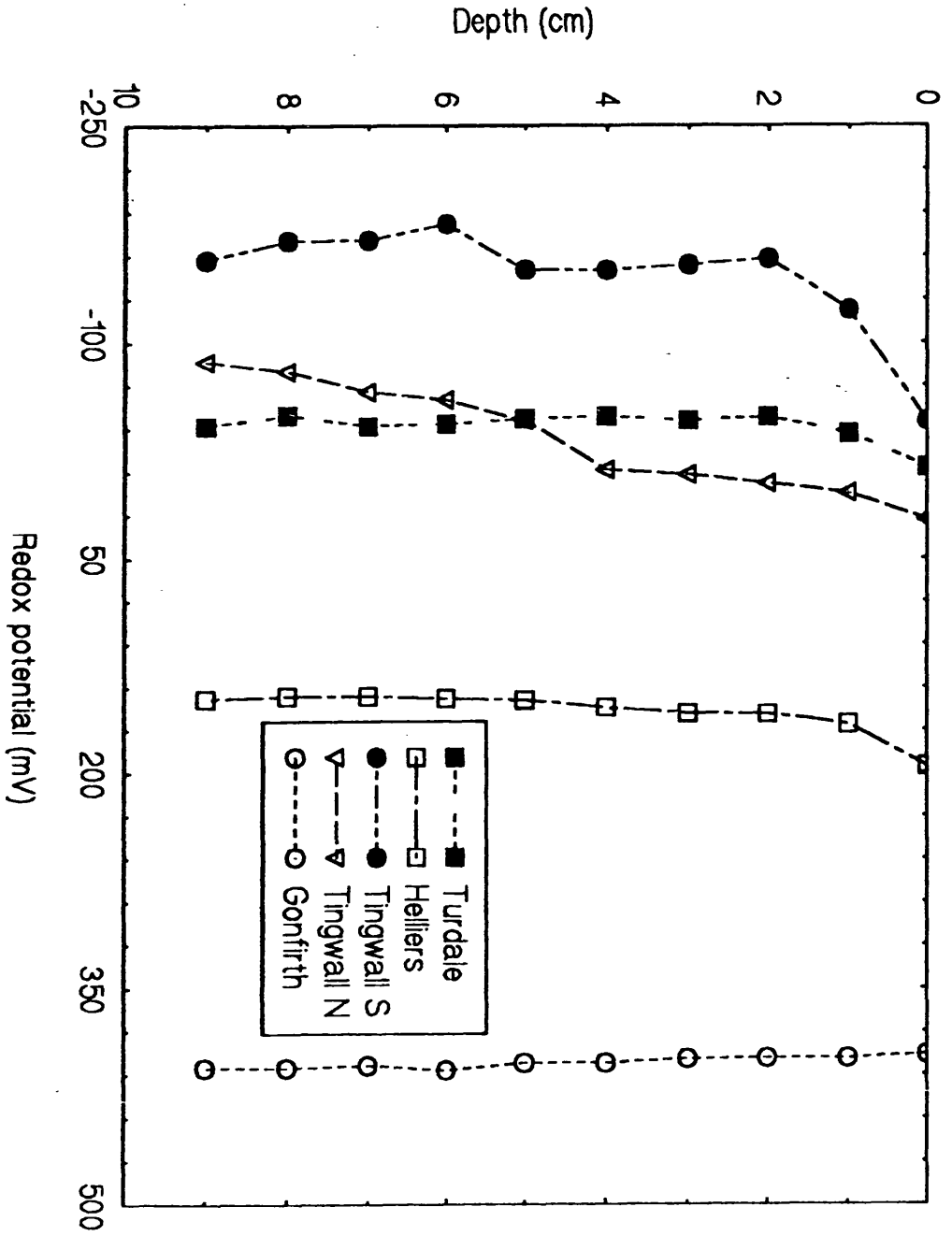


Table 3.2 Characteristics of Sandy Loch sediment collected in 1992

Parameter	% content
Loss on ignition	63.60
Carbon	36.70
Nitrogen	1.49
Phosphorus	0.06

Table 3.3 Significance matrix (paired sign test) of sediment characteristics

Bulk density (g cm^{-3})

		Gonfirth	Helliers	Ting N	Ting S	Turdale
	Gonfirth		<0.001	<0.01	<0.01	<0.01
	Helliers	<0.001		n.s.	n.s.	<0.01
%LOI	Ting N	<0.001	<0.01		n.s.	n.s.
	Ting S	<0.001	<0.01	<0.01		n.s.
	Turdale	<0.001	n.s.	n.s.	n.s.	

% N content

		Gonfirth	Helliers	Ting N	Ting S	Turdale
	Gonfirth		<0.001	<0.001	<0.001	<0.01
	Helliers	<0.001		<0.01	<0.01	<0.05
%C	Ting N	<0.001	<0.01		n.s.	<0.01
	Ting S	<0.001	<0.05	n.s.		<0.01
	Turdale	<0.001	n.s.	n.s.	n.s.	

% P content

		Gonfirth	Helliers	Ting N	Ting S	Turdale
	Gonfirth		n.s.	<0.05	n.s.	n.s.
	Helliers			n.s.	n.s.	<0.05
	Ting N				<0.05	<0.05
	Ting S					<0.05
	Turdale					

Compared to the sediment from the other sites, Gonfirth sediment also had a low proportion of N in its structure. The %N present was within the range 0% at 4-5 cm to 0.54% at 7.5-9 cm (Figure 3.5). The difference was highly significant between Gonfirth sediment and that from Helliers Water and Loch of Tingwall ($p < 0.001$), though the dissimilarity from Turdale Water sediment was of lower magnitude ($p < 0.01$) (Table 3.3).With respect to %P content, Loch of Gonfirth deposits were similar to Helliers Water, Loch of Tingwall (South) and Turdale Water mud. Greatest %P content of any of the samples was 0.34% recorded in sediment from 4-5 cm depth, the minimum for this loch being 0.05% in sediment from 0-2 cm depth. A gradient from the maximum %P content to surface mud was noted (Figure 3.7).

Proportionally, P present in Gonfirth sediment was slightly different from that found in Loch of Tingwall (North), the latter incorporating less P ($p < 0.05$) (Table 3.3).

The Eh values in Loch of Gonfirth cores ranged from +336 to +458 mV. Eh values were higher in the Loch of Gonfirth sediment than in the bottom deposits of the other loch basins where cores were taken (Figure 3.4).

3.3.1.2 Helliers Water

The range of BD values down Helliers Water sediment cores was from 0.62 g cm^{-3} at 3-4 cm to 1.13 g cm^{-3} at 7.5-9 cm depth (Figure 3.2). There was no significant difference between BD in mud from Helliers Water and Loch of Tingwall, although the former was found to be less dense than sediment from Turdale Water ($p < 0.01$). Organic content in Helliers Water sediment was similar to that in Turdale Water bottom deposits, though greater than that in Loch of Tingwall samples ($p < 0.01$). %LOI determinations ranged from 26.2% of sediment at 1-2 cm to 35% at 7.5-9 cm depth. The general depth-distribution pattern appears relatively similar in sediment cores from Helliers Water and Turdale Water (Figure 3.3). Distribution of %LOI and %C content in Helliers Water sediment appears relatively similar when plotted with depth. Maximum recorded %C content of 15.77% at 7.5-9 cm was determined in Helliers Water sediment, minimum for this loch being 12.3% at 5-6 cm depth. A decrease in %C content in the sediment occurred between 4-5 cm (15.73% C) and surface mud (Figure 3.5). As for %LOI, Helliers and Turdale sediments were similar, whilst %C content was significantly smaller in Tingwall North ($p < 0.01$)

and Tingwall South ($p < 0.05$) (Table 3.3). The %N in Helliers Water sediment cores was found to differ between 0.97% at 5-6 cm and 1.22% at 1-2 cm depth (Figure 3.6). %N content was slightly greater in Helliers sediment than in Turdale bottom deposits ($p < 0.05$), though significantly smaller than in Tingwall mud ($p<0.01$) (Table 3.3).

The %P content in Helliers Water sediment was not significantly different from that of Loch of Tingwall cores, though there was a small difference between Helliers and Turdale, the latter containing more P ($p<0.05$) (Table 3.3). A decrease in %P content occurred from the maximum percentage of 0.09% at 3-4 cm to a proportion of 0.06% in sediment taken from the surface. Minimum %P content of 0.04% was located in the 6-7.5 cm core section (Figure 3.6).

Eh values in Helliers Water sediment ranged from +124 to +187 mV (Figure 3.7). Of the sediments sampled, the conditions in Helliers Water bottom deposits were less reducing than those observed in Loch of Tingwall and Turdale Water cores.

3.3.1.3 Loch of Tingwall North

Tingwall North was not significantly different from Tingwall South nor Turdale Water in terms of sediment core BD (Table 3.3). The range was from 0.63 g cm^{-3} in sediment from 0-1 cm to 1.68 g cm^{-3} at 7.5-9 cm depth. Depth distribution of sediment density for Tingwall North appears very similar to those of Tingwall South and Helliers Water (Figure 3.2). There was little change in %LOI throughout the depth sampled. It ranged from 22.5% (0-1 cm and 6-7.5 cm depth) to 24.2% (7.5-9 cm depth). The depth profiles of %LOI for Tingwall North and South appeared very similar though Tingwall South had the significantly greater organic content of the two sites ($p < 0.01$) (Figure 3.3 and Table 3.3). Conversely, although the depth-%LOI profile of sediment from Tingwall North did not appear similar to that of Turdale Water in terms of the fluctuations of %LOI with depth, these two sites were similar when considering organic content of the entire core.

From below 2-3 cm depth, the increases and decreases in %C content with sediment depth in Tingwall North contrasted with those of Tingwall South, but there was no significant difference between these sites with respect to %C content. Neither was

there any difference between Tingwall North and Turdale Water cores (Figure 3.5 and Table 3.3). Proportion of sediment composed of C varied from 10.08% at the surface to 24.2% in the deepest segment of the cores. From 3-4 cm depth, there was a general gradation to lower %C content at the surface. A decrease in %N content occurred from 3-4 cm depth to sediment surface in Tingwall North cores (Figure 3.5). Maximum %N was found in the 3-4 cm sediment, minimum in mud from 0-1 cm. These determinations were 1.42% and 1.12% respectively. Although Tingwall North bottom deposits were similar to those of the southern basin, the proportion of N in the former was significantly greater than that encountered in sediment from Turdale Water. As with %C content, there was a tendency for variations in %N content of Tingwall North sediment to be similar, but opposite to those of Tingwall South.

The %P content of mud from Tingwall North was less than that of sediment from both Tingwall South and Turdale Water ($p < 0.05$) and ranged from 0.07% at 4-5 cm to 0.03 at 5-6 cm depth. An increase in %P content was noted from surface sediment (0.04% P) to 4-5 cm depth (0.07% P) (Figure 3.6).

Mean sediment Eh values observed in Tingwall North were similar to those of Turdale Water bottom deposits (Figure 3.7). The range of Eh values in Tingwall North sediments was from -123 to +42 mV and a discontinuity in mean Eh occurred below 4-5 cm depth. From the surface of sediment cores to 5 cm depth, less reducing conditions were observed in Tingwall North sediment, whereas in deeper sediment, conditions were more reducing in Tingwall North than in Turdale Water cores.

3.3.1.4 Loch of Tingwall South

BD was lowest at 0.49 g cm^{-3} in surface deposits of Tingwall South. Maximum density at this site (1.67 g cm^{-3}) was determined in the deepest section of the cores (7.5-9.0 cm) (Figure 3.2). Tingwall South was not significantly different from Turdale Water with reference to BD or %LOI of sedimented material. %LOI varied within the sediment between 23.7% and 25.3% in 1-2 cm and 5-6 cm segments respectively (Figure 3.3). Tingwall South and Turdale Water were also similar in terms of %C content, the range of this parameter in sediment from the southern basin being 11.77% (0-1 cm) to 13.7% (6-7.5 cm)(Figure 3.4). In contrast, %N content of

Tingwall South mud was significantly greater than that incorporated in Turdale Water bottom deposits. Its range was 1.13% in the deepest section to 1.46% at the surface of the core.

The %P content was lowest at 0.06% in sediment from 3-4 cm depth, but rose to 0.08% in sections of 0-1 cm and 4-5 cm. Turdale Water sediment was found to contain more P than sediment collected from Tingwall South ($p < 0.05$)(Figure 3.6).

Tingwall South sediment cores exhibited the most reducing conditions of the bottom deposits examined. Eh values measured ranged from -241 to +90 mV (Figure 3.7). Sediment from all five coring sites, except Loch of Gonfirth, had higher Eh values at the surface of the sediment than deeper in the core. The most marked decrease in Eh in the surface layers occurred in Tingwall South cores.

3.3.1.5 Turdale Water

The depth-distribution pattern for BD in Turdale Water deposits appeared similar to that for Loch of Gonfirth (Figure 3.2). BD in Turdale sediment was highest at 1.63 g cm^{-3} in sediment from 1-2 cm depth, lowest in the surface deposits (0.74 g cm^{-3}). %LOI varied from 18.4% at 1-2 cm depth to 31.5% in the 7.5-9 cm section. %C content depth profile is similar to that of organic matter for Turdale Water sediment (Figure 3.3). Proportion of C present in Turdale cores peaked at 15.31% in the deepest sediment section. The lowest %C content was found to be 9.11% in sediment at 3-4 cm depth. Depth profile shapes of %C and %N content were found to be alike and maximum and minimum %C and %N occurred at the same sediment depths (Figures 3.4 and 3.5). These %N values were 1.16% and 0.48% respectively. Percentage of Turdale sediment which was P ranged from 0.06% in the 1-2 cm section to 0.24% at 3-4 cm depth. A gradient of decreasing %P therefore occurred from 3-4 cm depth to near surface (Figure 3.6). Eh values measured in Turdale Water cores ranged from -131 to +41 (Figure 3.7).

Turdale Water sediment has been compared in the above sections to bottom deposits of the other loch sediment samples taken.

Table 3.4 Mean (±2 s.e.) bulk density and loss on ignition of sediments used for incubation experiments

Site	Date	Bulk density ($g\ cm^{-3}$)	Loss on ignition (%)
Gonfirth	31.07.93	0.20±0.00	33.2±1.00
Helliers	02.08.93	0.14±0.01	29.1±0.59
Tingwall	04.08.93	0.22±0.01	25.5±0.41
Turdale	04.08.93	0.20±0.04	39.0±1.45

Table 3.5 Mean (±2 s.e.) phosphorus release from sediment incubation experiments ($n=5$)

Site	Date	Mean release ($\mu g\ P\ g^{-1}$)
+0 $\mu g\ P\ L^{-1}$		
Gonfirth	31.07.93	+0.17±0.06
Helliers	02.08.93	0.00±0.00
Tingwall	04.08.93	+0.34±0.04
Turdale	04.08.93	+0.52±0.11
+10 $\mu g\ P\ L^{-1}$		
Gonfirth	31.07.93	-0.03±0.03
Helliers	02.08.93	-0.11±0.01
+50 $\mu g\ P\ L^{-1}$		
Gonfirth	31.07.93	-0.24±0.18
Helliers	02.08.93	-0.54±0.02
Tingwall	04.08.93	-0.44±0.02

KEY:
+ refers to release of P
- refers to uptake of P

3.3.1.6 Sandy Loch

%C and %N of Sandy Loch sediment were the highest of all sites surveyed at 36.7% and 1.49% of sediment dry weight. There was a correspondingly high %LOI of 63.6%, which was also the greatest figure recorded. The %P was not high, a figure of 0.06% being comparable with many of the results for the sediment of the other lochs (Table 3.2).

3.3.2 Characteristics of loch sediment collected in 1993

Sediment BD and %LOI results are presented in Table 3.4 and those of the P release/adsorption experiments in Table 3.5. All ± figures reported below represent ± 2 standard errors. A positive adsorption value represents a release of P from sediments to the overlying water, whilst a negative value indicates P removal from overlying water to the sediments.

3.3.2.1 Loch of Gonfirth

Cores take from Loch of Gonfirth in 1993 appeared different from those sampled during 1992. Sediment from 0-5 cm was less dense and %LOI was greater in 1993 cores. In sediment taken in 1992, BD varied in the first 5 cm of core from 1.55 g cm^{-3} to 3.2 g cm^{-3} (Figure 3.2), but in 1993 density was only 0.19 g cm^{-3} to 0.21 g cm^{-3} (Table 3.4). %LOI ranged from only 3.1% to 4.4% in the surface 5 cm of cores in 1992, compared to 30.3% to 37.4% in the 1993 0-5 cm bulk samples (Figure 3.3 and Table 3.4). Sediment collected during 1992 appeared more minerogenic than that of the 1993 survey, which on visual inspection, was peaty in nature.

A general pattern of increasing P adsorption with increasing water P concentration was observed. When no addition of P was made to the sediment from Loch of Gonfirth, DRP release ranged between +0.11 and +0.25 μg P g^{-1} with a mean of +0.17±0.06 (Table 3.5). Addition of P to raise loch water DRP concentration by 10 μg P L^{-1} resulted in average uptake of -0.03 ±0.03 μg P g^{-1}. Assimilation increased to -0.24 ±0.18 μg P g^{-1} when loch water DRP concentration was elevated by 50 μg P L^{-1}. Uptake ranged from -0.01 to -0.48 μg P g^{-1} at this treatment level (Table 3.5).

3.3.2.2 Helliers Water

BD of Helliers Water sediment was less than that of the other sediments examined.

It was found to range from 0.13-0.15 g cm^{-3}. %LOI determinations were of the same order of magnitude as in 1992, minimum organic content being 26.4%, maximum 31.2% (Table 3.4).

There was no detectable release of DRP from cores of Helliers Water sediment, except in one core with an adsorption of +0.02 μg P g^{-1} (Table 3.5). As with Loch of Gonfirth sediment, there appeared to be an increase in P uptake with increasing DRP concentration in the water. In loch water+10 μg P L^{-1} treatment, mean adsorption was -0.11 $\pm$0.01 μg P g^{-1}, whilst in the +50 μg P L^{-1} treatment, adsorption increased to -0.54 $\pm$0.02 μg P g^{-1}. As indicated by the error values, Helliers Water sediment cores were relatively uniform in their P sorption/desorption characteristics. Mean uptake of P at both enrichment levels was greater for Helliers Water sediment than that from Loch of Gonfirth. In none of the three experiments did adsorption/release figures for Helliers Water and Loch of Gonfirth occur in the same range, indicating that sediment from these two lochs was dissimilar in terms of P sorption capacity (Table 3.5).

3.3.2.3 Loch of Tingwall

Loch of Tingwall sediment bulk density varied from 0.2-0.23 g cm^{-3} in the top 5 cm of cores. %LOI was determined as being between 24.4% and 26.3% (Table 3.4). Release of DRP from Loch of Tingwall bottom deposits appeared greater than that from either Helliers Water or Loch of Gonfirth sediment as release figures for all five cores were greater than those of either Helliers Water or Loch of Gonfirth. Mean adsorption was +0.34 $\pm$0.04 μg P g^{-1} (Table 3.5). In the loch water+50 μg P L^{-1} treatment, mean adsorption was determined as -0.44 $\pm$0.02 μg P g^{-1}. This was greater than mean DRP uptake in Gonfirth sediment, but less than the P adsorption capacity of Helliers Water mud at this enrichment level. The range of adsorption values associated with Loch of Tingwall sediments did not overlap those of Helliers Water, indicating that Helliers Water sediments probably have a higher P sorption capacity at this treatment level. Loch of Tingwall P uptake results do however all occur within the range of Loch of Gonfirth P adsorption data. This is because of one Gonfirth data point only, Loch of Tingwall taking up more P on a mean basis than Loch of Gonfirth bottom deposits in +50 μg P L^{-1} loch water. There was relatively little variation between each of the five cores in each treatment for Loch of Tingwall

(Table 3.5).

3.3.2.4 Turdale Water

BD of Turdale Water sediment ranged from 0.17 g cm^{-3} to 0.27 g cm^{-3}, with a mean of 0.02 g cm^{-3}. The corresponding organic content of these samples had a maximum value of 41.0% and a minimum of 36.4%, resulting in mean %LOI of 39% (Table 3.4). Ranging from +0.37 to +0.65 μg P g^{-1}, DRP release from Turdale Water sediment cores had a mean of +0.52 $\pm$0.11 μg P g^{-1} (Table 3.5). Despite the variability of these results, release figures for Turdale Water coincided with those of neither Loch of Gonfirth nor Helliers Water. Turdale Water release rates are therefore probably greater than those of either Loch of Gonfirth or Helliers Water. P release rates from Loch of Tingwall sediment are similar to those at the lower end of the range of P release rates of Turdale Water sediment, although on average, P release from Turdale sediment was greater.

3.4 DISCUSSION

3.4.1 Relevance of sedimentary P determination technique

Sediment P characteristics have frequently been ascertained by utilising a sequential extraction technique (Pettersson *et al.*, 1988). Sequential extraction as developed by Hieltjes and Lijklema (1980), allows determination of different fractions of sedimentary P, efficiency of each extraction depending on the way in which P has been assimilated. Successive solubilisation of P is undertaken using the following compounds: NH_4Cl, NaOH and HCl. These reagents release loosely and $CaCO_3$-bound, Fe- and Al-bound and Ca-bound P respectively.

In peaty sediment, NaOH has been found to extract not only Al- and Fe-bound P, but also much of the humic-bound fraction, thereby suggesting that this procedure is inadequate under such conditions (Klapwijk *et al.*, 1982).

Attempts have also been made to chemically extract the bioavailable P fraction from sediment. Nitrilotriacetic acid (NTA) extractable P has been shown to be an estimate of phytoplankton available P in some sediments. However, available P may be over estimated due to presence of organic or Ca-bound P (Golterman, 1977; 1982b). NTA extractable P was found to be 4-90 times greater than that removed by *Scenedesmus*

quadricauda from clay, sand/peat and peat sediment. A correlation was found between available P and NTA and NaOH extractable P, but a stronger relationship was found between available P and TP (H_2SO_4-persulphate digest) (Klapwijk *et al.*, 1982).

None of the extraction techniques used in sediment chemistry determine definable P compounds, but give an estimate of the amount of a group of P compounds extractable by a particular method. In addition, the accuracy of results is highly dependent upon sediment type (Pettersson *et al.*, 1988). Difficulties associated with measuring different P fractions, combined with the fact that the purpose of P determination was to estimate the total quantity of P bound in the sediment, regardless of the form in which it was present, meant that the nitric-perchloric-sulphuric acid digestion of sediment samples was the most suitable for the present study. The hot acid digestion results in destruction of all organic matter present, although there is little breakdown of silicates. Procedures involved in this technique are relatively simple and the methodology has been utilised repeatedly for determination of quantities of P and N in previous studies of sediment nutrient content (Allen *et al*, 1974; Grimshaw, 1985).

3.4.2 Characteristics of sediments in the five water bodies

Shetland sediment analysed may have incorporated P in a number of forms, both inorganic and organic. The range of values calculated, of %P in the sediments tested (*i.e.* 0.03 to 0.34% P), was found to be comparable with information on sediment %P content in published literature (Table 3.6). There did not appear to be a simple relationship between organic content of the sediments and the quantity of P bound in the sediment (Figure 3.3 and 3.6). This could be because, although P may be loosely bound in organic matter, it may also be easily lost. In addition, there may be other processes to consider, such as the availability of other types of binding site. For example, if there was a considerable proportion of P immobilised by organic matter, but the Fe content of the sediment was low, then the total P bound in the sediment would not necessarily be particularly high.

Table 3.6 The phosphorus content of sediments recorded in published literature

Sediment P content (%)	Reference
0.15-0.25	Granéli (1978)
0.06-0.16	Boström and Petersson (1982)
0.03-0.48	Klapwijk *et al.* (1982)
0.14-0.18	Boström (1984)
0.11-0.37	Wiśniewski and Planter (1985)
0.09-0.20	Boström (1988)
0.10-0.65	Boström *et al.* (1988)
0.08-0.19	Gächter *et al.* (1988)
0.12-0.32	Jensen and Andersen (1990)
0.04-0.49	Jensen *et al.* (1992)
0.21-0.39	Eckerrot and Pettersson (1993)
0.05-0.10	Kleeberg and Schlungbaum (1993)
0.03-0.39	Lopez and Morgui (1993)
0.07	Waara *et al.* (1993)

As Loch of Gonfirth sediment Eh remained above +200 mV it is assumed that the bottom deposits were aerated to some degree throughout the first 10 cm depth, *i.e.* reducing conditions were not occurring (Figure 3.7). Conditions in Helliers Water sediment were slightly reducing only. The relatively high organic content in Helliers Water sediment may account for the lower Eh values in sediment from this water body compared to those of Loch of Gonfirth. Much of the organic matter in the Helliers Water bottom deposits is likely to have resulted from the presence of plant material, as there is much macrophyte growth in this water body.Sediments from Helliers Water and Loch of Gonfirth were the only two which exhibited positive Eh values throughout core depth (Figure 3.7). The more favourable Eh values in Loch of Gonfirth and Helliers Water are to be expected, owing to the low anthropogenic inputs of organic matter to these loch systems. Under the Eh conditions observed, P binding within the sediment is likely to be affected little in Loch of Gonfirth. However, the type of sediment retrieved from this water body in 1993 may have different characteristics to that sampled during 1992. In the slightly reducing conditions observed in Helliers Water sediment, there may have been some denitrification and reduction of Mn^{4+} occurring, depending upon sediment pH (Schwoerbel, 1987; Meadows and Campbell, 1988).

There was no significant difference in BD, %LOI or %C between cores of Tingwall North, Tingwall South and Turdale Water (Table 3.3). %LOI and %C are not necessarly good indicators of organic enrichment in freshwater sediments, as both are influenced by the presence of peaty material. Although %N was greater in Tingwall South than Turdale Water sediment, there was no significant difference between bottom deposits from the two Tingwall basins in terms of %N. The difference in redox conditions may be attributable to the characteristics of the external organic inputs. The discharges to Tingwall South incorporate complex organic compounds which cause a high oxygen demand, whereas a high proportion of anthropogenic inputs to Turdale Water contribute to the inorganic nutrient loading of the waterbody. It is possible that at the sediment Eh values observed, the processes of denitrification and reduction of Mn^{4+} and Fe^{3+} were occurring within the sediment profiles of Tingwall South, Tingwall North and Turdale Water, although stability of ion species in sediments is also pH dependent (Schwoerbel, 1987; Meadows and Campbell, 1988). As Fe and Mn do not bind with P in their reduced forms, a proportion of the

total P within these bottom deposits was probably free within the sediments. There are several mechanisms by which this P could be released to the oxygenated water column, as decscribed in Section 3.1.3.1.

As observed with %P values, the %N (Granéli, 1979; Bŏstrom and Pettersson, 1982; Klapwijk *et al.*, 1982; Bŏstrom, 1988) and %C (Bŏstrom and Pettersson, 1982; Bŏstrom, 1988) contents of Shetland sediments were typical for freshwater lake bottom deposits (Table 3.6). Similarities were observed in sediment profiles of %N, %C and %LOI, such as in Turdale Water sediment cores. However, the distribution of %P in the cores followed a distinctive pattern (Figure 3.6). Sediment from each of the five lochs exhibited an elevated %P content toward the mid depth of the cores. In addition, in Helliers and Turdale Water, Loch of Gonfirth and the North basin of Loch of Tingwall, sediment %P content decreased from the mid depth of the core. If interstitial P is related to total P, then this implies a concentration gradient from depth to sediment surface, which may favour translocation of P to surface sediment. It is possible that the upper layers of sediment incorporate less P because of periodic resuspension of surface sediment in the water column.

It is likely that the low %P content of Helliers Water sediment was related to the low P concentration in the water column of this water body (Chapter 2). The sediment surface %P content in Loch of Gonfirth was also low, as would be expected from the low P concentrations in the water column. Cores taken in 1992 from Loch of Gonfirth were plastic and clay-like under the surface layers. The relatively high %P content observed mid core may have been related to clay present at this depth. Clay minerals are mainly hydrous silicates of Al, Mg and/or Fe and therefore have a high potential P binding capacity. Turdale Water sediment %P content tended to be relatively high in comparison with the other sediments examined (Figure 3.6). This water body has been subject to high P concentrations in the water column, so partly explaining elevated sediment %P content. Possible mechanisms of P binding in the sediments of the five lochs will be discussed further with reference to the P adsorption and release experiments of 1993.

3.4.3 P adsorption tests with sediment samples

P adsorption in Loch of Gonfirth sediment was not as efficient as that of Helliers

Water at either P enrichment treatment level (Table 3.5). Sediment from Loch of Gonfirth also assimilated less P than Loch of Tingwall sediment, when loch water P concentration was elevated by 50 μg P L^{-1}. Of the five lochs examined, water from Loch of Gonfirth was most acidic (mean pH: 6.36, 1991) and concentrations of water Ca and Mg were also low (3.2 mg Ca L^{-1} and 3.1 mg Mg L^{-1} respectively, 1991). Although more mineral sediment was found in 1992, sediment from Loch of Gonfirth in 1993 was the most organic of the four examined. (There was no sediment sample from Sandy Loch in 1993 upon which to comment).

The poor P adsorption capacity of this sediment was therefore perhaps due in part to lack of Ca and Mg binding sites. At the pH levels of this loch Fe-P would be more likely. However, effectiveness of Fe in immobilisation of P in peaty sediment may be limited because Fe is rapidly reduced. Consequently little Fe-P binding occurs (Keizer *et al.*, 1993). Release of P is greater from Loch of Gonfirth sediments than from those from Helliers Water (Table 3.5). This suggests that, in Loch of Gonfirth, P which is adsorped may be loosely bound in humic complexes. Loch of Gonfirth sediment collected in 1992 was not organic and perhaps would have had relatively good adsorption properties. However, owing to catchment soil types (Chapter 6), it is likely that sediment of a more organic nature is dominant in the loch system.

Turdale Water sediment was found to release more P than the other sediments tested (Table 3.5). This is most plausibly explained as the result of a combination of high loading of P from the catchment area and the inability of the sediment to immobilise P additions. Ca concentration in Turdale Water was found to be relatively high when considering the five study lochs (mean: 13.7 mg Ca L^{-1}, 1991). Turdale Water is situated on limestone of the Walls Formation. This loch also has the second highest Mg concentrations of the five lochs involved in the sediment study (mean: 8.8 mg Mg L^{-1}, 1991). Water pH values are also relatively high, indicating that P should theoretically be binding with Ca^{2+} and Mg^{2+}. However, the catchment area of Turdale Water incorporates peaty soil and sediment from this loch was more organic than that of the other lochs. In the peaty sediments of the Loosdrecht Lakes, The Netherlands, formation of vivianite in interstitial water is insignificant, conditions in peaty sediment precluding conversion of $CaCO_3$ to Ca-P compounds (Keizer *et al.*, 1993). It is suggested that a significant proportion of P immobilised by Turdale Water sediment

is only temporarily or loosely bound, in humic complexes.

Sediment of Helliers Water was relatively efficient at P adsorption, greater uptake occurring in this sediment than either of the other two tested (Table 3.5). Water of this loch has high Mg concentrations (10.5 mg Mg L^{-1}, 1991 mean), although Ca concentration is relatively low at 4.0 mg Ca L^{-1} (1991 mean). Situated on serpentine bedrock, Helliers Water catchment area would be expected to have soils and sediments high in Mg, Fe, Ni and Cr. A mean water pH of 7.23 in 1991 indicates that at the low Ca concentrations present, it is likely that P is binding with Mg, although some binding with Fe is possible, depending upon sediment conditions. Low bulk density figures associated with Helliers Water sediment suggest the possibility that penetration of dissolved oxygen may be relatively efficient, assisted also by growth of rooted macrophytes. This would augment P retention in the field situation. Organic content of Helliers Water sediment is likely to be influenced by the macrophyte growth present, rather than by humic materials, as Helliers Water is a clear water loch.

Loch of Tingwall sediment was not as efficient in its immobilisation of P as that of Helliers Water, though it exhibited P uptake twice that of Loch of Gonfirth sediment (Table 3.5). Loch of Tingwall sediment also had the second highest P release of 0.34 μg P g^{-1} sediment. The latter may be as a consequence of there being a higher external P loading on Loch of Tingwall, than on either Loch of Gonfirth or Helliers Water. It is probable that Loch of Tingwall sediment P is binding with Ca, as loch water is slightly alkaline (pH 7.72, 1991 mean) and Ca concentration is high (33.7 mg Ca L^{-1}, 1991 mean). The west side of Loch of Tingwall is situated on limestone bedrock, so that sediment Ca content is likely to be elevated.

The organic content of Sandy Loch sediment was greatly in excess of that in sediment of the other four lochs (Table 3.2). Water in this loch is highly coloured. This suggests that P adsorption capacity of Sandy Loch sediment is likely to be poor, P binding loosely with humic substances rather than directly with metals.

3.5 CONCLUSIONS

%C, %N and %P contents of the sediments examined were all within the ranges of

values observed elsewhere. Eh conditions in the sediments were generally in agreement with nutrient status information on the four basins *i.e.* Gonfirth sediment remained slightly aerated, whilst sediment conditions became more reducing in the following order: Helliers Water, Tingwall North, Turdale Water and Tingwall South. This is the same order as increasing nutrient status, with the exception of Tingwall South. As Eh values were smaller than expected from the trophic status of Loch of Tingwall, this suggests that the water body is under considerable influence of organic enrichment from anthropogenic sources within the catchment area.

It is apparent from the above results that, in Shetland lochs, the same sediment may act as both a sink and a source of P. There was a tendency for P stored in sediment to be present in highest quantities at approximately 3-5 cm sediment depth. A proportion of the P present in the upper 5 cm of sediment was in a readily releasable form, possibly loosely bound to humic substances, in sediment from Lochs of Gonfirth, Tingwall and Turdale Water. Sediment P content is not necessarly a good indicator of trophic status, since, as observed in the literature, %P can be highly variable, within the same loch and between different waterbodies exhibiting similar water column nutrient levels.

Turdale Water had the most elevated water column TP concentration, in addition to having the most organic sediment and the highest P release. Loch of Tingwall sediment had the lowest organic content, but the second highest water column TP concentration and sediment P release. This illustrates the importance of external P loading on sediment P dynamics. Sediment from Helliers Water did not release any P, unlike Loch of Gonfirth sediments. Considering the similarity of water column TP levels in these two water bodies, the inferior binding capacity of Loch of Gonfirth sediment may have been related to the higher organic content of this sediment.
Of the three sediments tested for P uptake, Helliers Water sediment had the highest adsorption capacity, followed by Lochs of Tingwall and Gonfirth. Therefore, sediment in Helliers Water assists in maintaining water column P concentration at levels lower than would be expected from P loading on the water body. In Loch of Gonfirth, the sediment has a comparatively small capacity for retaining P and may rerelease P to the water column. Sediment in Loch of Tingwall has a relatively good P binding capacity, but again, P may be rereleased to the water column from the

sediment. Although Turdale Water sediment may release P, there is such a high external P loading that this will not be of consequence, unless the external loading decreases. The peaty nature of Sandy Loch sediment suggests that it would not have a high P binding capacity. This would limit adsorptive capacity and lead to rapid water column changes in P concentration with increased external P loading.

It is concluded that, if the external P loadings were removed from Loch of Tingwall, Sandy Loch and Turdale Water, an internal P loading would remain. However, in Helliers Water, it is likely that the P immobilised in the sediment would be retained. Although Loch of Gonfirth sediment was found to release P, there has been no artificial loading on this water body, so that the internal loading is not considerable.

CHAPTER 4: PHYTOPLANKTON IN SHETLAND LOCHS

4.1 INTRODUCTION

4.1.1 Phytoplankton blooms

As phytoplankton are primary producers *i.e.* organisms at the base of the aquatic food chain, effects of shifting nutrient status due to anthropogenic influences within the catchment are often detectable in the algal population before differences are evident in communities of herbivorous or carnivorous organisms. As well as subtle changes in size and species of phytoplankton present, nutrient enrichment may cause great increases in algal numbers. Skulberg *et al.* (1984) suggest that moderate to high nutrient levels, especially of nitrate and ammonia, water temperatures of 15-20°C and pH 6-9 are ideal conditions for blooms to occur, whilst Boyd *et al.* (1978) stress the importance of wind action in the distribution of blue-green algae in the water column, as it prevents formation of localised areas of particularly high biomass. Dense populations of phytoplankton occur in surface waters when weather conditions are calm. Blue-green algae actively regulate their buoyancy (Fay, 1983; Fogg and Walsby, 1971), so that they may remain in the photic zone of a water body; therefore, if wind circulation stops, buoyancy is overcompensated, resulting in large concentrations of phytoplankton in water surface layers. Incidences of algal bloom problems in Scotland have not been restricted to recent years, occurring annually in many small lochs such as Balgavies Loch (NGR: 533 508), Fingask Loch (NGR: 165 430), Lindores Loch (NGR: 265 165) Loch Marlee (NGR: 143 444), Monikie Island pond (NGR: 505 380), Loch Rescobie (NGR: 515 515) and White Loch (NGR: 170 428) (Richard *et al.*, 1981).

Although any algal group may create blooms, increased biomass is often in the form of blue-green species (Cyanophyceae, cyanophytes or cyanobacteria) such as *Oscillatoria*, *Anabaena*, *Aphanizomenon*, or *Microcystis* (Gorham and Carmichael, 1980; Carmichael, 1982; NRA, 1990), other cyanophytes which have been known to cause problems being *Gomphosphaeria*, *Coelosphaerium*, *Nodularia*, *Nostoc* and *Cylindrospermum* (Lawton and Codd, 1991). Assessment of cyanophyte blooms from nearly 300 British sites between 1981 and 1989 indicated that 45-75% were toxic (Lawton and Codd, 1991), although of those blue-green blooms examined in 1989, approximately 60-70% of cases were found to involve lethal substances. Cyanophyte toxins may be divided into three groups: neurotoxins (some of which are alkaloids),

hepatotoxins (peptides) and lipopolysaccharides (fats and sugars). Neurotoxins are produced by species of *Anabaena*, *Aphanizomenon* and *Oscillatoria*, hepatotoxins by strains of species of *Microcystis*, *Oscillatoria* and *Anabaena*. The latter are also known as microcystins and consist of a cyclic structure containing seven amino acids and having a molecular weight of about 1000 (NRA, 1990). Lipopolysaccharides differ from the other toxin types as they form as essential components of cyanobacterial cells, rather than substances produced within those cells.

Animal poisoning incidents involving blue-green algal toxins have been reviewed (Ingram and Prescott, 1954), deaths having occurred in livestock, birds and fish (Gorham and Carmichael, 1980; Hunt, 1984). During investigations of toxicity of *Microcystis aeruginosa* to rainbow trout (*Oncorhynchus mykiss*), fish exposed to dense populations of this algal species for ten days demonstrated no ill-effects, although interperitoneal injection of *Microcystis* extract caused mortality (Phillips *et al.*, 1985). It is possible therefore, that chronic effects could occur in fish through exposure to blue-green colonies. During 1992, brown trout (*Salmo trutta*) in Loch Leven (Fife, Scotland) were found dead after senescence of a bloom of *Anabaena flos-aquae*. Pathology of the gill epithelium revealed a change in mucus consistency and acute irritation. Liver pathology was "consistent with the effects of potent hepatotoxin(s)" and similar to that induced in rainbow trout through injection of *Microcystis* extract by Phillips *et al.* (1985) (Rodger *et al.*, 1994). Whereas liver damage was directly attributable to a toxic effect, gill irritation may have occurred through elevated water pH, concentration of blue-green algae, a direct toxic effect or an association of these potential causes (Rodger *et al.*, 1994). Although no human deaths have resulted from contact with blooms, skin rashes, eye irritation, vomiting, diarrhoea, fever, liver disorders, painful joints and muscles can occur in man (NRA, 1990). Obviously in these cases blooming would severely limit the amenity value of the affected water body.

Instances of any algal bloom can also significantly reduce dissolved oxygen concentrations in the water column both overnight and when the bloom dies. The increased BOD resulting from algal dieoff is perhaps a more likely cause of fish mortality than toxin production, as avoidance strategies may be employed by these organisms to deal with the latter. Fish, however may also encounter difficulties

through gill clogging during dense phytoplankton growth, thereby creating further gaseous exchange problems. Large populations of phytoplankton can also result in great changes in pH of standing water bodies. For example, Brook (1958), recorded a change in waters of pH 6-7 to pH 8-10 during blooms of Cyanophyceae and Chlorococcales. Further to these problems are the elevated levels of ammonia associated with bloom death (Reynolds, 1984a), increased turbidity in the water column and taste taint in fish flesh.

4.1.2 Phytoplankton of freshwater lochs in Shetland

In a study of Shetland freshwater algae from Bressay and Mainland (West and West, 1904) algal groups which were found, in order of decreasing numbers were Chlorophyceae, Bacillariophyceae and Cyanophyceae. Of these, the green phytoplankton were most diverse. The study included the sites of Loch Asta, Neugles Water, Sandy Loch, Trebister Loch, Beosetter Loch and Brindister Loch and it was concluded that plankton was not very rich, partly due to the wetness of the season (West and West, 1904). There was, however, only one trip made (in August) so that any successional effects cannot be identified.

In a second study of Shetland algae from standing freshwaters (Carter and Bailey-Watts, 1981), over 400 species of phytoplankton in a total of 53 lochs were found, each loch in detail being unique. In nearly every water, the two algal groups represented by most species were those of Chrysophyceae and Chlorococcales. Overall numbers of species found in each group are shown in Table 4.1.

In 80% of lochs, chrysophytes exceeded green algae in both numbers of species and density of individuals. Phytoplankton of the Chrysophyceae do not tend to form major blooms, although *Dinobryon* and *Mallomonas* may be associated with taste and odour problems (APHA, 1989). Chrysophytes are believed to be unaffected by considerations of loch volume, surface area, mixing depth and epilimnetic water temperature, but other factors which have been associated with this algal type include low to moderate productivity, low nutrient availability, low alkalinity, low conductivity and neutral to slightly acid pH (Sandgren, 1988). Chrysophytes are often associated with peaty waters, though possibly due to their wide tolerance of water colour rather than their restricted range.

Table 4.1 **Numbers of species found from different algal groups in samples from 53 Shetland lochs (Carter and Bailey-Watts, 1981)**

Algal type	Number of species
Chrysophyceae	82
Chlorococcales	92
Bacillariophyceae	47
Volvocales	34
Desmidaceae	32

However, though conditions in the Shetland lochs examined in the study were favourable to chrysophyte growth, samples were taken in September only. As a consequence of phytoplankton periodicity, dominance of the algal community by Chrysophyceae could be transitory. No record of Cyanophyceae was made in the 53 lochs sampled in September, 1974 (Carter and Bailey-Watts, 1981), suggesting that these algae were not important in a large proportion of lochs at that time. However, this could also be a seasonal effect.

4.1.3 Aims

In the present study, the aims of examining the phytoplankton in Shetland lochs were as follows.

(a) Identify and enumerate phytoplankton present in the thirty one lochs studied during summer 1991.

(b) Using environmental data collected at the same time (Chapter 2), assess whether the successful growth of different algae was associated with specific conditions within the water column.

(c) Assess which environmental parameters are likely to be linked with excessive production of cyanobacteria, in particular, *Anabaena*.

(d) Assess the possible effects of nutrient enrichment on the standing freshwaters of Shetland.

(e) Examine the phytoplankton in five lochs of different water chemistry in terms of succession and periodicity.

4.2. MATERIALS AND METHODS

4.2.1 Chlorophyll *a*

Chlorophyll *a* was determined by the method described in Chapter 2.

Correlations were examined between mean summer chl *a* concentration and environmental data of mean summer pH, mean summer concentrations of TP, TDP, TON, TAN, Ca, Mg, Na and K.

4.2.2 Phytoplankton populations

In 1991, samples for phytoplankton were taken and composited as described for water chemistry (Chapter 2) although three phytoplankton samples were not examined,

apparently having been lost in transit. These samples were from Loch of Gonfirth 07/91, Loch of Cliff 07/91, and Lunga Water 07/91. During 1992 and 1993, phytoplankton samples were taken from Lochs of Gonfirth (Site 2) and Tingwall (Site 1, North; Site 2, South), Sandy Loch (Site 3) and Helliers (Sites 1-3) and Turdale Water (Sites 1-3). Samples were then composited after concentration. For each survey date at Turdale and Helliers Water, three surface samples were amalgamated, whereas samples from 0, 2 and 5 m at each site of the remaining three lochs were combined. Phytoplankton in the surface waters of each of the five lochs were enumerated in order to examine changes in numbers and dominance of different algal groups from March to October.

Phytoplankton in each 250 mL water sample were preserved with approximately 0.5 mL Lugol's iodine (Beveridge, 1985). In the laboratory, samples were transferred to 250 mL glass measuring cylinders and allowed to stand undisturbed for at least 1 week. In order to allow phytoplankton to settle and concentrate in the bottom of each cylinder, a sinking rate of 1 cm every 4 hours was assumed, as Margalef (1969) supposed an algal descent of 1 cm every 3 hours for nanoplankton. Overlying water was then removed to leave 20-30 mL undisturbed concentrated phytoplankton sample. When phytoplankton was particularly sparse, samples were centrifuged at 1,000 r.p.m. for 20 minutes (Beveridge, 1985), before removal of supernatant, to leave a concentrated sample, of 5 mL volume.

From a concentrated sample it was possible to identify and count phytoplankton present. After resuspension of the algae, sample examination was carried out at a magnification of x400, using a compound microscope. Algae in samples from 1991, 1992 and 1993 samples were examined in terms of identification of individuals and numbers of algae per sample. Samples were pipetted into a Lund chamber (Lund, 1959) and the number of phytoplankton units in each randomly chosen microscope field identified and enumerated until at least 100 units and 30 fields (depending on concentration of phytoplankton) had been counted. A review of published literature revealed that generally workers elsewhere have counted up to 100 units and 40 fields (Venrick, 1978). Each discrete colony or cell was regarded as 1 unit. From the sample concentration factor, dimensions of the chamber and field of view, counts were expressed as phytoplankton units mL^{-1} (PU mL^{-1}). Identifications of specimens

were carried out using standard phytoplankton keys (Barber and Haworth, 1981; Belcher and Swale, 1978; 1979; Bourrelly, 1966; 1968; 1970; Cleve-Euler, 1968; Pentecost, 1984; Prescott, 1962; 1970; Lind and Brook, 1980; Smith, 1950).

At Brough (Yell) and Bu Water during 1991, localised areas of algal scum were noted near to the shore. A sample of the scum was taken in each case. After preservation, the phytoplankton present were identified as above.

4.2.3 Data analysis of 1991 phytoplankton numbers

CANOCO is a FORTRAN program designed to carry out canonical community ordination using several methods, including Principal Components Analysis, Correspondence Analysis, Detrended Correspondence Analysis and Canonical Correspondence Analysis (CCA) (Ter Braak 1986; 1988; 1989). In the present study, CCA was used to undertake canonical community ordination of the phytoplankton data. Environmental data and phytoplankton numbers for each field visit in 1991 were analysed. Environmental parameters which were found to have a variance inflation factor (VIF) of > 19 were excluded from the data analysis. VIF is calculated as follows:

$$\text{VIF} \times (\text{residual variance})/(n\text{-}q\text{-}1) = \text{variance of the estimated regression coefficient}$$

where:

n = number of samples

q = number of environmental variables

VIF = $1/(1 - pmc)$

where

pmc = (partial) multiple correlation between one environmental variable and the other environmental variables in the calculations

Therefore, as the VIF of a parameter increases it indicates a higher correlation with other environmental variables. Environmenal parameters with high VIFs were removed as they would not confer singular information to the analysis. Consequently,

conductivity, water colour and TDP were not included because of their relationships with divalent cations, light attenuation and TP respectively. As the majority of lochs exhibited concentrations of DRP < 1.0 μg P L^{-1}, this parameter was also rejected from CCA. In addition, several samples were disregarded as their influence values were > 15, *i.e.* these samples had a disproportionately large effect on the analysis. These samples were: Loch of Brow (8/91), Mill Pond (7/91), Strand Loch (7/91 and 8/91) and Turdale Water (9/91).

From environmental information, CCA determined a number of ordination axes, which accounted for most of the variability in the sample (site plus date) and phytoplankton data. The greater the eigen value of an axis, the more variance in the data was accounted for by that axis. Scores (eigenvectors) were calculated by the program for both phytoplankton taxa and sites on each sampling date. These scores were then plotted in relation to the first two CCA ordination axes (Axis 1 and Axis 2 accounted for most variability in the data) on two separate figures (Figures 4.1a&b and 4.2a&b). Figures 4.1a&b represent phytoplankton groups along environmental gradients, whilst Figures 4.2a&b represent the site positions along the same gradients.

Interset correlations from the CANOCO output were converted to intraset correlations by division of the former with the species-environment correlations (Brown *et al.*, 1993). The significance of the intraset correlations was then investigated by comparing the *t*-values of the regression coefficients with the *t* distribution. Examination of the regression coefficients and the intraset correlations facilitated understanding of the ordination axes, through clarification of the most important environmental variables in the Shetland phytoplankton community distribution.

Biplot scores of environmental variables were used to illustrate environmental gradients on each biplot. Each environmental parameter included in the CCA analysis was represented as an arrow, the bearing of which portrayed the direction of maximum change within that parameter. Lengths of environmental gradient arrows were linked to their importance in terms of their influence on phytoplankton and site location in the biplots *i.e.* increased length was equated with greater correlation with the ordination axes. A perpendicular line dropped from phytoplankton type to environmental arrow indicated its location along that environmental gradient, relative

to other points on the biplot. Approximate rankings of phytoplankton taxa along the most influential environmental gradients were therefore ascertained. Similarity of site or phytoplankton points were assessed through the similarity of coordinates on the biplot.

4.3 RESULTS

4.3.1 Chlorophyll *a*

From the results of the 1991 survey (n=93), correlation of chl *a* with each environmental variable in turn revealed significant positive correlations between chl *a* and TP ($r = 0.49$; $p < 0.001$), chl *a* and pH ($r = 0.31$; $p < 0.01$), chl *a* and Na ($r = 0.47$; $p < 0.001$) and chl *a* and K ($r = 0.47$; $p < 0.001$). A strong positive relationship between chl *a* and total algal counts was not observed (Figure 4.1b). However, this was likely to have been an artifact which occurred as a result of the method of algal enumeration used in the present study (Section 4.4.1).

4.3.2 Phytoplankton distribution with respect to environmental parameters

4.3.2.1 Summary of CCA characteristics

Table 4.2 presents the summary of the CCA analysis. 38% of the species-environment correlation was in the first two axes. The eigenvalues associated with Axis 1 and Axis 2 were 0.510 and 0.456 respectively and the decrease in eigenvalues from Axis 1 to Axis 4 exhibited a low gradient. The ratio of the sum of unconstrained eigenvalues (7.206) and the sum of canonical eigenvalues (2.543) was relatively high.

The intraset correlations of environmental variables with the Axes (Table 4.3) indicated that TP, TAN and chl *a* were positively correlated with Axis 1, whilst TON and total algal count were negatively correlated with the same Axis. TP, TAN and TON were also positively correlated with Axis 2. Water pH values were negatively correlated with this Axis. Significance of the *t*-values (assigned as if using a conventional *t*-test) indicated importance in Axis 1 of TP, TON, TAN, K, chl *a* and phytoplankton numbers, in addition to TP, TAN, TON, pH, Ca, Mg, chl *a* and phytoplankton numbers in Axis 2. All other *t*-values were < 2.1 and therefore did not explain an important proportion of the varition in the data (Ter Braak, 1988).

Table 4.2 Summary data of CCA data analysis

Axes	1	2	3	4	Total inertia
Eigenvalues	0.510	0.456	0.351	0.293	7.206
Species environment correlations	0.929	0.911	0.895	0.782	
Cumulative % variance of:					
species data	7.1	13.4	18.3	22.3	
species-environment relation	20.1	38.0	51.8	63.3	
Sum of all unconstrained eigenvalues					7.206
Sum of all canonical eigenvalues					2.543

KEY TO FIGURES 4.1a AND 4.1b

Phytoplankton taxa active in the CCA analysis

CCA number	Phytoplankton active in CCA	Phytoplankton class
01	*Anabaena*	Cyanophyceae
02	*Aphanothece*	Cyanophyceae
03	*Ankyra*	Chlorophyceae
04	*Asterionella*	Bacillariophyceae
05	*Aulomonas*	Chrysophyceae
06	*Botryococcus*	Chlorophyceae
07	*Diceras*	Chrysophyceae
08	*Treubaria*	Chlorophyceae
10	*Cosmarium*	Chlorophyceae (Desmidiaceae)
11	*Closterium*	Chlorophyceae (Desmidiaceae)
12	*Chlamydomonas*	Chlorophyceae
13	*Cyclotella*	Bacillariophyceae
14	centric diatoms	Bacillariophyceae
15	*Cryptomonas*	Cryptophyceae
16	*Cylindrospermum*	Cyanophyceae
17	*Chroococcus*	Cyanophyceae
18	*Ceratium*	Dinophyceae
19	*Coelosphaerium*	Cyanophyceae
20	*Chrysolykos*	Chrysophyceae
21	Chrysoflagellates	Chrysophyceae
23	*Dictyosphaerium*	Chlorophyceae
24	*Dinobryon*	Chrysophyceae
25	*Eudorina*	Chlorophyceae
26	*Elakatothrix*	Chlorophyceae
27	*Euastrum*	Chlorophyceae (Desmidiaceae)
28	*Eutetramorus*	Chlorophyceae
29	*Fragilaria*	Bacillariophyceae
30	*Gomphosphaeria*	Cyanophyceae
31	*Gymnodinium*	Dinophyceae
32	unicellular greens	Chlorophyceae
33	*Koliella* (1)	Chlorophyceae
34	*Koliella* (2)	Chlorophyceae
35	*Kephyrion*	Chrysophyceae
36	*Lagerheimia*	Chrysophyceae
37	*Lyngbya*	Cyanophyceae
38	*Merismopedia*	Cyanophyceae
39	*Melosira*	Bacillariophyceae
40	*Monoraphidium* (1)	Chlorophyceae
41	*Monoraphidium* (2)	Chlorophyceae
42	*Mougeotia*	Chlorophyceae
43	*Oocystis*	Chlorophyceae
44	*Oscillatoria*	Cyanophyceae
45	*Pediastrum*	Chlorophyceae

KEY TO FIGURES 4.1a AND 4.1b (cont.)

Phytoplankton taxa active in the CCA analysis

CCA number	Phytoplankton active in CCA	Phytoplankton class
47	*Peridinium*	Dinophyceae
49	*Rhodomonas*	Cryptophyceae
50	*Scenedesmus* (2 cell)	Chlorophyceae
51	*Synedra*	Bacillariophyceae
53	*Staurastrum*	Chlorophyceae (Desmidiaceae)
55	*Sphaerocystis*	Chlorophyceae
57	*Spirogyra*	Chlorophyceae
58	*Schroederia*	Chlorophyceae
59	*Tabellaria*	Bacillariophyceae
60	*Xanthidium*	Chlorophyceae (Desmidiaceae)
62	filamentous A	
63	filamentous B	
64	Strand diatom	Bacillariophyceae
65	*Selenastrum*	Chlorophyceae
66	unknown A	
67	*Euglena*	Euglenophyceae
68	*Crucigenia*	Chlorophyceae
69	Brow filament A	
70	Brow filament B	
71	*Scenedesmus* (4 cell)	Chlorophyceae
74	*Trachelomonas*	Euglenophyceae
75	unknown E	
76	*Tabellaria /Fragilaria*	Bacillariophyceae
77	*Kirchneriella*	Chlorophyceae

NOTE: **Axis 1** is the horizontal axis (*i.e.* in the "x axis" position), **Axis 2** is the vertical position (*i.e.* in the "y axis" position) on the biplot

Figure 4.1a CCA biplot of phytoplankton distribution along environmental gradients

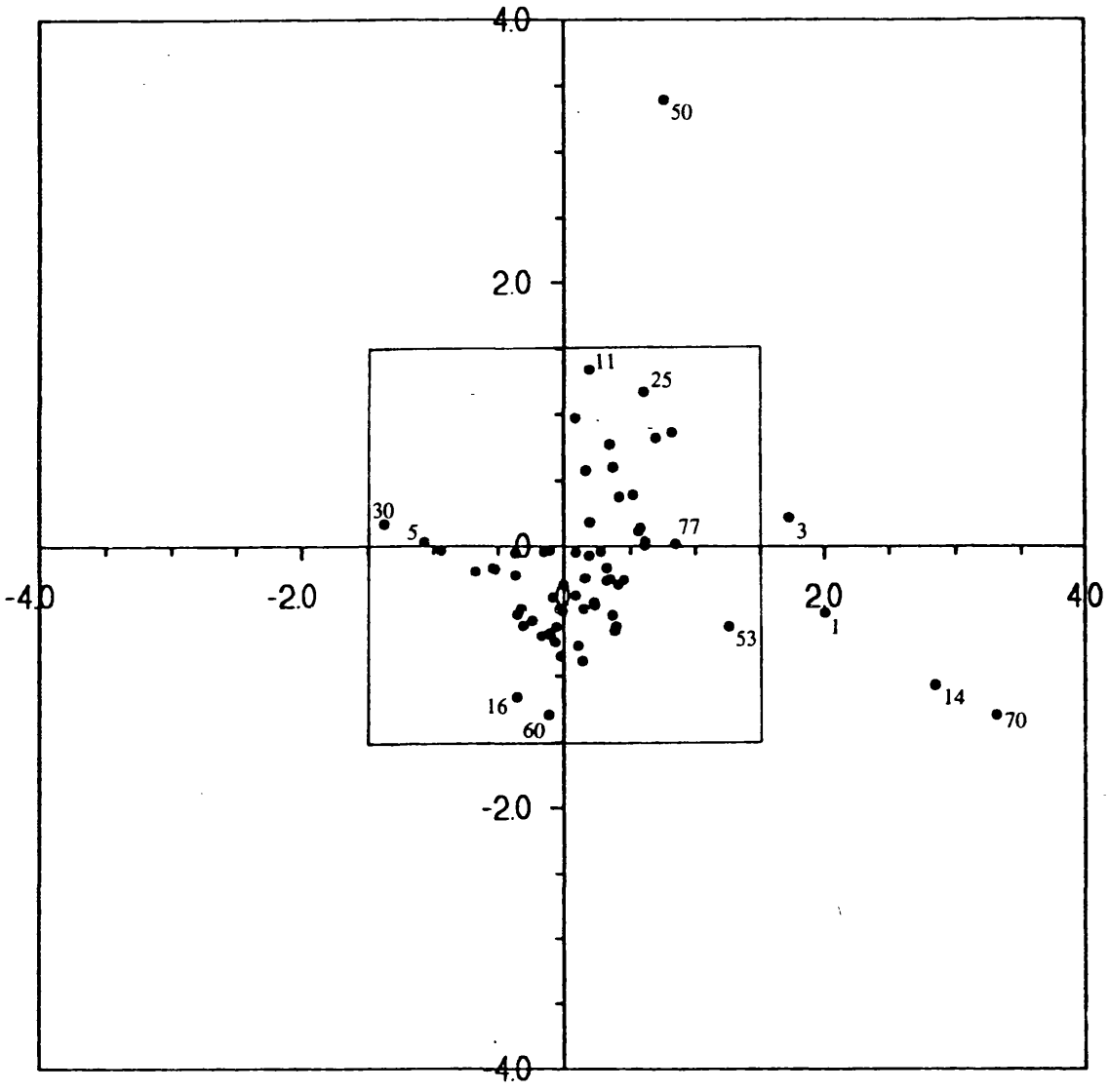
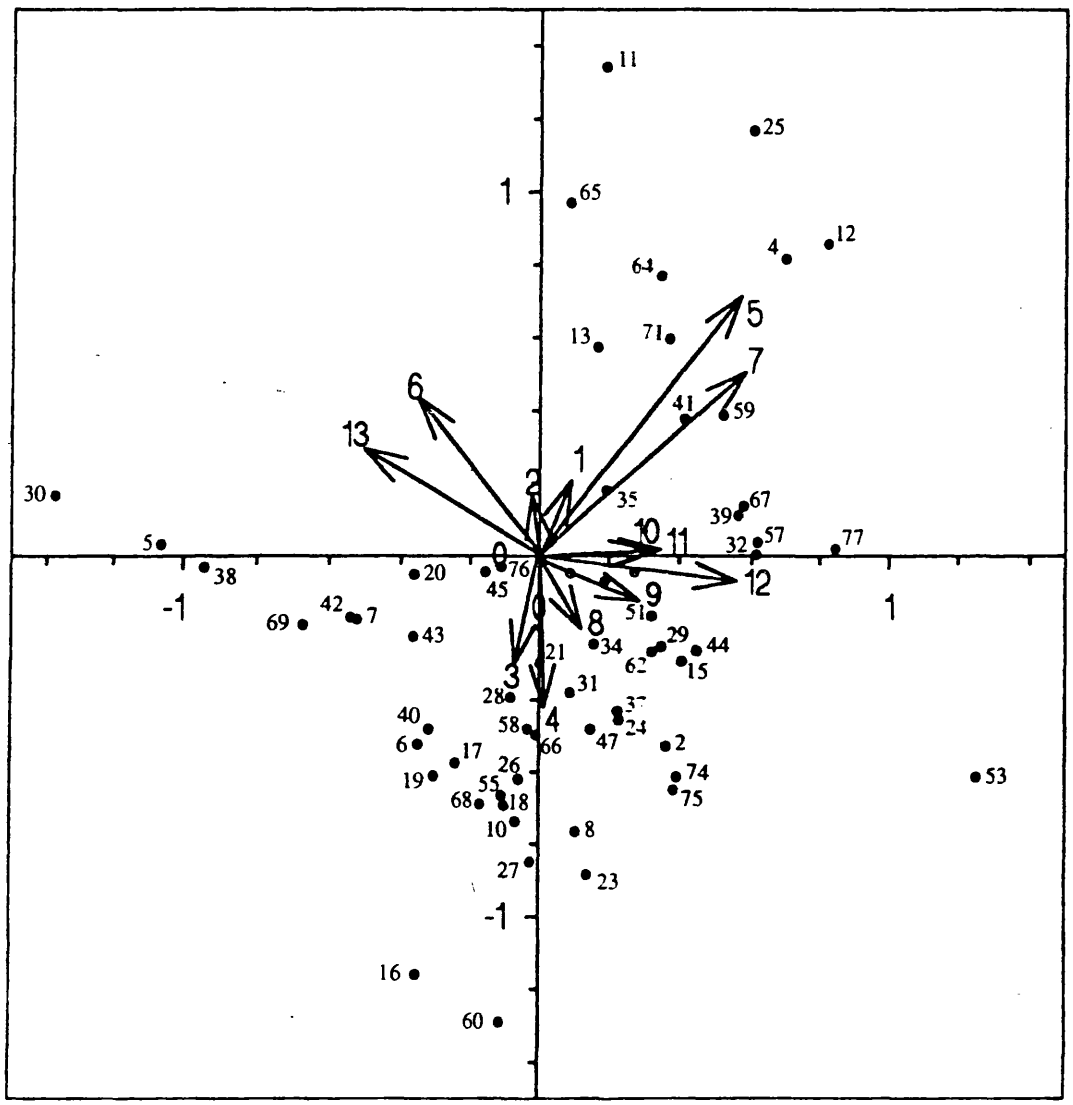


Figure 4.1b Detail of Figure 4.1a



Key to environmental gradients

1:	LAC	**2:**	Dissolved oxygen	**3:**	Temperature
4:	pH	**5:**	TP	**6:**	TON
7:	TAN	**8:**	Calcium	**9:**	Magnesium
10:	Sodium	**11:**	Potassium	**12:**	Chlorophyll *a*
13:	Total algal count				

KEY TO FIGURES 4.2a AND 4.2b

Shetland loch samples included in the CCA analysis

CCA no.	Water body	Sampling date
01	Arthurs Loch	07/91
02		08/91
03		09/91
04	Bu Water	07/91
05		08/91
06		09/91
07	Loch of Brindister	07/91
08		08/91
09		09/91
10	Loch of Brough	07/91
11	(Bressay)	08/91
12		09/91
13	Loch of Brough	07/91
14	(Yell)	08/91
15		09/91
16	Loch of Brow	07/91
17		09/91
18	Loch of Cliff	08/91
19		09/91
20	Eela Water	07/91
21		08/91
22		09/91
23	Loch of Gonfirth	08/91
24		09/91
25	Gorda Water	07/91
26		08/91
27		09/91
28	Gossa Water	07/91
29		08/91
30		09/91
31	Helliers Water	07/91
32		08/91
33		09/91
34	Loch of Huesbreck	07/91
35		08/91
36		09/91
37	Loch of Huxter	07/91
38		08/91
39		09/91
40	Loch of Kettlester	07/91
41		08/91
42		09/91

KEY TO FIGURES 4.2a AND 4.2b (cont.) Shetland loch samples included in the CCA analysis

CCA no.	Water body	Sampling date
43	Lunga Water	08/91
44		09/91
45	Mill Pond	08/91
46		09/91
47	Papil Water	07/91
48		08/91
49		09/91
50	Punds Water	07/91
51		08/91
52		09/91
53	Roer Water	07/91
54		08/91
55		09/91
56	Sand Water	07/91
57		09/91
58	Sandy Loch	07/91
59		08/91
60		09/91
61	Skutes Water	07/91
62		08/91
63		09/91
64	Loch of Snarravoe	07/91
65		08/91
66		09/91
67	Loch of Spiggie	07/91
68		08/91
69		09/91
70	Strand Loch	09/91
71	Loch of Tingwall	07/91
72		08/91
73		09/91
74	Turdale Water	07/91
75		08/91
76	Loch of Ustaness	07/91
77		08/91
78		09/91
79	Loch of Watlee	07/91
80		08/91
81		09/91
82	Whitelaw Loch	07/91
83		08/91
84		09/91
85	Sand Water	08/91

NOTE: **Axis 1** is the horizontal axis (*i.e.* in the "x axis" position), **Axis 2** is the vertical position (*i.e.* in the "y axis" position) on the biplot

Figure 4.2a CCA biplot of loch sites along environmental gradients

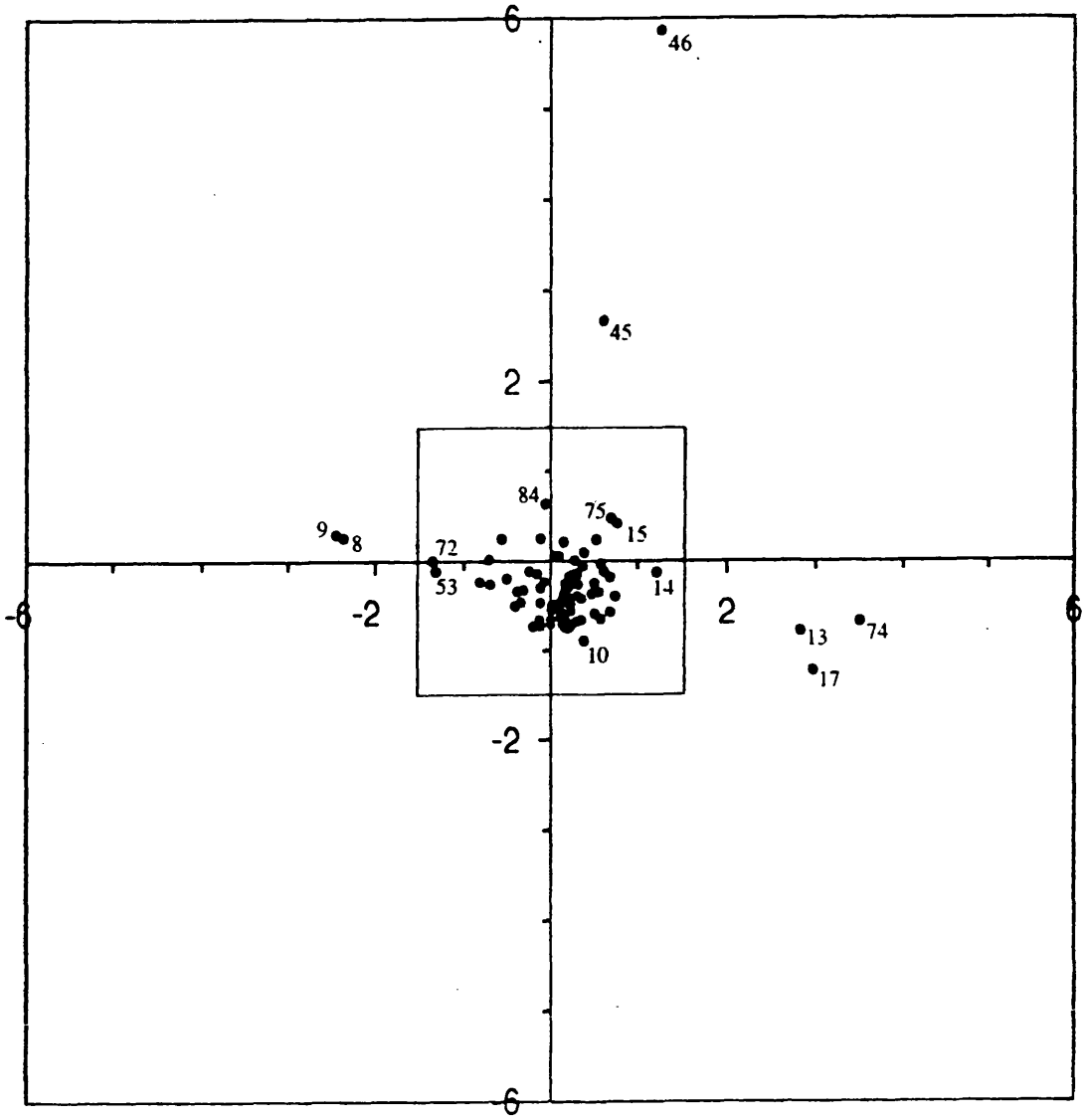
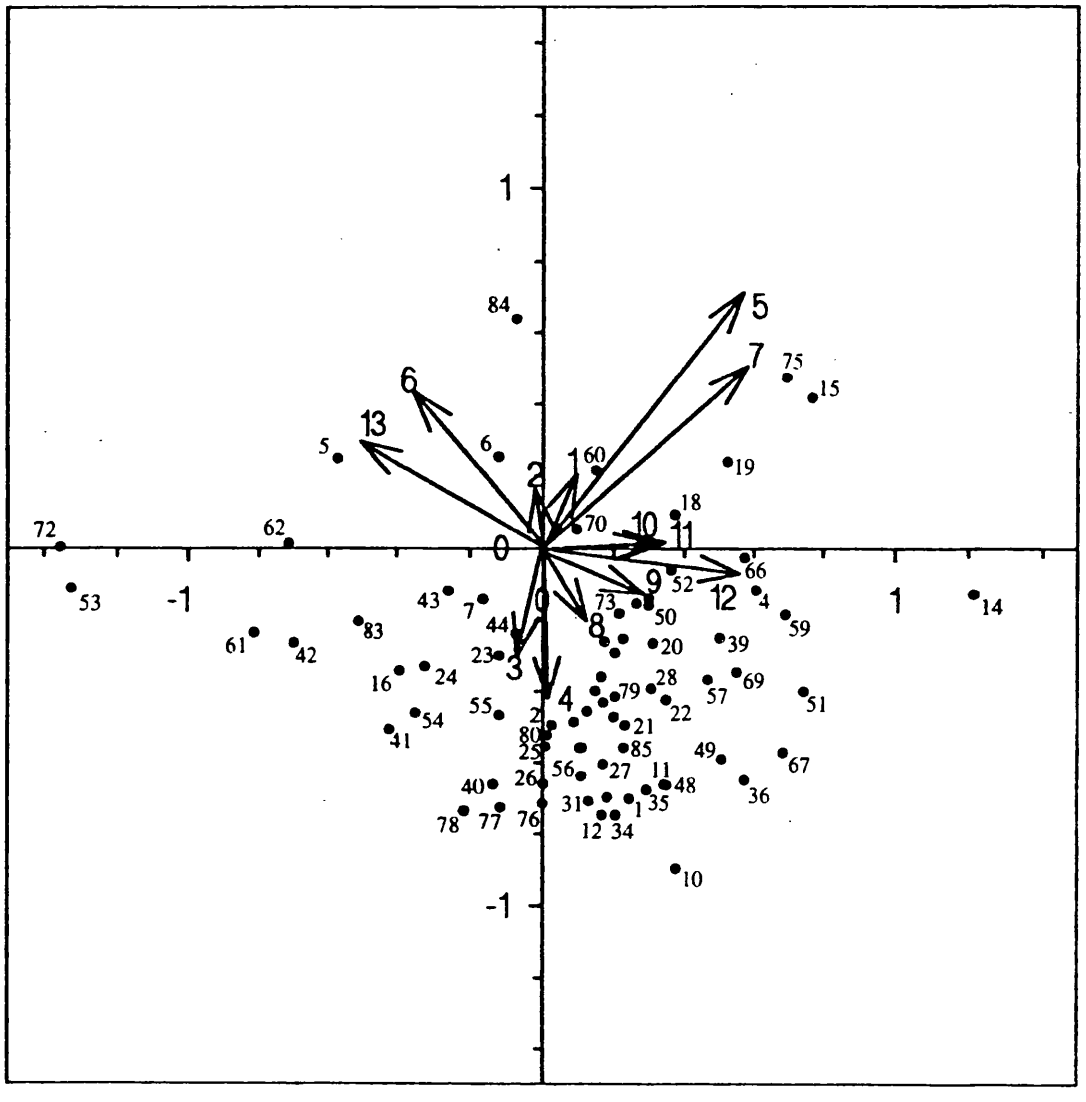


Figure 4.2b Detail of Figure 4.2a



Key to environmental gradients

1:	LAC	**2:**	Dissolved oxygen	**3:**	Temperature
4:	pH	**5:**	TP	**6:**	TON
7:	TAN	**8:**	Calcium	**9:**	Magnesium
10:	Sodium	**11:**	Potassium	**12:**	Chlorophyll *a*
13:	Total algal count				

Table 4.3 **Intraset correlations of environmental variables with CCA Axes 1 and 2 and significance of regression coefficient *t*-values**

Variable	Axis 1	Significance	Axis 2	Significance
LAC	0.095	ns	0.203	ns
Temperature	-0.070	ns	-0.294	ns
DO	-0.019	ns	0.166	ns
pH	0.013	ns	-0.426	***
TP	0.571	***	0.711	***
TON	-0.347	**	0.417	*
TAN	0.589	**	0.502	*
Ca	0.123	ns	-0.203	***
Mg	0.291	ns	-0.123	***
Na	0.317	ns	0.017	ns
K	0.350	***	0.025	ns
Chl *a*	0.527	***	-0.060	***
Algal count	-0.509	***	0.291	***

*** $p < 0.001$
** $p < 0.01$
* $p < 0.05$

Axis 1 was therefore related to P and N enrichment, whilst Axis 2 was related to water pH and hardness.

4.3.2.2 Positioning of phytoplankton data along CCA environmental gradients

Approximate (several phytoplankton taxa might be located at similar coordinates on the biplot) positions of phytoplankton taxa along important environmental gradients are presented in Table 4.4. Phytoplankton which were associated with high TP levels also tended to be associated with increased concentrations of TAN. Algal taxa for which this was the case were (in order of decreasing TP levels) *Scenedesmus* (two cell), *Eudorina*, *Ankyra*, *Chlamydomonas*, *Closterium*, *Asterionella*, small centric diatoms and *Anabaena*. Similarly, the phytoplankton taxa which were associated with low TP levels were also linked with low TAN concentrations. These algae included *Cylindrospermum*, *Xanthidium*, *Gomphosphaeria*, *Euastrum*, *Coelosphaerium*, *Crucigenia*, *Aulomonas*, *Botryococcus*, *Cosmarium* and *Merismopedia*, (in order of increasing TP concentration). However, although green algae, cyanobacteria and chrysophytes were all represented when TP and TAN concentrations were low, none of the diatom taxa observed in this study were associated with these water column conditions. Certain genera of green algae and blue-green phytoplankton were also linked with high concentrations of TP and TAN in the water column, as were individual diatom taxa. In contrast, chrysophytes were not associated with high water column TP and TAN levels.

The inferred ranking of phytoplankton on the TON gradient indicated that *Scenedesmus* (two cell), *Gomphosphaeria*, *Closterium*, *Aulomonas*, *Selenastrum*, *Merismopedia*, *Eudorina*, *Cyclotella* and *Scenedesmus* (four cell) were associated with increased levels of TON in the water column. In contrast, small centric diatoms, *Anabaena*, *Staurastrum*, *Ankyra*, *Xanthidium*, *Dictyosphaerium*, *Trachelomonas*, *Cylindrospermum* and *Treubaria* were linked with low water TON concentrations. Algae which were successful in waters with the combination of high TP, TAN and TON concentrations were few. Only green phytoplankton were ranked highly on all three gradients: *Scenedesmus*(two cell), *Closterium*, *Eudorina* and *Selenastrum*. Certain phytoplankton which were observed at low TP and TAN concentrations were, in contrast, ranked highly on the TON gradient.

Table 4.4 Ranking inferred by CCA of phytoplankton along environmental gradients of TP, TAN and TON

TP	TAN	TON
Scenedesmus (2 cell)	*Scenedesmus* (2 cell)	*Scenedesmus* (2 cell)
Eudorina	Centric diatoms	*Gomphosphaeria*
Ankyra	*Ankyra*	*Closterium*
Chlamydomonas	*Eudorina*	*Aulomonas*
Closterium	*Anabaena*	*Selenastrum*
Asterionella	*Chlamydomonas*	*Merismopedia*
Centric diatoms	*Asterionella*	*Eudorina*
Anabaena	*Closterium*	*Cyclotella*
Selenastrum	*Selenastrum*	*Scenedesmus* (4 cell)
Scenedesmus (4 cell)	*Scenedesmus* (4 cell)	*Mougeotia*
Tabellaria	*Kirchneriella*	*Diceras*
Monoraphidium (2)	*Tabellaria*	*Chrysolykos*
Cyclotella	*Monoraphidium* (2)	*Asterionella*
Kirchneriella	*Staurastrum*	*Chlamydomonas*
Melosira	*Cyclotella*	*Pediastrum*
Spirogyra	*Melosira*	*Oocystis*
Unicellular greens	*Spirogyra*	*Tabellaria/Fragilaria*
Staurastrum	Unicellular greens	*Monoraphidium* (2)
Kephyrion	*Kephyrion*	*Kephyrion*
Lagerheimia	*Lagerheimia*	*Tabellaria*
Oscillatoria	*Oscillatoria*	*Koliella* (1)
Synedra	*Synedra*	Monoraphidium (1)
Rhodomonas	*Cryptomonas*	*Rhodomonas*
Cryptomonas	*Fragilaria*	*Botryococcus*
Fragilaria	*Rhodomonas*	*Lagerheimia*
Koliella (1)	*Koliella* (1)	Chrysoflagellates
Tabellaria/Fragilaria	*Koliella* (2)	*Eutetramorus*
Koliella (2)	*Aphanothece*	*Melosira*
Pediastrum	*Tabellaria/Fragilaria*	*Coelosphaerium*
Aphanothece	*Trachelomonas*	*Koliella* (2)
Lyngbya	*Lyngbya*	*Chroococcus*
Dinobryon	*Dinobryon*	*Synedra*
Chrysoflagellates	*Pediastrum*	*Schroederia*
Trachelomonas	*Gymnodinium*	*Gymnodinium*
Gymnodinium	Chrysoflagellates	*Spirogyra*
Chrysolykos	*Peridinium*	Unicellular greens
Peridinium	*Chrysolykos*	*Fragilaria*
Eutetramorus	*Eutetramorus*	*Crucigenia*
Schroederia	*Schroederia*	*Elakatothrix*
Oocystis	*Oocystis*	*Sphaerocystis*
Diceras	*Treubaria*	*Peridinium*
Mougeotia	*Elakatothrix*	*Ceratium*
Elakatothrix	*Dictyosphaerium*	*Lyngbya*
Treubaria	*Diceras*	*Cryptomonas*
Monoraphidium (1)	*Sphaerocystis*	*Oscillatoria*
Sphaerocystis	*Mougeotia*	*Dinobryon*
Chroococcus	*Ceratium*	*Kirchneriella*
Ceratium	*Cosmarium*	*Cosmarium*
Dictyosphaerium	*Monoraphidium* (1)	*Aphanothece*
Merismopedia	*Chroococcus*	*Euastrum*
Cosmarium	*Euastrum*	*Treubaria*
Botryococcus	*Crucigenia*	*Cylindrospermum*
Aulomonas	*Botryococcus*	*Trachelomonas*
Crucigenia	*Coelosphaerium*	*Dictyosphaerium*
Coelosphaerium	*Merismopedia*	*Xanthidium*
Euastrum	*Aulomonas*	*Ankyra*
Gomphosphaeria	*Gomphosphaeria*	*Staurastrum*
Xanthidium	*Xanthidium*	*Anabaena*
Cylindrospermum	*Cylindrospermum*	Centric diatoms

These algae were *Gomphosphaeria*, *Aulomonas*, *Merismopedia*. The opposite was also the case, as there were phytoplankton associated with high TP and TAN concentrations, but which were ranked near to the bottom of the TON concentration gradient. Such algae were small centric diatoms, *Anabaena* and *Ankyra*.

4.3.2.2.1 Summary of information on TP, TAN and TON and different algal groups

Green algae were ubiquitous in their distribution, occurring in all conditions of TP, TAN and TON described by the biplot (Figures 4.1a&b). The most commonly occurring and numerically important chrysophytes in the Shetland lochs studied, the chrysoflagellates, occurred at low to intermediate levels on all three of the gradients of water TP, TAN and TON concentrations. *Dinobryon* was located at a slightly more elevated position in the TP and TAN rankings, but was lower on the TON scale. Cyanophytes were not associated with the combination of high concentrations of TP, TAN and TON together, but were included in all other varieties of conditions, such as low TP and TAN and high TON. Dinoflagellates were associated with low to intermediate concentrations of all three parameters. *Peridinium* and *Gymnodinium* occupied similar positions on the TP and TAN gradients to the chrysoflagellates and *Dinobryon*, although chrysoflagellates were located at a higher level on the TON gradient than either of these dinoflagellates. Of the Bacillariophyceae, only small centric diatoms were found at particularly low TON levels and no diatoms were situated near the bottom of the TP and TAN gradients.

4.3.2.2.2 Inferred rankings of phytoplankton on pH, Ca and Mg concentration gradients

When considering pH, Ca and Mg concentration gradients, which were important in terms of the second CCA axis, inferred rankings of algae from the CCA analysis indicated the following points (Table 4.5). Small centric diatoms, *Anabaena*, *Ankyra*, *Staurastrum* and *Trachelomas* were associated with high levels of both Ca and Mg, whilst *Aulomonas*, *Gomphosphaeria*, *Merismopedia*, *Closterium* and *Selenastrum* were located at the bottom of these scales.

Table 4.5 Ranking inferred by CCA of phytoplankton along environmental gradients of pH, Ca and Mg

pH	Ca	Mg
Xanthidium	Centric diatoms	Centric diatoms
Centric diatoms	*Anabaena*	*Anabaena*
Cylindrospermum	*Staurastrum*	*Ankyra*
Dictyosphaerium	*Xanthidium*	*Staurastrum*
Euastrum	*Dictyosphaerium*	*Kirchneriella*
Treubaria	*Cylindrospermum*	*Trachelomonas*
Cosmarium	*Trachelomonas*	Unicellular greens
Ceratium	*Euastrum*	*Spirogyra*
Crucigenia	*Treubaria*	*Aphanothece*
Staurastrum	*Ankyra*	*Oscillatoria*
Sphaerocystis	*Aphanothece*	*Cryptomonas*
Trachelomonas	*Cosmarium*	*Melosira*
Elakatothrix	*Ceratium*	*Dictyosphaerium*
Anabaena	*Sphaerocystis*	*Chlamydomonas*
Coelosphaerium	*Dinobryon*	*Fragilaria*
Chroococcus	*Crucigenia*	*Xanthidium*
Aphanothece	*Elakatothrix*	*Treubaria*
Botryococcus	*Peridinium*	*Dinobryon*
Peridinium	*Lyngbya*	*Lyngbya*
Schroederia	*Cryptomonas*	*Synedra*
Dinobryon	*Oscillatoria*	*Asterionella*
Monoraphidium (1)	*Kirchneriella*	*Tabellaria*
Lyngbya	*Schroederia*	*Peridinium*
Eutetramorus	*Fragilaria*	*Euastrum*
Gymnodinium	*Gymnodinium*	*Lagerheimia*
Cryptomonas	*Chroococcus*	*Koliella* (2)
Chrysoflagellates	*Coelosphaerium*	*Monoraphidium* (2)
Oscillatoria	Unicellular greens	*Gymnodinium*
Fragilaria	*Synedra*	*Cosmarium*
Koliella(2)	*Eutetramorus*	*Rhodomonas*
Oocystis	*Koliella* (2)	*Elakatothrix*
Synedra	*Spirogyra*	*Ceratium*
Diceras	*Botryococcus*	*Sphaerocystis*
Mougeotia	Chrysoflagellates	*Schroederia*
Rhodomonas	*Monoraphidium* (1)	*Cylindrospermum*
Lagerheimia	*Melosira*	Chrysoflagellates
Koliella (1)	*Lagerheimia*	*Scenedesmus* (4 cell)
Pediastrum	*Rhodomonas*	*Crucigenia*
Chrysolykos	*Koliella* (1)	*Kephyrion*
Tabellaria/Fragilaria	*Oocystis*	*Koliella* (1)
Unicellular greens	*Tabellaria/Fragilaria*	*Eudorina*
Kirchneriella	*Pediastrum*	*Eutetramorus*
Spirogyra	*Kephyrion*	*Chroococcus*
Merismopedia	*Tabellaria*	*Coelosphaerium*
Aulomonas	*Diceras*	*Cyclotella*
Melosira	*Monoraphidium* (2)	*Tabellaria/Fragilaria*
Ankyra	*Mougeotia*	*Monoraphidium* (1)
Kephyrion	*Chrysolykos*	*Botryococcus*
Gomphosphaeria	*Chlamydomonas*	*Pediastrum*
Tabellaria	*Scenedesmus* (4 cell)	*Oocystis*
Monoraphidium (2)	*Asterionella*	*Selenastrum*
Cyclotella	*Cyclotella*	*Chrysolykos*
Scenedesmus (4 cell)	*Merismopedia*	*Closterium*
Asterionella	*Aulomonas*	*Diceras*
Chlamydomonas	*Eudorina*	*Mougeotia*
Selenastrum	*Selenastrum*	*Schroederia*
Eudorina	*Gomphosphaeria*	*Merismopedia*
Closterium	*Closterium*	*Aulomonas*
Scenedesmus (2 cell)	*Scenedesmus* (2 cell)	*Gomphosphaeria*

According to the rankings, in the most alkaline waters, the following algae were observed: *Xanthidium*, small centric diatoms, *Cylindrospermum*, *Dictyosphaerium*, *Euastrum*, *Treubaria* and *Cosmarium*, whereas *Scenedesmus* (two cell), *Closterium*, *Eudorina*, *Selenastrum*, *Chlamydomonas*, *Asterionella*, *Scenedesmus* (four cell) and *Cyclotella* occupied positions at the more acid end of the pH gradient. Chrysoflagellates were again associated with intermediate positions in these three gradients, although *Dinobryon* appeared to have a preference for harder and more alkaline waters than the chrysoflagellates. Dinoflagellates were successful at intermediate to higher water pH and Ca levels and toward the middle of the ranking on the water Mg concentration scale. Green and blue-green algae were represented throughout the range of conditions of water pH and hardness. Although diatoms were not situated at the extreme lower end of the Ca and Mg gradients (with the exception of the diatom species which was found in Strand Loch only and was likely to be of marine origin), they were present throughout the majority of conditions of water hardness and the the pH gradient.

4.3.2.3 Positioning of lochs along CCA environmental gradients

Approximate positions of loch samples along the important environmental gradients of TP, TAN and TON are presented in Table 4.6. Lochs which were associated with high TP levels were Mill Pond, Loch of Brough (Yell), Loch of Brow, Turdale Water, Loch of Cliff, Whitelaw Loch, Loch of Snarravoe, Sandy Loch, Bu, Punds and Gossa Water. These lochs were also ranked highly on the CCA TAN scale. Water bodies which were observed at the top of the TON gradient were as follows: Mill Pond, Lochs of Brindister and Tingwall, Roer and Bu Water, Whitelaw Loch, Skutes Water and Loch of Kettlester. Only Mill Pond, Bu Water and Whitelaw Loch were ranked at relatively high positions on all three environmental gradients.

Loch of Brindister, Roer Water, Lochs of Tingwall and Ustaness, Skutes Water, Lochs of Kettlester and Brow, Gorda Water and Whitelaw Loch were all linked with low TP levels on the CCA biplot. These water bodies also occupied positions at the lower end of the TAN scale. Loch of Brow, Turdale Water, Lochs of Brough (Yell and Bressay), Spiggie, Huesbreck, Papil and Helliers Water, Arthurs and Sandy Lochs, were all situated at a low level on the CCA TON ranking.

Table 4.6 Ranking inferred by CCA of sites along environmental gradients of TP, TAN and TON

TP	TAN	TON
Mill 3	Mill 3	Mill 3
Mill 2	Mill 2	Brindister 3
Turdale 1	Turdale 1	Brindister 2
Brough (Yell) 1	Brough (Yell) 1	Mill 2
Brow 3	Brow 3	Tingwall 2
Brough (Yell) 3	Brough (Yell) 3	Roer 1
Turdale 2	Turdale 2	Bu 2
Brough (Yell) 2	Brough (Yell) 2	Whitelaw 3
Cliff 3	Cliff 3	Skutes 2
Whitelaw 3	Snarravoe 3	Skutes 1
Snarravoe 3	Sandy 2	Bu 3
Cliff 2	Bu 1	Kettlester 3
Sandy 2	Whitelaw 3	Whitelaw 3
Bu 1	Cliff 2	Lunga 2
Sandy 3	Punds 2	Sandy 3
Punds 3	Sandy 3	Skutes 3
Gossa 3	Punds 3	Brindister 1
Punds 2	Huxter 3	Brow 1
Huxter 3	Gossa 3	Strand 3
Bu 3	Spiggie 3	Gonfirth 3
Strand 3	Spiggie 1	Turdale 2
Snarravoe 1	Snarravoe 1	Kettlester 2
Spiggie 3	Punds 1	Roer 2
Skutes 3	Sand 3	Lunga 3
Punds 1	Strand 3	Gonfirth 2
Sand 3	Watlee 3	Cliff 3
Tingwall 3	Bu 3	Cliff 2
Eela 1	Eela 1	Gossa 3
Spiggie 1	Skutes 3	Brough (Yell) 3
Snarravoe 2	Tingwall 3	Roer 3
Huxter 2	Huesbreck 3	Tingwall 3
Sandy 1	Snarravoe 2	Punds 3
Eela 3	Papil 3	Watlee 3
Gossa 1	Eela 3	Snarravoe 1
Papil 3	Gossa 1	Huxter 2
Huesbreck 3	Sandy 1	Punds 1
Bu 2	Huxter 2	Snarravoe 2
Tingwall 1	Tingwall 1	Sandy 1
Watlee 1	Watlee 1	Tingwall 1
Brindister 1	Eela 2	Snarravoe 3
Gossa 2	Gossa 2	Arthurs 2
Spiggie 2	Spiggie 2	Gossa 2
Lunga 3	Huxter 1	Eela 1
Eela 2	Papil 2	Watlee 2
Huxter 1	Brough (Bressay) 2	Kettlester 1

Table 4.6 (cont.)

TP	TAN	TON	
Lunga 2		Sand 2	Ustaness 3
Huxter 1		Arthurs 3	Whitelaw 1
Arthurs 3		Lunga 3	Arthurs 3
Sand 2		Huesbreck 2	Gorda 1
Papil 2		Brindister 1	Spiggie 2
Brough (Bressay) 2		Whitelaw 1	Watlee 1
Gonfirth 2		Gorda 3	Ustaness 2
Whitelaw 1		Arthurs 1	Bu 1
Huesbreck 2		Lunga 2	Huxter 1
Helliers 2		Helliers 2	Helliers 2
Gorda 3		Bu 2	Gossa 1
Arthurs 2		Helliers 3	Helliers 3
Helliers 3		Gonfirth 2	Gorda 2
Arthurs 1		Brough (Bressay) 1	Huxter 3
Watlee 2		Arthurs 2	Eela 2
Gorda 1		Papil 1	Ustaness 1
Sand 1		Watlee 2	Eela 3
Papil 1		Huesbreck 1	Sand 1
Roer 3		Sand 1	Gorda 3
Skutes 2		Gorda 1	Sand 2
Huesbreck 1		Brough (Bressay) 3	Sand 3
Gonfirth 3		Helliers 1	Sandy 2
Brough (Bressay) 1		Roer 3	Spiggie 3
Helliers 1		Gorda 2	Helliers 1
Brough (Bressay) 3		Gonfirth 3	Papil 1
Whitelaw 2		Ustaness 1	Brough (Bressay) 3
Gorda 2		Brow 1	Arthurs 1
Brow 1		Whitelaw 2	Huesbreck 1
Ustaness 1		Kettlester 1	Huesbreck 2
Roer 2		Skutes 2	Brough (Bressay) 2
Kettlester 1		Ustaness 2	Papil 2
Ustaness 2		Roer 2	Papil 3
Kettlester 3		Ustaness 3	Punds 2
Kettlester 2		Kettlester 2	Huesbreck 3
Skutes 1		Kettlester 3	Spiggie 1
Ustaness 3		Skutes 1	Brough (Yell) 2
Tingwall 2		Tingwall 2	Brough (Bressay) 1
Roer 1		Roer 1	Brough (Yell) 1
Brindister 2		Brindister 2	Turdale 1
Brindister 3		Brindister 3	Brow 3

NOTE:

1 sampling date, 07/91
2 sampling date, 08/91
3 sampling date, 09/91

Of these water bodies, Loch of Brow, Turdale Water, Loch of Brough (Yell), Punds Water and Sandy Loch were also located at the top of the CCA TP and TAN gradients.

The CCA analysis indicated that certain water bodies did not occupy the same approximate position on the biplot on each sampling date. Nutrient levels changed between sampling trips and differences were of sufficient magnitude to result in movement of samples (sites on a sampling date) to a different general area of the biplot. It was therefore possible for a water body be located at various positions on the same environmental gradient, during different sampling dates. For example, Turdale, Punds, Gossa and Bu Water, Sandy Loch, Lochs of Brow and Brough (Yell) were found to change position considerably on the TON gradient. Papil Water, Lochs of Brow, Tingwall, Watlee and Brindister and Whitelaw Loch are examples of sites which differed within the TAN ranking. In terms TP ranking, Lochs of Brow, Tingwall and Brindister, Whitelaw Loch and Skutes Water are examples of water bodies which changed position considerably through the period of observation.

4.3.3 Changes in numbers of the main phytoplankton taxa in the five water bodies chosen for further study

4.3.3.1 Loch of Gonfirth

4.3.3.1.1 1991

During 1991, greatest number of phytoplankton was counted in the sample from 01/06/91 and totalled 808 PU mL^{-1}. In August the phytoplankton density had decreased to 668 PU mL^{-1}. Changes in numbers of the main phytoplankton taxa in Loch of Gonfirth are described below. In addition, variations in the abundance of the most numerically important taxa observed in 1992 are included in Figure 4.3.

4.3.3.1.1.1 Chrysophytes, cryptophytes and diatoms

Chrysoflagellate numbers increased from 193 PU mL^{-1} in June to 240 PU mL^{-1} in August and were least abundant at 164 PU mL^{-1} in the September sample. *Dinobryon* was countable in the June sample only, when it had a density of only 12 PU mL^{-1}. Although not abundant, presence of *Aulomonas* in the assemblage in all samples should be noted. Diatom flora was mainly of *Cyclotella*. Peak abundance of this genus was noted in June (64 PU mL^{-1}), lowest density in September (35 PU mL^{-1}).

Cryptomonas was absent from the June sample, though *Rhodomonas* abundance was 64 PU mL^{-1}. Maximum count for the latter came to 94 PU mL^{-1}.in the August sample, dropping to 59 PU mL^{-1} in September. *Cryptomonas* increased to 12 PU mL^{-1} in August, greatest concentration of 29 PU mL^{-1} occurring in September.

4.3.3.1.1.2 Green and blue-green algae

Cyanobacteria were present throughout the samples taken.

Anabaena, *Gomphosphaeria*, *Merismopedia* and *Aphanothece* were all represented, though only the latter was present in sufficient numbers to be enumerated in all three samples. In June *Anabaena* was at its greatest concentration of 6 PU mL^{-1}, being undetectable in the other samples. Maximum concentrations of *Aphanothece* and *Merismopedia* occurred in August, numbers totalling 41 PU mL^{-1} and 59 PU mL^{-1} respectively. In September greatest blue-green numbers were accounted for by *Gomphosphaeria* at 59 PU mL^{-1}. Chlorophytes which were important in their abundance in the samples were *Monoraphidium* (1), *Koliella* (1), *Selenastrum* and *Oocystis*. *Selenastrum* and *Oocystis* both showed peak abundance of 76 PU mL^{-1} in the 01/06/91 sample, declining to minima in August of 29 PU mL^{-1} and 18 PU mL^{-1} respectively. *Koliella* showed a similar pattern, exhibiting a concentration of 23 PU mL^{-1} in June, but could not be located in the August sample. Greatest individual algal count for this loch in 1991 was 152 PU mL^{-1} for *Monoraphidium* in September. Abundance of this alga in June was 105 PU mL^{-1}, decreasing to 47 PU mL^{-1} during August.

4.3.3.1.2 1992

Total phytoplankton abundance in samples taken in 1992 ranged from 284 PU mL^{-1} in August to 597 PU mL^{-1} in May. Changes in numbers of the main phytoplankton taxa in the Loch are described below. In addition, the counts of the algal taxa observed to exhibit greatest numbers are presented in Figure 4.4.

4.3.3.1.2.1 Chrysophytes, cryptophytes and diatoms

In March, chrysoflagellates were present at 94 PU mL^{-1}, but by May their density had increased to 135 PU mL^{-1}. Numbers then decreased to 19 PU mL^{-1} in October. *Dinobryon* remained in the plankton intermittently, whilst *Aulomonas* was present in every sample.

Figure 4.3 Changes in numbers of the main phytoplankton taxa in Loch of Gonfirth during summer, 1991 (composite samples, n=9)

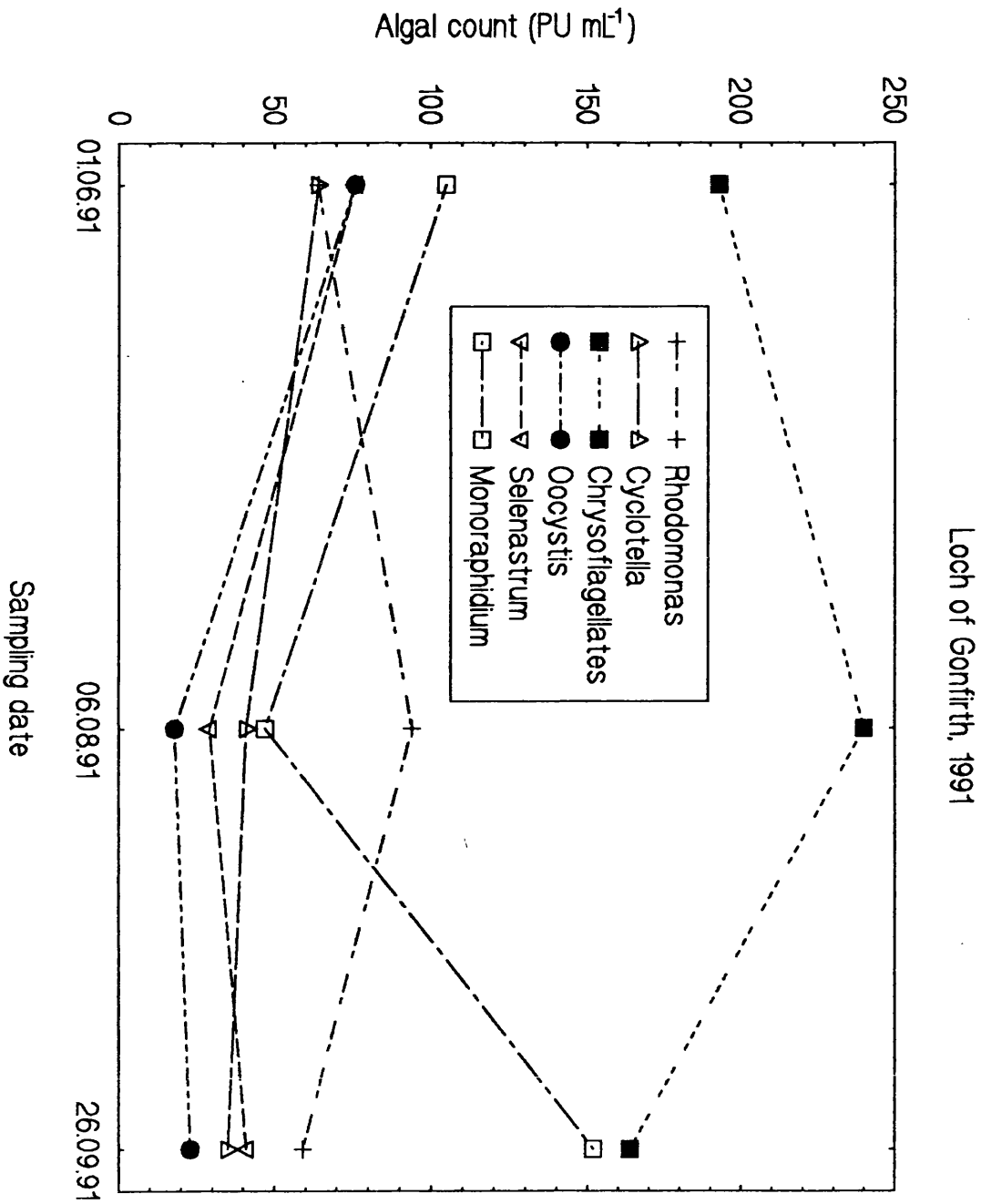
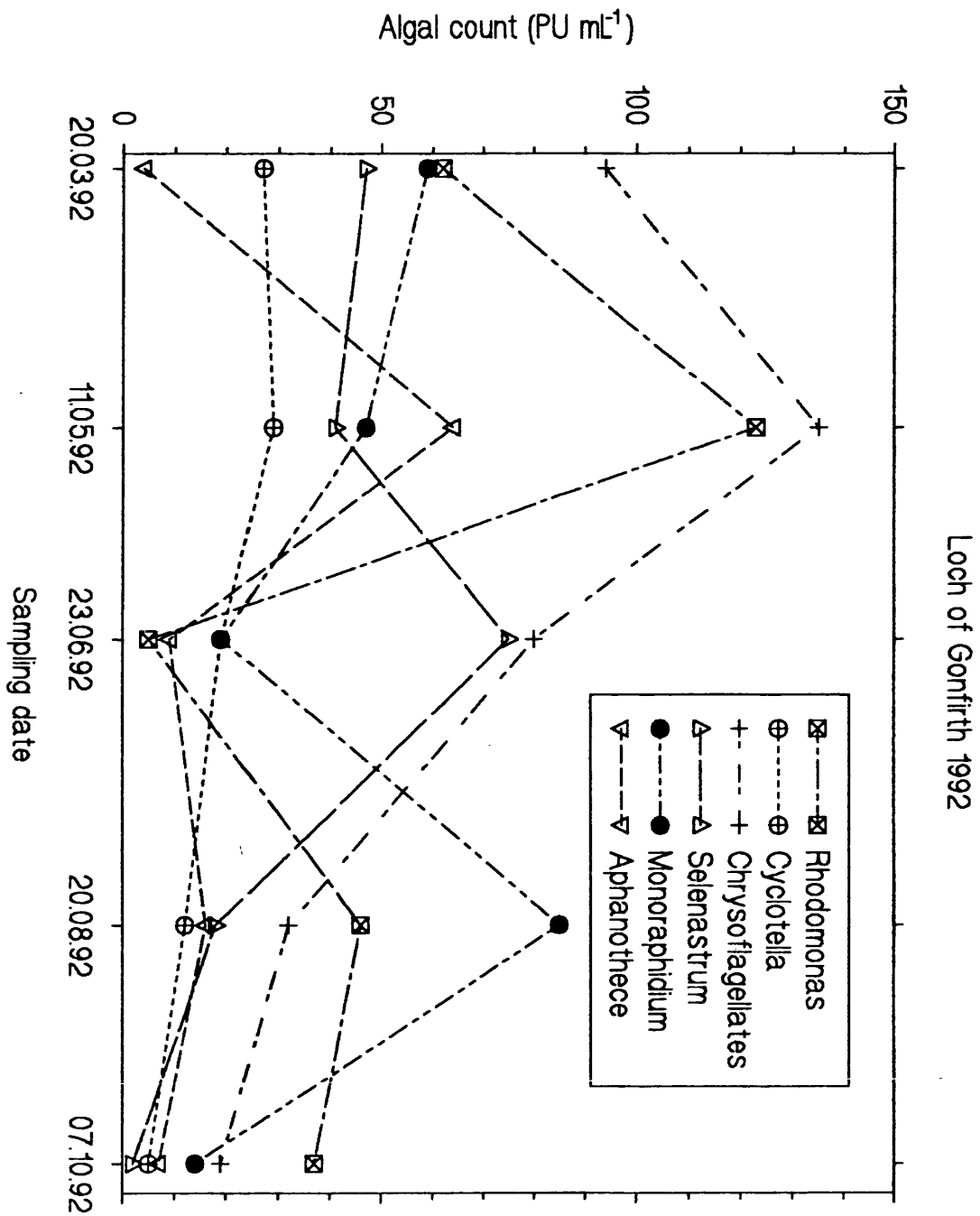


Figure 4.4 **Changes in numbers of the main phytoplankton taxa in Loch of Gonfirth during the 1992 sampling season (composite samples, n=3)**



Production of neither genus achieved a high proportion of the phytoplankton assemblage. *Cyclotella* continued to be the dominant diatom present in Loch of Gonfirth, although small centric diatoms had increased in importance. Concentration of *Cyclotella* remained similar in March and May, but peak numbers were present in May (29 PU mL^{-1}). The lowest count of 5 *Cyclotella* PU mL^{-1} was observed in the October sample. Small centric diatoms were absent in March and May, but present during August (32 PU mL^{-1}). *Rhodomonas* and *Cryptomonas* both exhibited maximum numbers in May. These totalled 123 PU mL^{-1} and 35 PU mL^{-1} respectively. *Rhodomonas* numbers were lowest in June (5 PU mL^{-1}), whilst *Cryptomonas* concentration was 4 PU mL^{-1} in March, August and October.

4.3.3.1.2.2 Green and blue-green algae

Of blue-green algae present, *Aphanothece* exhibited greatest numbers. Its range of abundance was 4 PU mL^{-1} during March to 64 PU mL^{-1}, during May. *Merismopedia* was no longer numerically important, being absent from all but the August sample, where its density was 2 PU mL^{-1}. In addition, *Gomphosphaeria* and *Anabaena* were absent from all samples in 1992. *Monoraphidium*, *Selenastrum* and *Oocystis* remained the dominant green phytoplankton in Loch of Gonfirth. Maximum count for each genus was observed in a different sample. *Monoraphidium* exhibited two peaks of 59 PU mL^{-1} and 85 PU mL^{-1} in March and August respectively, minimum count occurring in October (12 PU mL^{-1}). *Selenastrum* ranged from 2 PU mL^{-1} in October, to 75 PU mL^{-1} during June. Peak abundance of *Oocystis* totalled 23 PU mL^{-1} in May, whereas only 2 PU mL^{-1} were counted in the October sample.

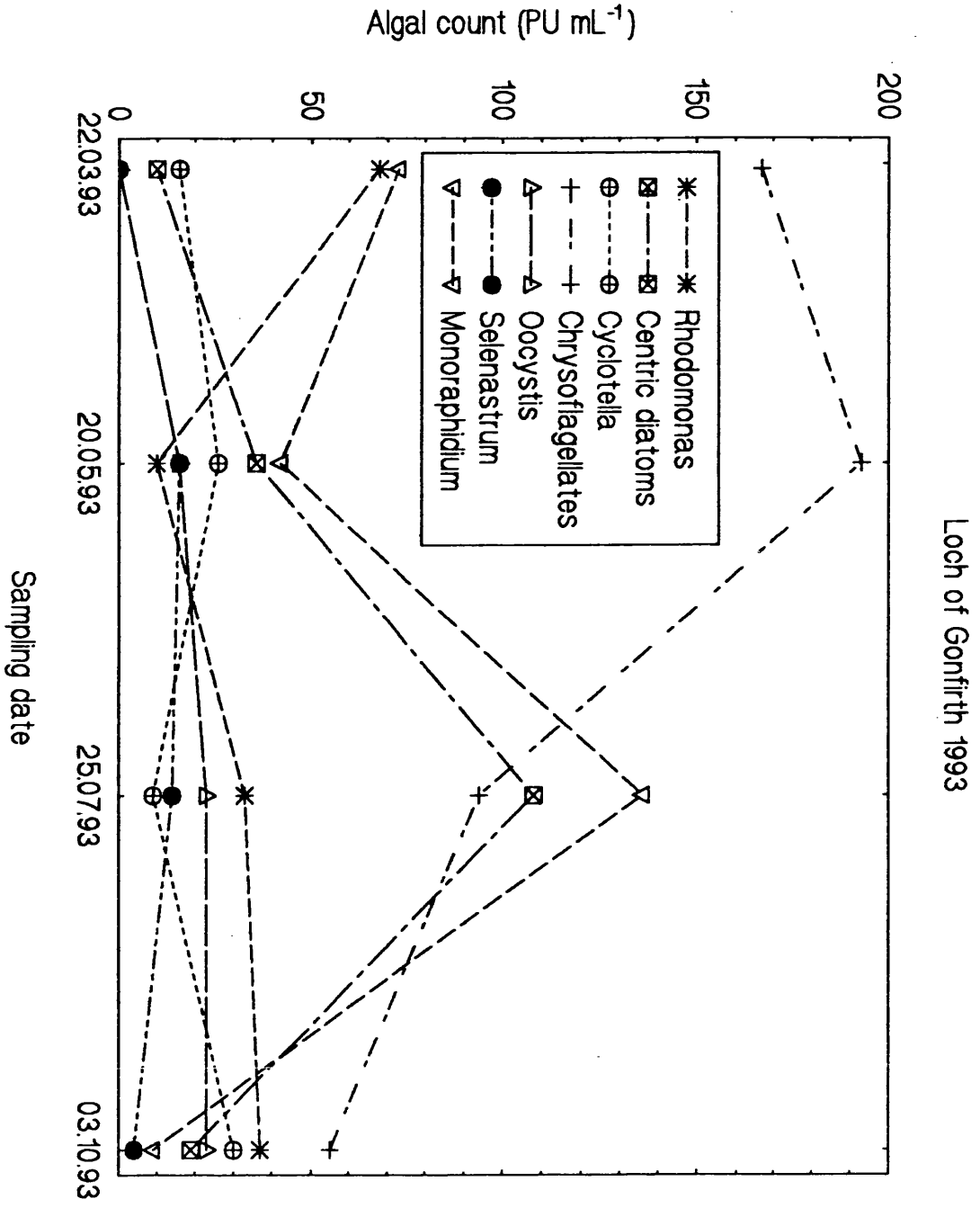
4.3.3.1.3 1993

Total phytoplankton count in 1993 ranged from 309 PU mL^{-1} in October to 521 PU mL^{-1} during May. Peak abundance was observed in May or early June in all three years of the study. Variations in the numbers of the the main phytoplankton taxa during 1993 are described below. In addition, the numbers of the algal taxa observed to exhibit greatest abundances are presented in Figure 4.5.

4.3.3.1.3.1 Chrysophytes, cryptophytes and diatoms

Chrysoflagellate numbers in 1993 ranged from 55 PU mL^{-1} in October to 193 PU mL^{-1} in May.

Figure 4.5 **Changes in numbers of the main phytoplankton taxa in Loch of Gonfirth during the 1993 sampling season (composite samples, n=3)**



Aulomonas became more important, maximum of 57 PU mL^{-1} decreasing to uncountably low levels in July, before population recovery to a concentration of 19 PU mL^{-1}. Small centric diatoms became relatively abundant in 1993, their count increasing from 10 PU mL^{-1} in March, to 108 PU mL^{-1} in July. In October, 19 PU mL^{-1} were enumerated. *Cyclotella* was a consistent member of the phytoplankton assemblage, its numbers remaining constant throughout the survey. Maximum values of 26 PU mL^{-1} and 30 PU mL^{-1} were observed in May and October respectively. *Cryptomonas* was undetectable by the counting procedure in 1993. *Rhodomonas* numbers fell to a minimum of 10 PU mL^{-1} in May, after achieving a maximum count of 68 PU mL^{-1} in March. The density of *Rhodomonas* subsequently increased to 37 PU mL^{-1} in October.

4.3.3.1.3.2 Green and blue-green algae

Gomphosphaeria was discovered once only in 1993, achieving an abundance of 5 PU mL^{-1}. *Aphanothece* increased from being undetectable in March to 19 PU mL^{-1} during July, decreasing to 14 PU mL^{-1} in October. *Merismopedia* numbers remained low. Greatest concentration of 2 PU mL^{-1} was found in the October sample. Again, *Monoraphidium*, *Selenastrum* and *Oocystis* were the most abundant forms of green algae in Loch of Gonfirth. *Oocystis* increased from undetectable levels in March to 23 PU mL^{-1} in August and October. *Monoraphidium* exhibited peaks of 73 PU mL^{-1} and 136 PU mL^{-1} in March and July respectively. Lowest recorded density of 9 PU mL^{-1} occurred in October. From below detection in March, *Selenastrum* increased to 16 PU mL^{-1} in May, subsequently declining to 4 PU mL^{-1} during October.

4.3.3.2 Helliers Water

4.3.3.2.1 1991

In 1991 total count of algae in Helliers Water rose from the minimum value in June of 919 PU mL^{-1}, to peak abundance in August of 1523 PU mL^{-1}. Variations in the numbers of the the main phytoplankton taxa in Helliers Water are described below. In addition, the numbers of the algal taxa observed to exhibit greatest abundances are presented in Figure 4.6.

4.3.3.2.1.1 Chrysophytes, cryptophytes and diatoms

Members of the Chrysophyceae constituted a significant proportion of total

phytoplankton abundance. Greatest numbers were recorded for chrysoflagellates. Counts ranged from 358 PU mL^{-1} (18/07/91) to 789 PU mL^{-1} (20/08/91). *Dinobryon*, though undetectable in the sample taken on 04/06/91, totalled 72 PU mL^{-1}, 62 PU mL^{-1} and 33 PU mL^{-1} on the following three sampling dates respectively. The abundance of the cryptophyte *Rhodomonas* increased from 23 PU mL^{-1} during June to 234 PU mL^{-1} in August, before decreasing to 52 PU mL^{-1} in September. Diatom flora were dominated by *Cyclotella*, with the greatest count occurring in September (59 PU mL^{-1}), after numbers had decreased from 47 PU mL^{-1} (04/06/91), to < 1 PU mL^{-1} during August.

4.3.3.2.1.2 Dinoflagellates

The Dinophyceae remained in the phytoplankton in sufficient numbers to be counted throughout the sampling season. Maximum counts for *Peridinium* (234 PU mL^{-1}) and *Gymnodinium* (59 PU mL^{-1}) were observed during July, minimum counts occurring in August (16 PU mL^{-1}) and June (12 PU mL^{-1}) respectively.

4.3.3.2.1.3 Green and blue-green algae

Several desmid taxa were represented in this water body, though they did not consistently constitute a large proportion of total sample abundance. These were *Cosmarium*, *Euastrum*, *Sphaerozosma*, *Spondylosium*, *Staurastrum*, *Staurodesmus* and *Xanthidium*. The appearance of *Treubaria* in the phytoplankton in July was followed by its maximum numbers (16 PU mL^{-1}) in August. The Cyanophyceae were also represented, the following algae being present: *Aphanothece*, *Chroococcus*, *Gomphosphaeria*, *Merismopedia* and *Lyngbya*. Again, this phytoplankton group did not generally establish a critical fraction of total sample abundance. All were present in numbers below the limit of detection, with the exceptions of *Merismopedia* and *Lyngbya* (7 PU mL^{-1} of each were observed during July) and *Gomphosphaeria* (8 PU mL^{-1} during August).

4.3.3.2.2 1992

Total phytoplankton count in 1992 ranged from a peak of 1405 PU mL^{-1} in March down to 783 PU mL^{-1} in October. Variations in numbers of the main phytoplankton taxa in Helliers Water samples during 1992 are described below. The numbers of the phytoplankton taxa exhibiting greatest abundances are presented in Figure 4.7.

Figure 4.6 Changes in numbers of the main phytoplankton taxa in Helliers Water during summer, 1991 (composite samples, n=3)

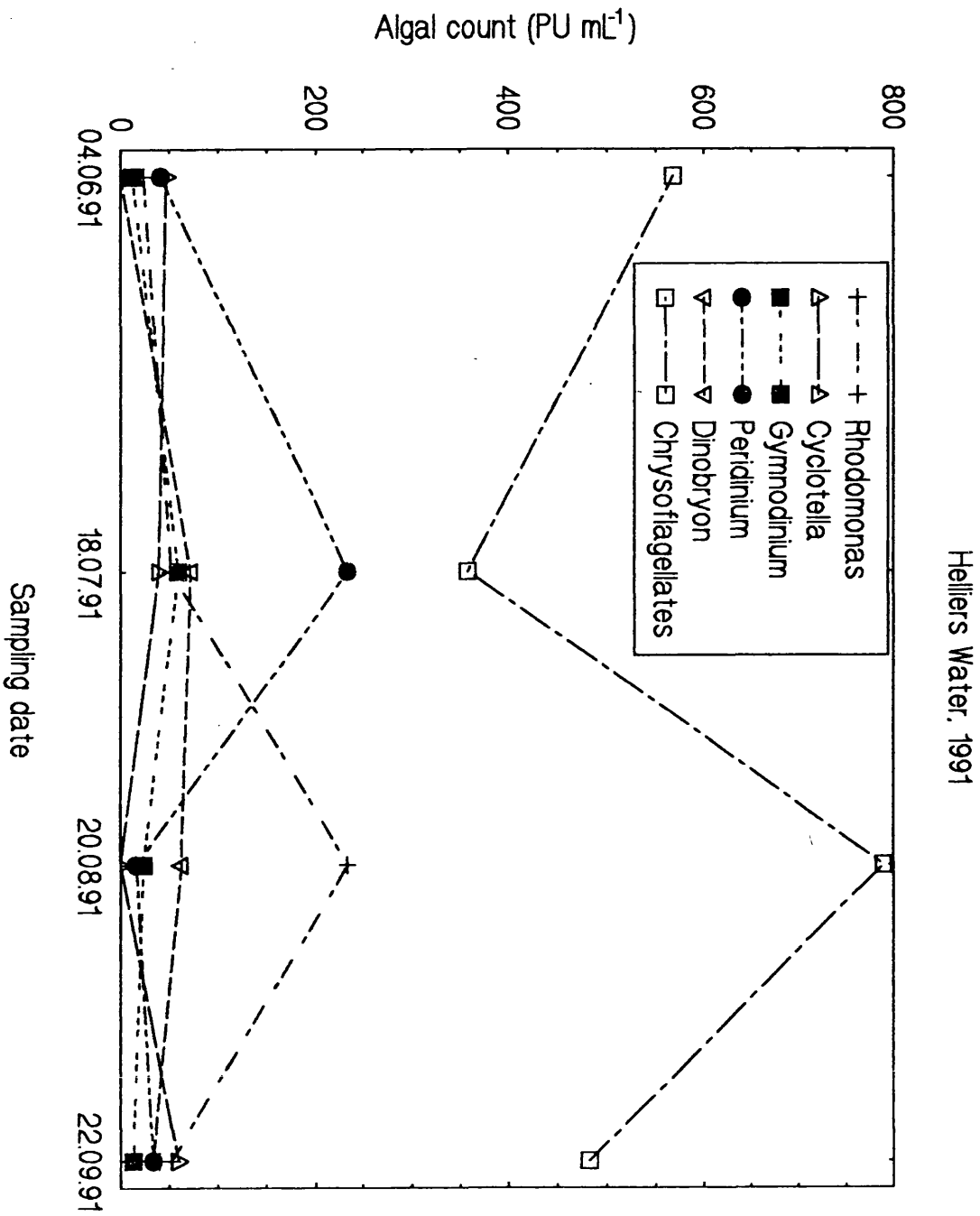
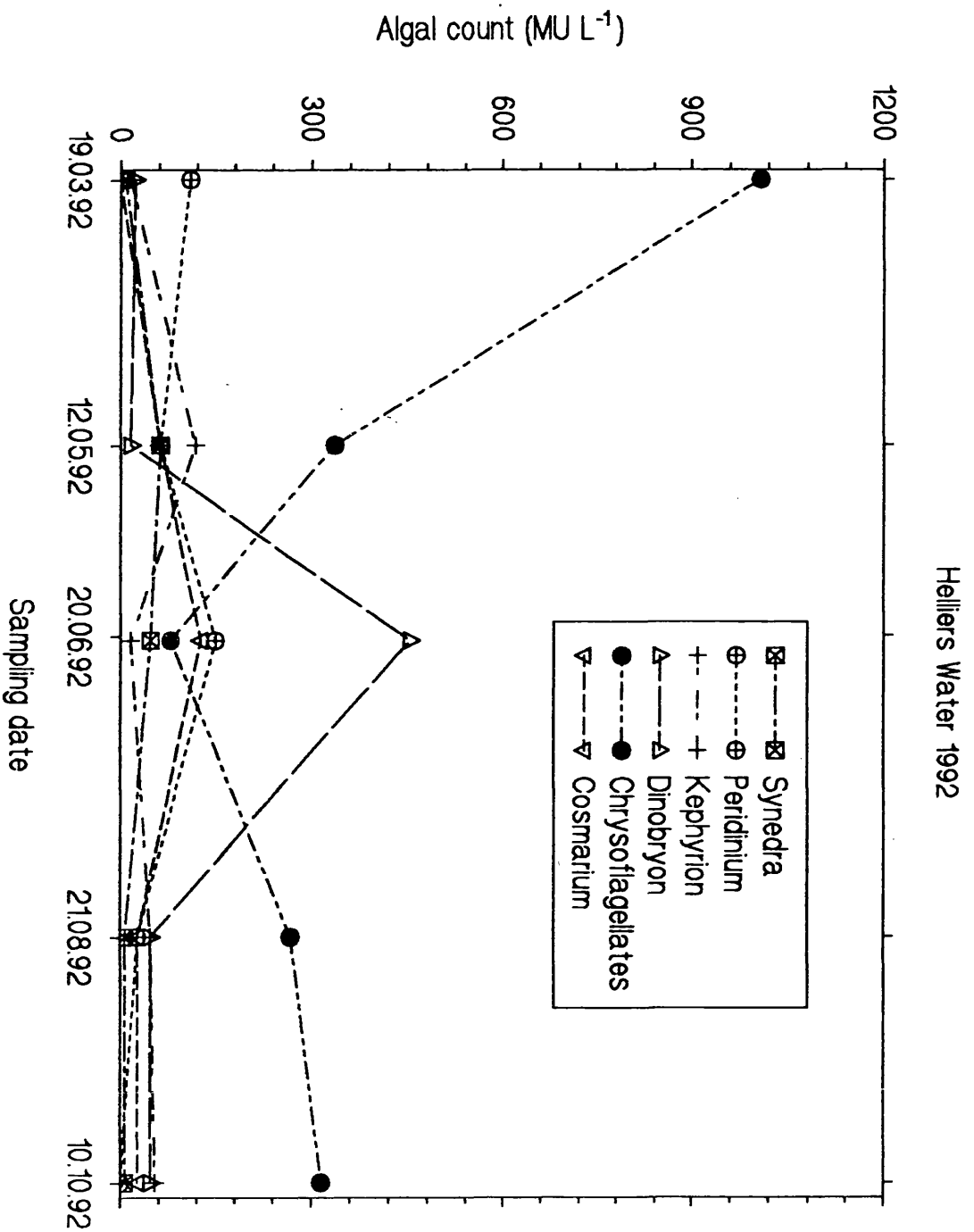


Figure 4.7 Changes in numbers of the main phytoplankton taxa in Helliers Water during the 1992 sampling season (composite samples, n=3)



4.3.3.2.2.1 Chrysophytes, cryptophytes and diatoms

As in 1991, the Chrysophyceae were again numerically important in Helliers Water. Chrysoflagellate density peaked in March (1007 PU mL^{-1}), declined to 78 PU mL^{-1} in June and subsequently increased to 315 PU mL^{-1} in October. A larger peak of *Dinobryon* units was noted than in 1991, the 21/06/92 sample exhibiting 453 PU mL^{-1}. In 1992, *Kephyrion* and *Chrysolykos* both appeared in the plankton. Importance of the cryptophyte *Rhodomonas* had decreased in 1992, being insignificant in May and reaching a peak of only 40 PU mL^{-1} in August. Numbers of *Cyclotella* observed in Helliers Water samples were not as great as in the previous year, *Synedra* having become the dominant diatom growth form. This genus reached maximum numbers in May (62 PU mL^{-1}), decreasing to 7 PU mL^{-1} in August and October.

4.3.3.2.2.2 Dinoflagellates

Phytoplankton of the Dinophyceae constituted a proportion of the algal assemblages sampled. Greatest number of *Gymnodinium* was detected in May (16 PU mL^{-1}), but this genus was not observed in August. The latter sample however, did exhibit 7 PU mL^{-1} *Ceratium*. Again, the dominant member of the Dinophyceae was *Peridinium*, maximum concentration of 148 PU mL^{-1} occurring in June, the minimum in October, when undetectable levels were present.

4.3.3.2.2.3 Green and blue-green algae

Cyanophytes were less important than in 1991; *Gomphosphaeria* and *Merismopedia* were not observed, whilst *Aphanothece*, *Chroococcus* and *Lyngbya* were not present in sufficient numbers to be counted. Of the desmids, however, *Cosmarium* had become a greater component part of phytoplankton abundance. Though not observed in March, numbers increased to 125 PU mL^{-1} in the June sample before declining to 27 PU mL^{-1} in August and October. *Treubaria* remained a feature of the 1992 assemblage.

4.3.3.2.3 1993

Timing of the maximum recorded phytoplankton count for Helliers Water was different in each year of the three year study. Maximum and minimum total counts in the three year study were observed in 1993, numbers being 1671 PU mL^{-1} (05/93) and 574 PU mL^{-1} (03/93) respectively. Variations in the numbers of the the main

phytoplankton taxa during 1993 are described below. In addition, the numbers of the algal taxa observed to exhibit greatest abundances are presented in Figure 4.8.

4.3.3.2.3.1 Chrysophytes, cryptophytes and diatoms

Greatest number of chrysoflagellates in Helliers Water samples was found in 1993. From 305 PU mL^{-1} in March, chrysoflagellate count increased to 1054 PU mL^{-1} in May, before declining to minimum of 234 PU mL^{-1} in October. Peak number of *Dinobryon* units again occurred after that of the chrysoflagellate group. A maximum concentration of 154 PU mL^{-1} was observed in October, when chrysoflagellate abundance was at its minimum. *Chrysolykos* continued to be present in the assemblage, although *Kephyrion* was not apparent after March. The cryptomonad, *Rhodomonas*, was present in numbers similar to those of 1992. The lowest count was observed in May (8 PU mL^{-1}), the highest in July (55 PU mL^{-1}). In 1993, *Synedra* continued to be the dominant member of the Bacillariophyceae, although *Cyclotella* was also important. Maxima were 172 PU mL^{-1} and 81 PU mL^{-1} respectively, with *Synedra* peaking in May and *Cyclotella* increasing from March to October. Minimum counts of these diatoms occurred coincidentally in March.

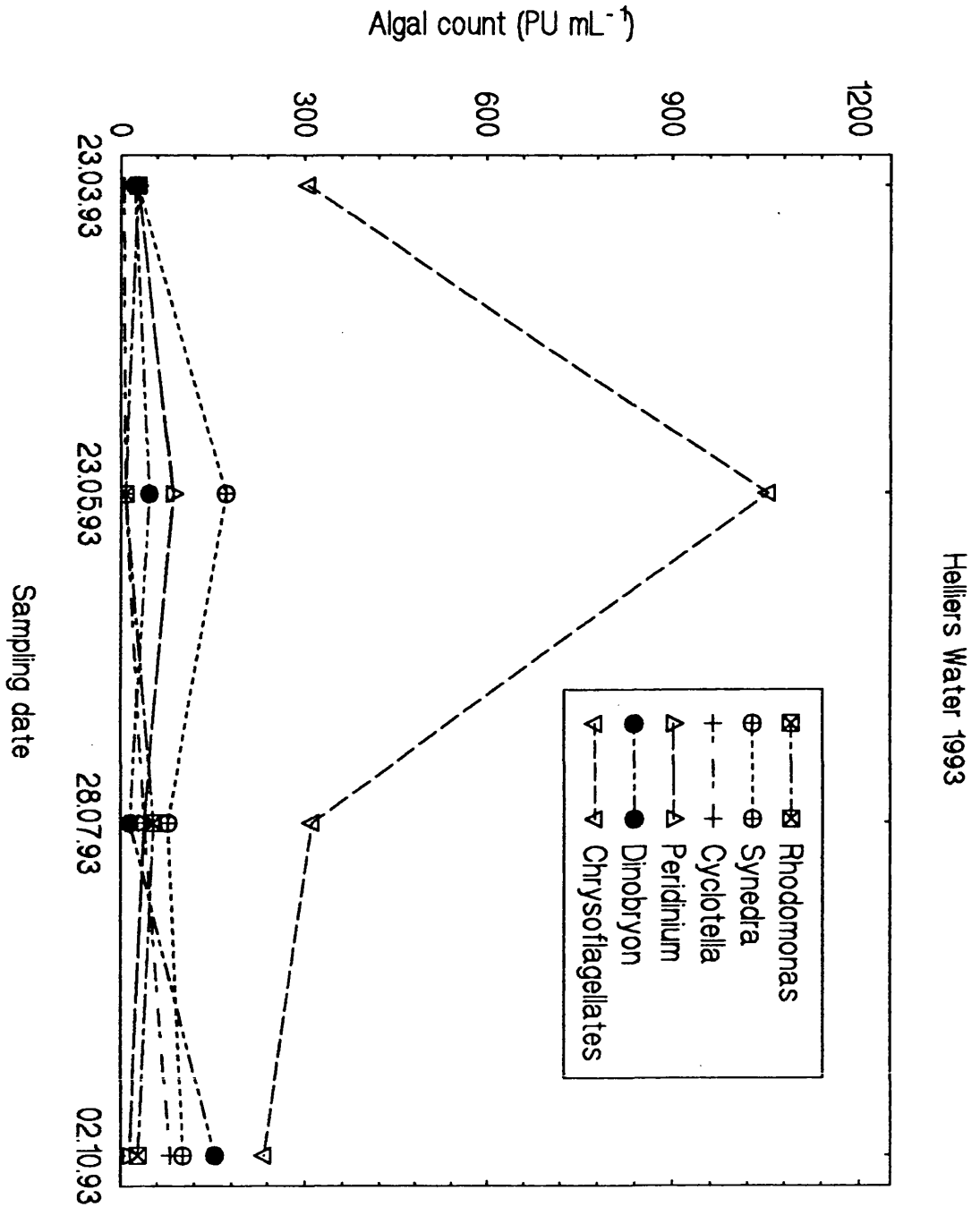
4.3.3.2.3.2 Dinoflagellates

The dinoflagellate, *Ceratium* was not found in phytoplankton samples in 1993. *Gymnodinium* concentration was < 1 PU mL^{-1} in July and October samples, although its maximum abundance of 47 PU mL^{-1} (05/93) was greater than that found in 1992. *Peridinium* density increased from 29 PU mL^{-1} in March to 86 PU mL^{-1} in May before falling to 15 PU mL^{-1} in October.

4.3.3.2.3.3 Green and blue-green algae

Blue-green algae once again reached detectable levels. In March, May, July and October samples there were 6 PU mL^{-1} *Chroococcus*, 8 PU mL^{-1} and 16 PU mL^{-1} *Gomphosphaeria* and 7 PU mL^{-1} *Aphanothece* respectively. *Cosmarium* and *Staurodesmus* were the most abundant desmids, on average, although the *Euastrum* count reached 16 PU mL^{-1} during July. *Staurodesmus* declined from 12 PU mL^{-1} in March to < 1 PU mL^{-1} and 7 PU mL^{-1} in July and October respectively. *Cosmarium* showed its maximum abundance (23 PU mL^{-1}) between May and October. *Treubaria* abundance was low, with the exception of 78 PU mL^{-1} observed in October.

Figure 4.8 **Changes in numbers of the main phytoplankton taxa in Helliers Water during the 1993 sampling season (composite samples, n=3)**



4.3.3.3 Loch of Tingwall

4.3.3.3.1 1991

During 1991, maximum total phytoplankton count observed occurred in July. Numbers decreased from 3610 PU mL^{-1} in July to 614 PU mL^{-1} in September. Variations in the numbers of the the main phytoplankton taxa during 1991 are described below. In addition, the numbers of the algal taxa observed to exhibit greatest abundances are presented in Figure 4.9.

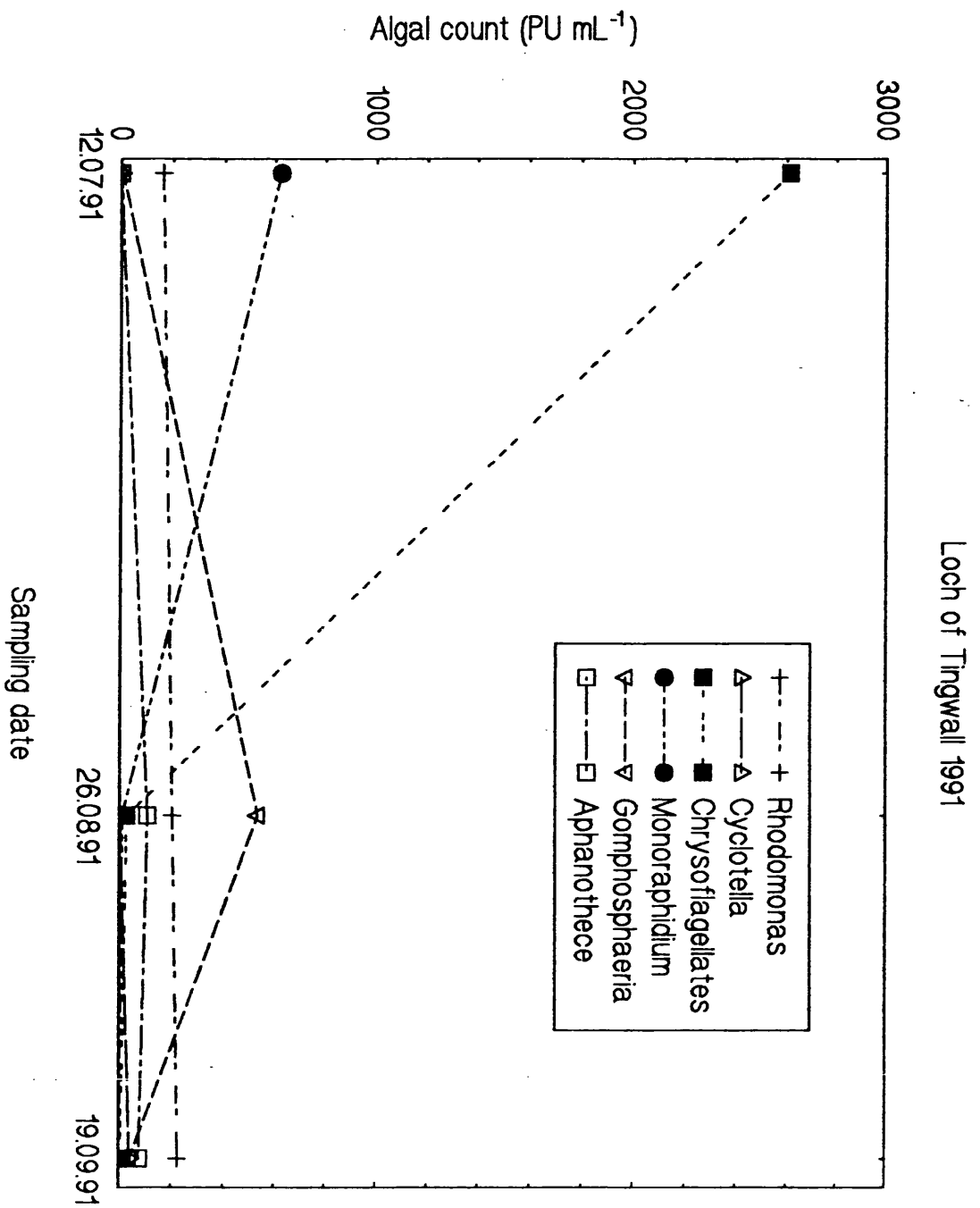
4.3.3.3.1.1 Chrysophytes, cryptophytes and diatoms

The peak of chrysoflagellate numbers, in July, coincided with the highest concentartion of *Monoraphidium*. A chrysoflagellate total of 2614 PU mL^{-1} accounted for the largest discrete count, of an individual algal type, found in Loch of Tingwall in 1991. Numbers fell to 26 PU mL^{-1} and 4 PU mL^{-1} in August and September samples respectively. Diatoms did not become numerically important until September, *Melosira*, *Synedra* and *Cyclotella* increasing in number. *Cyclotella* was most abundant at a concentration of 40 PU mL^{-1}. Concurrent with maximum *Gomphosphaeria* count in August was production of the greatest number of cryptophytes. Peak densities of *Cryptomonas* and *Rhodomonas* came to 31 PU mL^{-1} and 203 PU mL^{-1} respectively. These algae were also observed in May and July.

4.3.3.3.1.2 Green and blue-green algae

Cyanobacteria represented in the total counts were *Gomphosphaeria* and *Aphanothece*. Though absent from the July sample, *Aphanothece* produced 106 PU mL^{-1} in August and 75 PU mL^{-1} in September. Numbers of *Gomphosphaeria* were found to increase from 7 PU mL^{-1} in July to 534 PU mL^{-1} in August. These were present as single or double cells rather than colonies. During July, *Monoraphidium* (2) density was 622 PU mL^{-1}. However, these algae decreased to undetectable levels in September. *Sphaerocystis* colonies totalling 17 PU mL^{-1} and *Scenedesmus* (4 cell) accounting for 18 PU mL^{-1} appeared in the assemblage at this time.

Figure 4.9 **Changes in numbers of the main phytoplankton taxa in Loch of Tingwall during summer, 1991 (composite samples, 9)**



4.3.3.3.2 North Basin, 1992

In 1992 numbers were maximal in May, with a total phytoplankton density of 13244 PU mL^{-1}. Numbers fell to their lowest during August, the water column only supporting 766 PU mL^{-1}. By October algal concentration had risen to 1314 PU mL^{-1}. Changes in numbers of the main phytoplankton taxa in the North Basin of the Loch during 1992 are described below. In addition, the counts of the algal taxa observed to exhibit greatest numbers are presented in Figure 4.10.

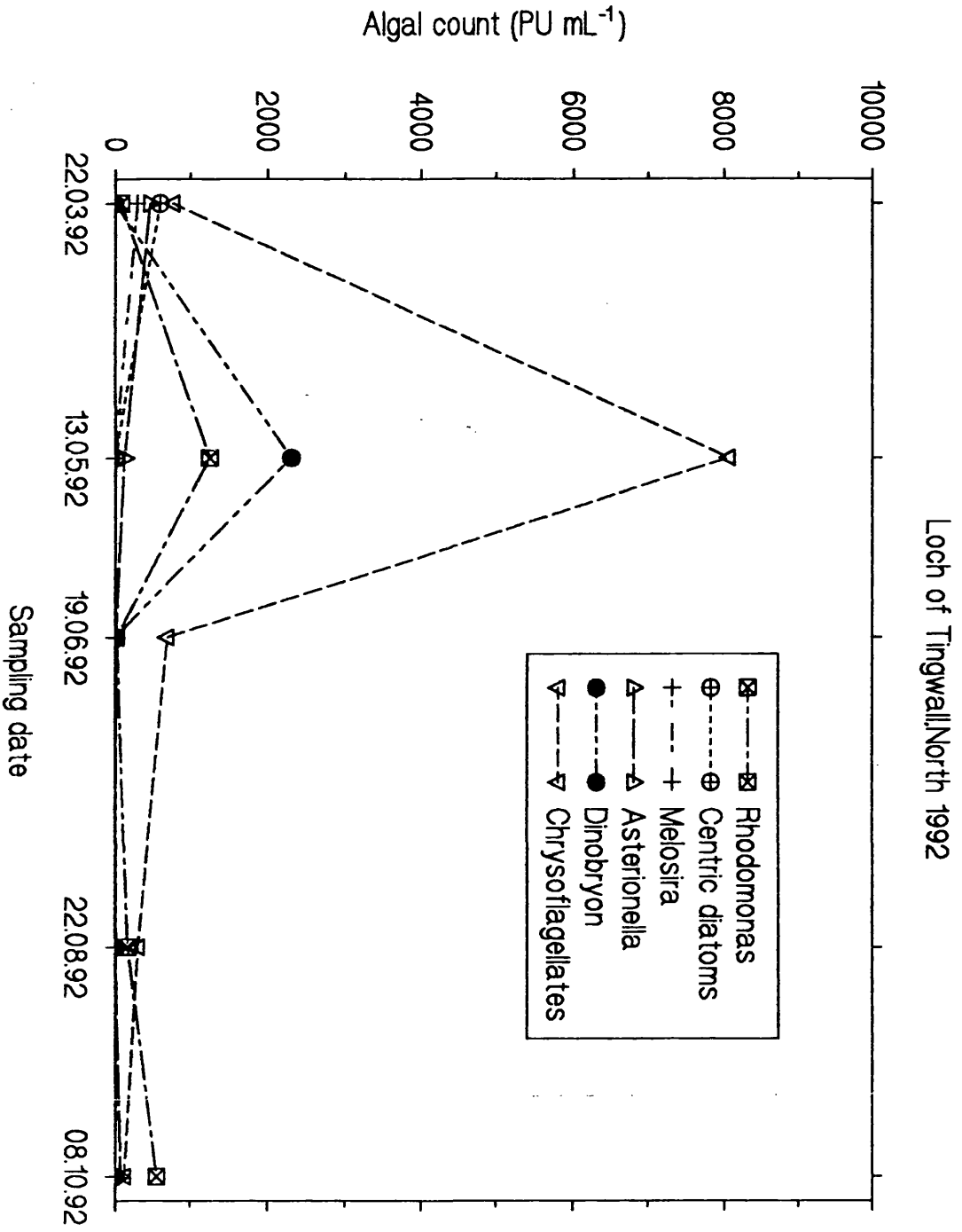
4.3.3.3.2.1 Chrysophytes, cryptophytes and diatoms

Chrysoflagellate count in March was 767 PU mL^{-1}. These phytoplankton increased to 8059 PU mL^{-1} during May, falling to a minimum of 127 PU mL^{-1} in October. Though absent from all but one other sample, *Dinobryon* produced 2311 PU mL^{-1} in May. Maximum number of cryptophytes coincided with *Dinobryon* and chrysoflagellate peaks. Both *Rhodomonas* and *Cryptomonas* were persistent in the phytoplankton throughout the sampling period. Greatest number of *Rhodomonas* was 1249 PU mL^{-1} and for *Cryptomonas*, 312 PU mL^{-1}. Minimum for each genus was 21 PU mL^{-1} in June. Phytoplankton of the Bacillariophyceae was dominated by centric diatoms, *Asterionella*, *Synedra* and *Melosira*, which numbered 596 PU mL^{-1}, 469 PU mL^{-1}, 341 PU mL^{-1} and 298 PU mL^{-1} respectively. Centric diatoms and *Melosira* were absent from subsequent samples. *Synedra* decreased to undetectably low levels in May, but numbers increased again to 10 PU mL^{-1} by August. *Asterionella* numbers decreased to undetectable levels in August, reappearing at 71 PU mL^{-1} in October.

4.3.3.3.2.2 Green and blue-green algae

Blue-green algae were represented by *Aphanothece* and *Anabaena*. The former was present at 60 PU mL^{-1} and 14 PU mL^{-1} in August and October respectively. *Anabaena* concentration in June accounted for 7 PU mL^{-1}. Phytoplankton of the Chlorophyceae were intermittently present in the plankton only. Unicellular greens, unicellular green flagellates, *Koliella* (1) and *Schroederia*, all showed March peaks of 298 PU mL^{-1}, 213 PU mL^{-1}, 85 PU mL^{-1} and 256 PU mL^{-1} respectively, before decreasing to levels below detection in the remaining samples. *Koliella* (2) was not found in March, June or October, but during May produced 187 PU mL^{-1}. *Monoraphidium* (2) was located in the October sample only, at a level of 64 PU mL^{-1}.

Figure 4.10 Changes in numbers of the main phytoplankton taxa in Loch of Tingwall, North Basin, during the 1992 sampling season (composite sample, n=3)



4.3.3.3.3 North Basin, 1993

Total phytoplankton numbers in samples taken in 1993 were not as high as those found in 1992 samples. From 5585 PU mL^{-1} in March, numbers increased to 8902 PU mL^{-1} in May, minimum levels of 742 PU mL^{-1} occurring in the October sample. Changes in numbers of the main phytoplankton taxa in Loch of Tingwall North Basin are described below. In addition, variations in the abundance of the most numerically important taxa observed in 1993 are included in Figure 4.11.

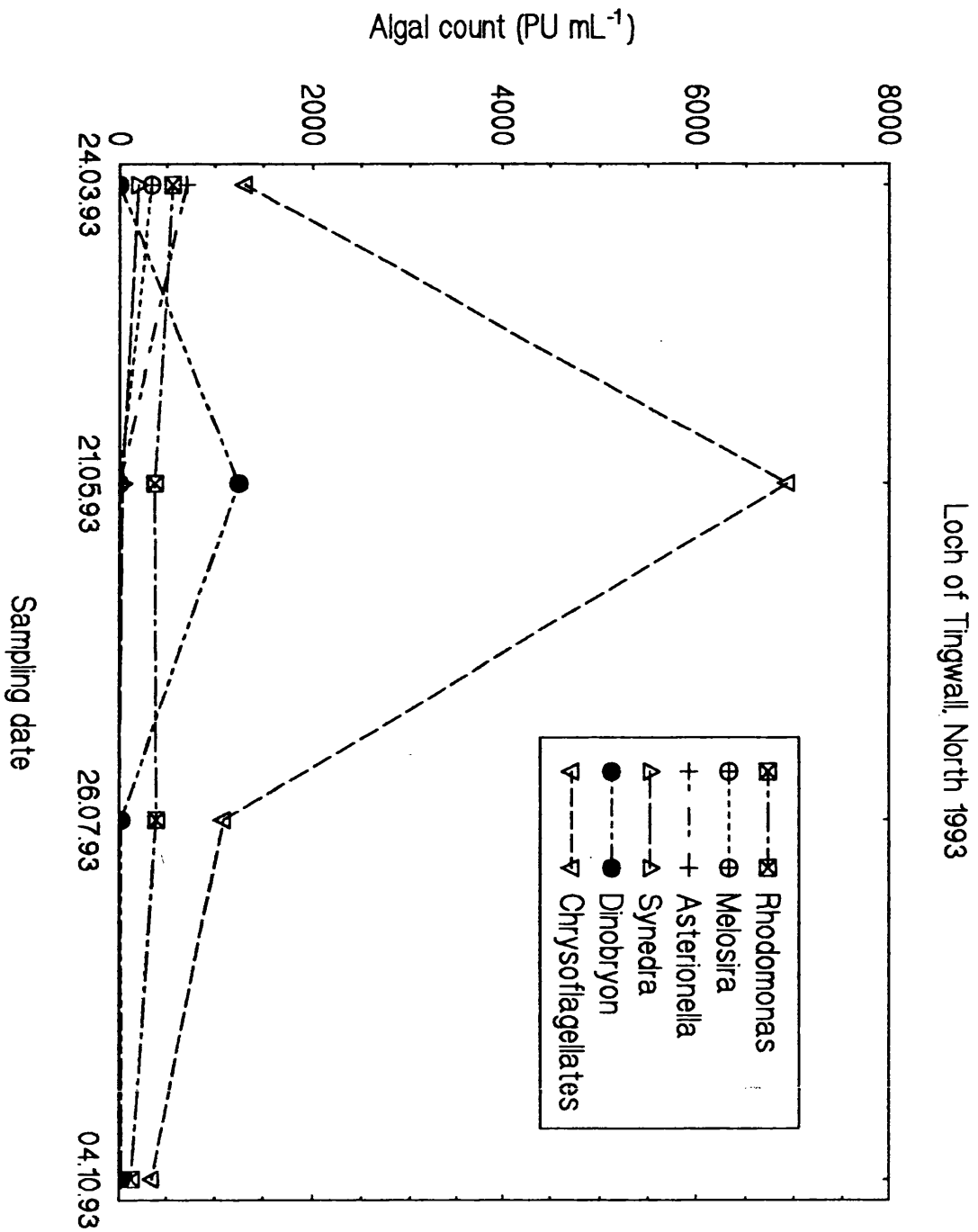
4.3.3.3.3.1 Chrysophytes, cryptophytes and diatoms

Chrysoflagellates were again the dominant phytoplankton in Loch of Tingwall, North Basin in 1993. Numbers ranged from 6934 PU mL^{-1} in the May sample, to 346 PU mL^{-1} in October. *Dinobryon* concentration was found to be below detection in March, rising to 1249 PU mL^{-1} in May, when the highest chrysoflagellate numbers were recorded. Small centric diatoms were not numerically important in 1993, although *Cyclotella* manifested itself in the community once more. It was present at 37 PU mL^{-1}, but during March only. *Melosira* numbers, after reaching 337 PU mL^{-1} in March, were reduced to undetectable levels during subsequent sampling trips. *Synedra* and *Asterionella* decreased from 187 PU mL^{-1} and 712 PU mL^{-1} respectively in March, to below detection during July, but reappeared in the phytoplankton assemblage in October. This year, maximum cryptophyte numbers occurred in March instead of May. *Cryptomonas* decreased from 75 PU mL^{-1} to a density below level of detection, whereas *Rhodomonas* concentration started at 562 PU mL^{-1} and fell to 120 PU mL^{-1}. Minimum cryptophyte density occurred in October.

4.3.3.3.3.2 Green and blue-green algae

Green and blue-green algae were again patchy in their distribution. *Koliella* (1) and (2) were present in March only, at levels of 75 PU mL^{-1} and 225 PU mL^{-1} respectively. *Monoraphidium* abundance ranged from 94 PU mL^{-1} in May down to below detection in July and October. Desmids increased in number during 1992. *Cosmarium* reached 62 PU mL^{-1} in May, though was present thereafter only in October (7 PU mL^{-1}). *Gomphosphaeria* was present as single or double cells in May only, reaching a density of 75 PU mL^{-1}. *Aphanothece* then appeared in July (16 PU mL^{-1}) and October (14 PU mL^{-1}).

Figure 4.11 Changes in numbers of the main phytoplankton taxa in Loch of Tingwall, North Basin, during the 1993 sampling season (composite sample, n=3)



4.3.3.3.4 South Basin, 1992

Total phytoplankton count in 1992 in Tingwall South Basin ranged from 4760 PU mL^{-1} in June down to 777 PU mL^{-1} in August. Variations in numbers of the main phytoplankton taxa in Loch of Tingwall South Basin are described below. In addition, variations in the numbers of the most abundant taxa observed in 1992 are included in Figure 4.12.

4.3.3.3.4.1 Chrysophytes, cryptophytes and diatoms

As occurred in the North Basin, the dominant phytoplankton in the South Basin were chrysoflagellates. A maximum number of 3973 PU mL^{-1} was detected in June, the minimum of 99 PU mL^{-1} occurring in August. *Dinobryon* was present in the May sample only, totalling 153 PU mL^{-1}. Though generally sparse or absent, *Diceras* totalled 17 PU mL^{-1} during May, 1992. *Melosira* and *Synedra* were present in the algal assemblage during March only, reaching concentrations of 281 PU mL^{-1} and 62 PU mL^{-1} respectively. Peak numbers of centric diatoms (187 PU mL^{-1}) and *Asterionella* (344 PU mL^{-1}) also occurred at this time, though in contrast, these algae reappeared in the October sample. The Cryptophyceae were persistent in the phytoplankton community throughout the 1992 study period. *Rhodomonas* concentration was greatest in August (403 PU mL^{-1}), when phytoplankton numbers were generally depressed, though cyanophyte numbers were elevated. It was lowest in March (281 PU mL^{-1}) when diatoms, dinoflagellates and green algae were at their greatest density. *Cryptomonas* concentration ranged from 102 PU mL^{-1} in May to 300 PU mL^{-1} during June.

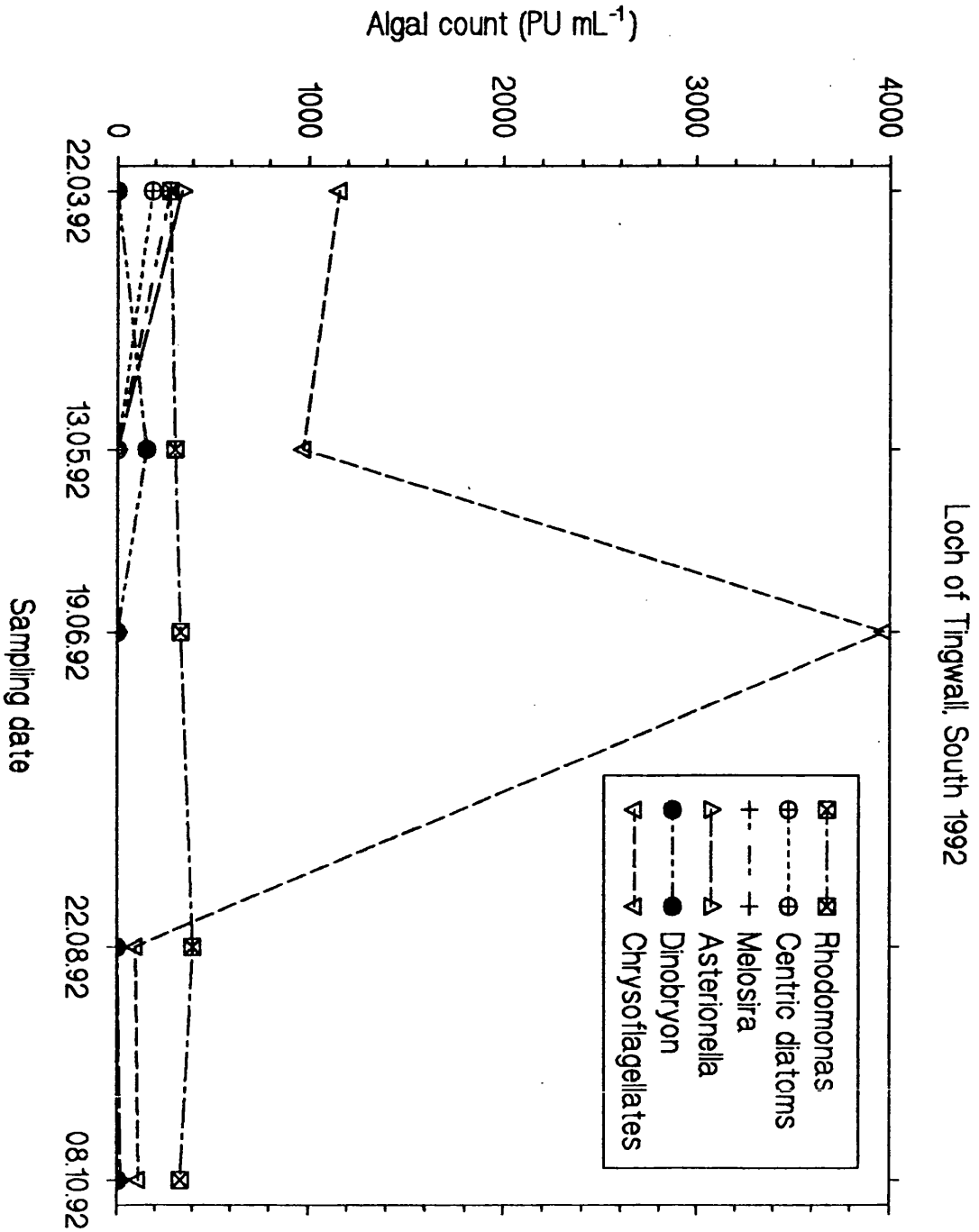
4.3.3.3.4.2 Dinoflagellates

The numbers of the Dinophyceae increased in Loch of Tingwall, South Basin, in 1992. Peak abundance was concurrent with that of the Bacillariophyceae in March. *Peridinium* concentration was 156 PU mL^{-1}, *Gymnodinium* 31 PU mL^{-1}. Lowest numbers occurred in October when neither genus was detectable.

4.3.3.3.4.3 Green and blue-green algae

Cyanophytes were mainly represented by *Aphanothece*, which ranged in abundance from below detection from March to June, to 120 PU mL^{-1} in August. *Chroococcus* accounted for 7 PU mL^{-1} in October.

Figure 4.12 Changes in numbers of the main phytoplankton taxa in Loch of Tingwall, South Basin, during the 1992 sampling season (composite sample, n=3)



Monoraphidium was not found in any of the samples from 1992, the dominant green genus being *Koliella*. *Koliella* (2) achieved greatest density simultaneously with diatoms during March (156 PU mL^{-1}) and lowest numbers in June and August when it was undetectable.

4.3.3.3.5 South Basin, 1993

In 1993 total phytoplankton abundance rose from 2041 PU mL^{-1} in March to 7590 PU mL^{-1} in July, minimum number occurring in October at a density of 636 PU mL^{-1}. Variations in numbers of the main phytoplankton taxa in Loch of Tingwall South Basin are described below. In addition, variations in the numbers of the most abundant taxa observed in 1993 are included in Figure 4.13.

4.3.3.3.5.1 Chrysophytes, cryptophytes and diatoms

Chrysoflagellates once again accounted for a great proportion of this total, maximum number of these algae occurring simultaneously with peak phytoplankton abundance. *Dinobryon* was found in May only, at a concentration of 156 PU mL^{-1}. *Diceras* was again found in the May sample in 1993, numbers totalling 31 PU mL^{-1}. As in 1992, diatoms, green algae and dinoflagellates were at their most important in March. *Melosira*, *Asterionella*, *Cyclotella*, centric diatoms, *Synedra* and *Fragilaria* were all constituents of the phytoplankton community at this time. *Asterionella* was dominant (521 PU mL^{-1}) followed by *Synedra* (187 PU mL^{-1}) and *Melosira* (125 PU mL^{-1}).

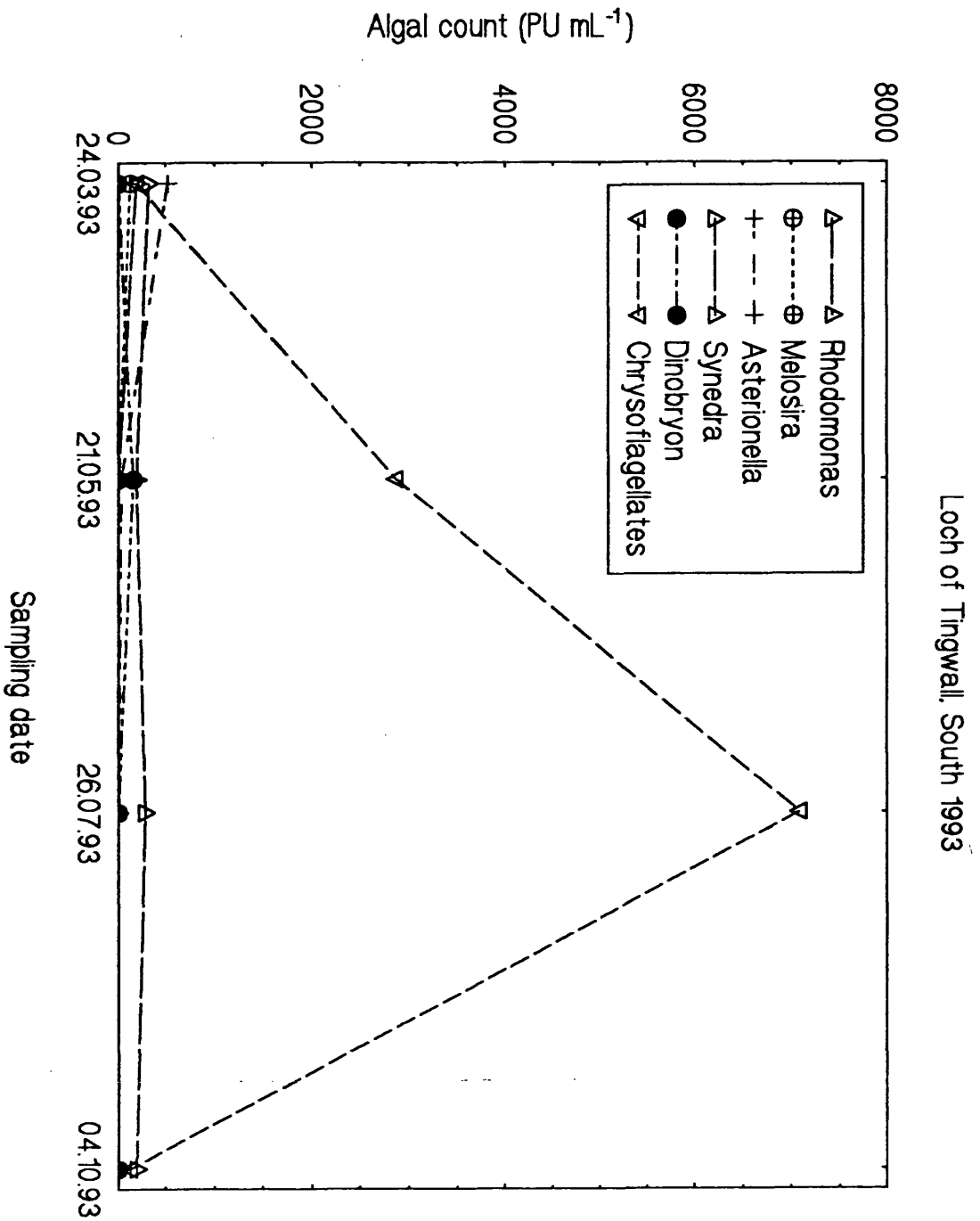
4.3.3.3.5.2 Dinoflagellates

Gymnodinium and *Peridinium* were both present at a concentration of 83 PU mL^{-1}, although only *Gymnodinium* was located in any other sample. In July its density was 31 PU mL^{-1}. During 1993 *Ceratium* became sufficiently abundant to allow counting. In October this dinoflagellate was present at 7 PU mL^{-1}.

4.3.3.3.5.3 Green and blue-green algae

In common with the 1992 algal assemblages, cyanobacteria were represented by *Aphanothece*, which reached maximum count in October of 42 PU mL^{-1}, although it had been absent in the July sample.

Figure 4.13 Changes in numbers of the main phytoplankton taxa in Loch of Tingwall, South Basin, during the 1993 sampling season (composite sample, n=3)



The green alga observed to be most abundant was *Koliella*. *Koliella* (2) was present in March, May and October at densities of 42 PU mL^{-1}, 62 PU mL^{-1} and 7 PU mL^{-1} respectively. *Monoraphidium* and *Scenedesmus* each numbered 21 PU mL^{-1} in the March phytoplankton sample, though only the latter was observeded subsequently, exhibiting a concentration of 7 PU mL^{-1} the following October.

4.3.3.4 Sandy Loch

4.3.3.4.1 1991

In 1991, maximum number of phytoplankton units (PU) was found in a sample taken on 25/05/91. The count recorded for this water sample was 3163 PU mL^{-1}. The minimum tally for a Sandy Loch sample in 1991 was 685 PU mL^{-1}, noted for 12/07/91. Number of PU mL^{-1} increased then in the following samples from 15/08/91 and 08/09/91. Changes in numbers of the main phytoplankton taxa in Sandy Loch are described below. In addition, variations in the abundance of the most numerically important taxa observed in 1991 are included in Figure 4.14.

4.3.3.4.1.1 Chrysophytes, cryptophytes and diatoms

Chrysoflagellate numbers were greatest in the 29/05/91 sample at 234 PU mL^{-1}, but decreased from May to the minimum recorded count in September of 86 PU mL^{-1}. Maximum numbers of *Rhodomonas* (246 PU mL^{-1}) were noted in July when green and chrysoflagellate numbers had decreased. A second peak of this alga occurred in September (234 PU mL^{-1}). *Cryptomonas* numbers followed the same pattern, but were much less abundant. Diatoms were most abundant in the 08/09/91 sample. *Melosira*, *Asterionella* and *Cyclotella* numbers were observed as 78 PU mL^{-1}, 39 PU mL^{-1} and 47 PU mL^{-1}, respectively.

4.3.3.4.1.2 Green and blue-green algae

In May, the phytoplankton assemblage was dominated by green algae. Most numerous was *Monoraphidium* (2) with 1335 PU mL^{-1}. There were also 141 PU mL^{-1} of *Koliella* (2). This alga did not represent a large proportion of the total count in the remaining samples in 1991. *Monoraphidium* (2) exhibited its lowest abundance in the 12/07/91 sample (53 PU mL^{-1}). Numbers increased from 12/07/91 to 08/09/91, when *Monoraphidium* (2) numbers reached 187 PU mL^{-1}. Blue-green algae were most abundant in the 08/09/91 sample, which incorporated 141 PU mL^{-1} *Gomphosphaeria*

and 8 PU mL^{-1} *Anabaena.*

4.3.3.4.2 1992

In 1992, two peaks in total phytoplankton abundance were recorded, the first in May, the second in August. The count of 5719 PU mL^{-1} in the sample from 10/05/92 was the greatest recorded for Sandy Loch during this study, the second peak in 1992 reaching only 2733 PU mL^{-1}. Variations in numbers of the main phytoplankton taxa in Sandy Loch are described below. In addition, changes in the numbers of the most abundant taxa observed in 1992 are included in Figure 4.15.

4.3.3.4.2.1 Chrysophytes, cryptophytes and diatoms

Greatest diatom numbers were found in a sample from 21/03/92, when *Melosira* was present at 344 PU mL^{-1}. *Melosira* became depleted and by 10/05/92, diatom dominance had passed to *Cyclotella* (97 PU mL^{-1}) and *Asterionella* (32 PU mL^{-1}). *Rhodomonas* (1260 PU mL^{-1}) also reached maximum abundance in the 10/05/92 sample, after *Melosira* numbers had been depleted. In contrast to *Rhodomonas*, *Cryptomonas* did not show peak abundance (141 PU mL^{-1}) in the samples until 23/06/92 and maximum chrysoflagellate abundance (364 PU mL^{-1}) occurred in August. *Melosira* and *Cyclotella* which had been undetectable in the 23/06/92 sample, accounted for 156 PU mL^{-1} and 78 PU mL^{-1} respectively in the August sample. By October, the majority of diatom biomass was to be found as *Asterionella*, numbers accounting for 196 PU mL^{-1}. At this time chrysoflagellate and *Rhodomonas* numbers were at their lowest and total phytoplankton count was the lowest of all Sandy Loch samples in the study.

4.3.3.4.2.2 Green and blue-green algae

Monoraphidium (2) (3490 PU mL^{-1}) and *Koliella* (2) (258 PU mL^{-1}) both reached maximum abundance in the 10/05/92 sample, after *Melosira* numbers had been depleted. *Monoraphidium* numbers were also elevated in August (937 PU mL^{-1}), when chrysoflagellates were abundant. Also concurrent with the peak chrysoflagellate numbers was the *Anabaena* bloom (521 PU mL^{-1}). *Anabaena* remained in the phytoplankton after the bloom declined, abundance falling to 13 PU mL^{-1} in October.

Figure 4.14 Changes in numbers of the main phytoplankton taxa in Sandy Loch during summer, 1991 (composite sample, n=8)

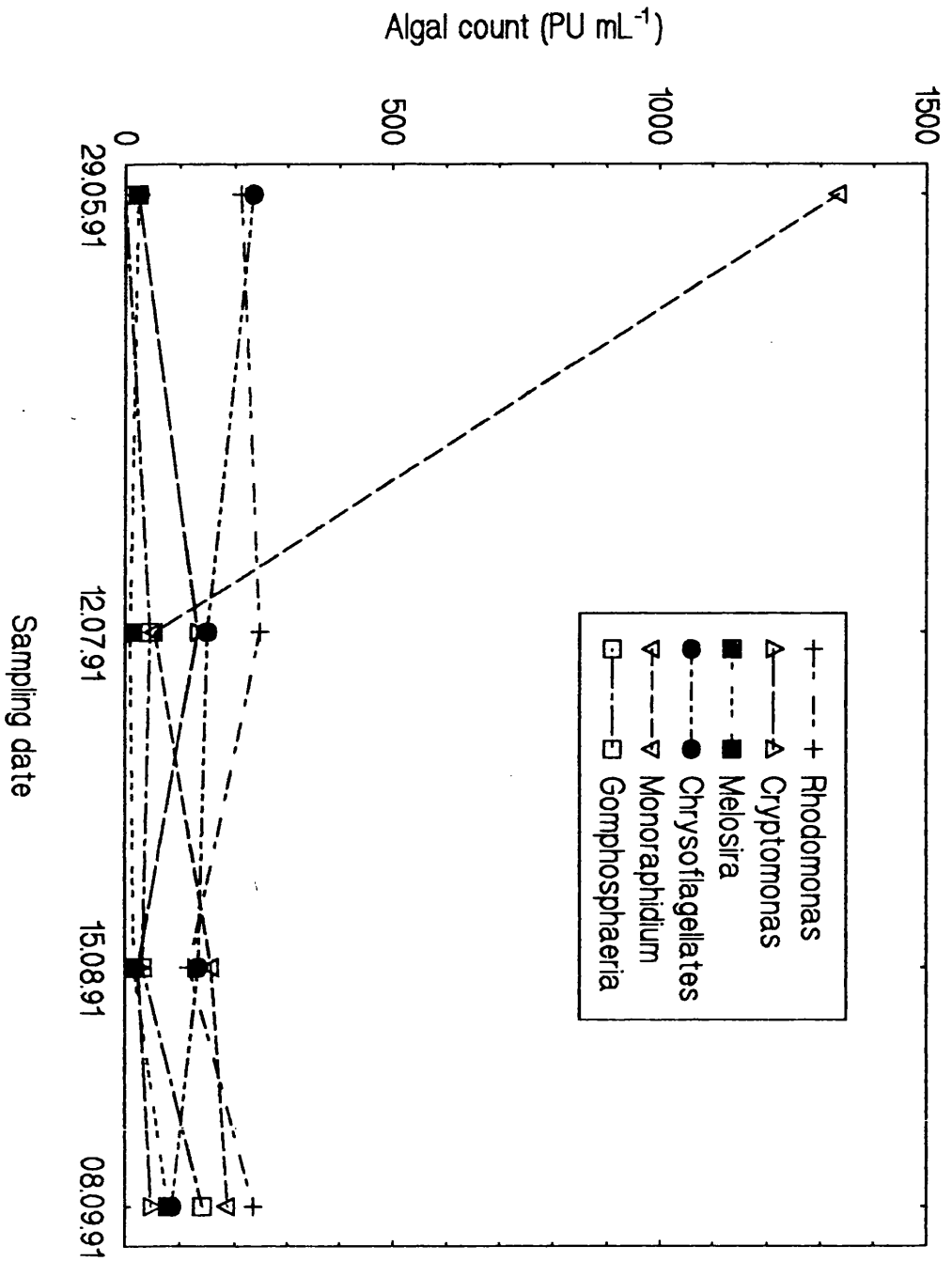
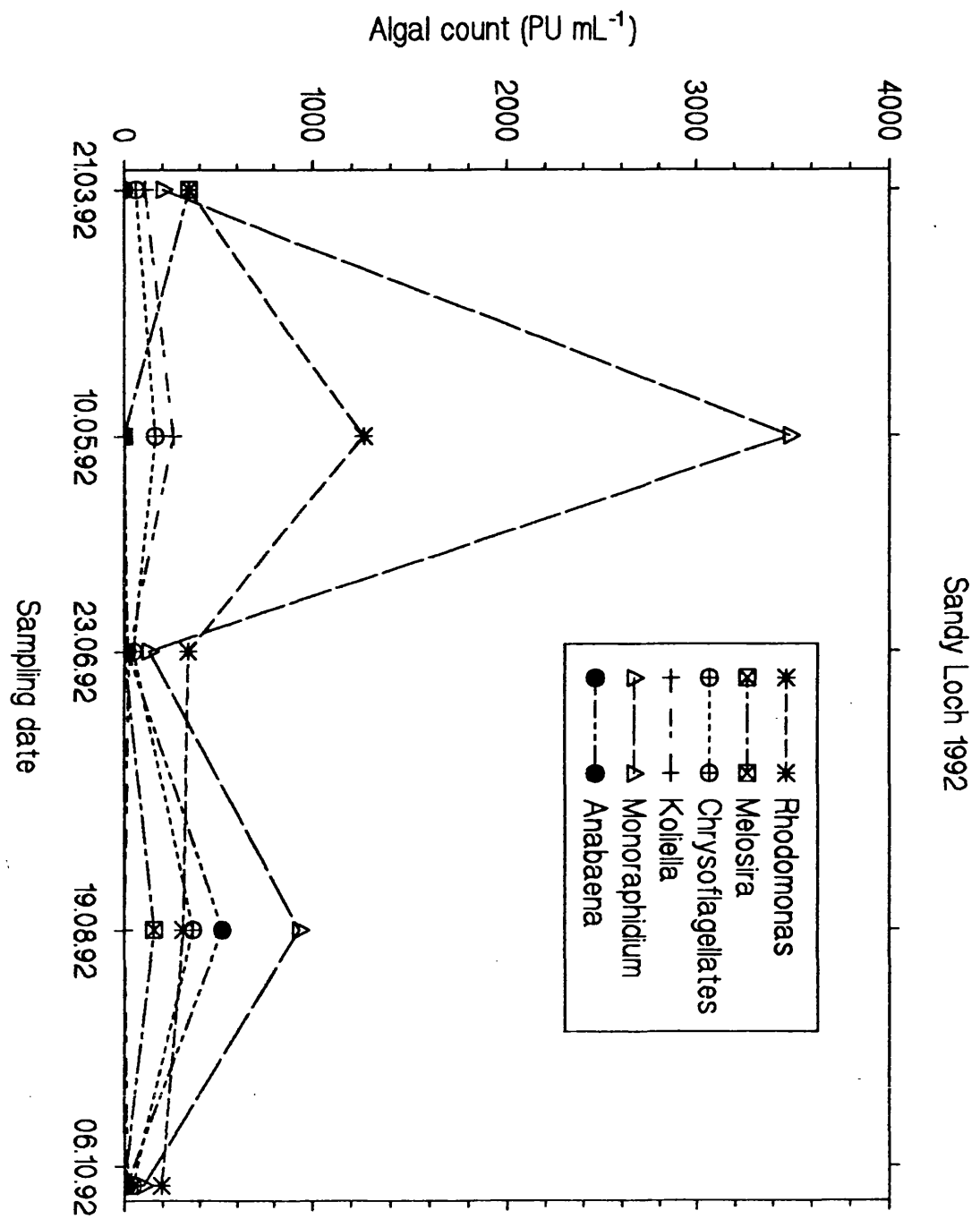


Figure 4.15 Changes in numbers of the main phytoplankton taxa in Sandy Loch during the 1992 sampling season (composite sample, n=3)



4.3.3.4.3 1993

In the three year study of Sandy Loch, maximum annual number of units was always recorded in May. In 1993, phytoplankton numbers were consistent through the sampling programme, ranging from 1218 PU mL^{-1} in the October sample to 1874 PU mL^{-1} in the May sample. Variations in the numbers of the main phytoplankton taxa in Sandy Loch are described below. In addition, changes in the numbers of the most commonly observed taxa in 1993 are included in Figure 4.16.

4.3.3.4.3.1 Chrysophytes, cryptophytes and diatoms

Highest number of units recorded for a single alga was 776 PU mL^{-1} for *Melosira* in the sample from 03/93. *Melosira* concentration in the water column in May was not sufficient for abundance to be estimated, though a peak occurred in July (172 PU mL^{-1}). *Asterionella* concentration rose continually from <1 PU mL^{-1} in March, to 187 PU mL^{-1} in October. Chrysoflagellate numbers peaked in May (312 PU mL^{-1}), with a second, lesser peak occurring in October (117 PU mL^{-1}). *Rhodomonas* numbers rose from 27 PU mL^{-1} in March to 750 PU mL^{-1} during May, before declining to 398 PU mL^{-1} in October, whereas *Cryptomonas* peaked in July (187 PU mL^{-1}).

4.3.3.4.3.2 Green and blue-green algae

Monoraphidium abundance remained consistently elevated, ranging from 203 PU mL^{-1} (07/93) to 422 PU mL^{-1} (05/93). Conversely, *Koliella* showed its greatest numbers in March, declining thereafter. *Anabaena* was not observed in any of the phytoplankton samples taken during 1993.

4.3.3.5 Turdale Water

4.3.3.5.1 1991

The greatest total count for phytoplankton samples in 1991 was 2628 PU mL^{-1}, in a sample taken in September. In the August sample, phytoplankton concentration was at its lowest (1033 PU mL^{-1}). Changes in the abundance of the main phytoplankton taxa in Turdale Water during 1991 are described below. In addition, variations in the numbers of the most commonly observed taxa are included in Figure 4.17.

Figure 4.16 Changes in numbers of the main phytoplankton taxa in Sandy Loch during the 1993 sampling season (composite sample, n=3)

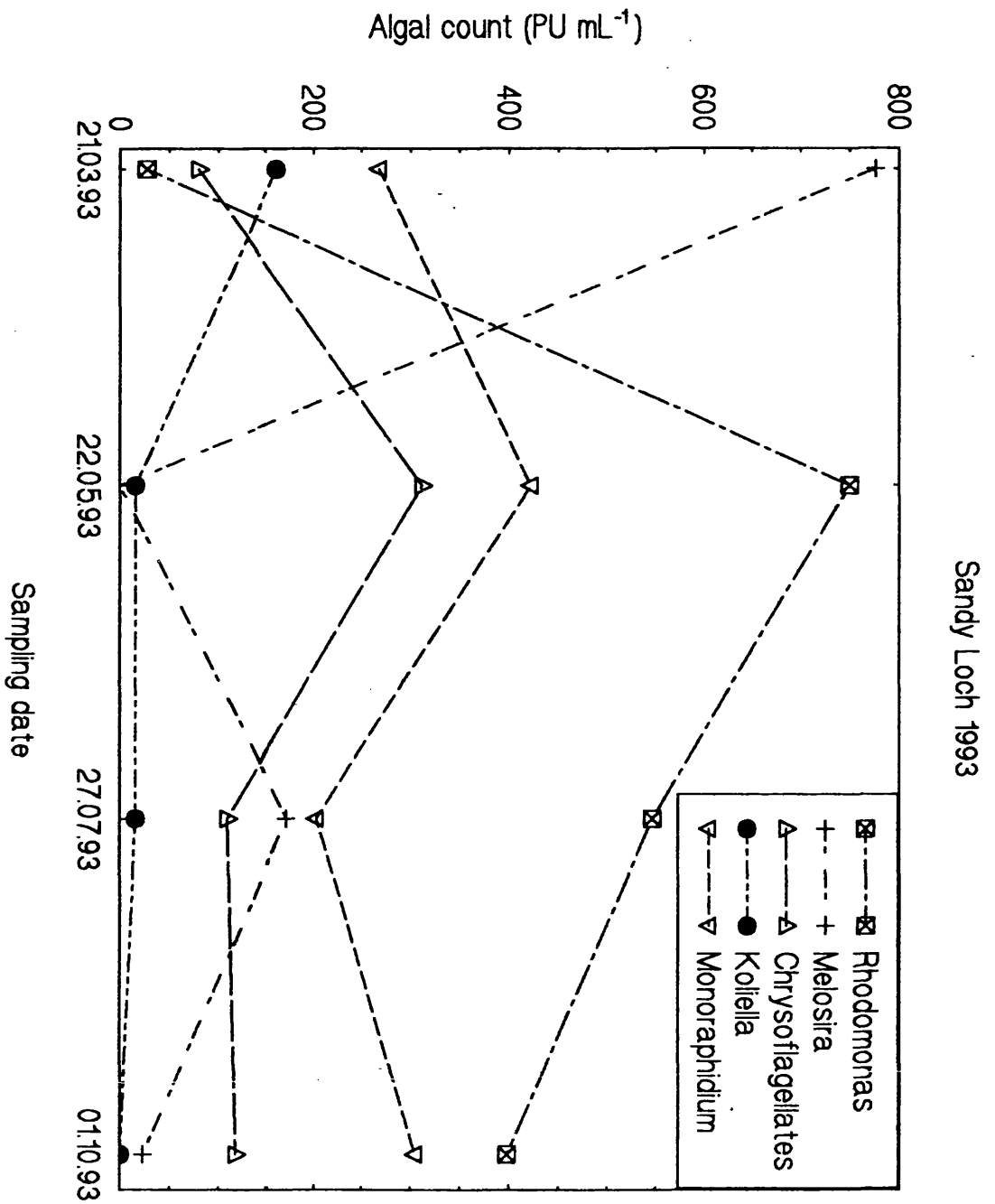
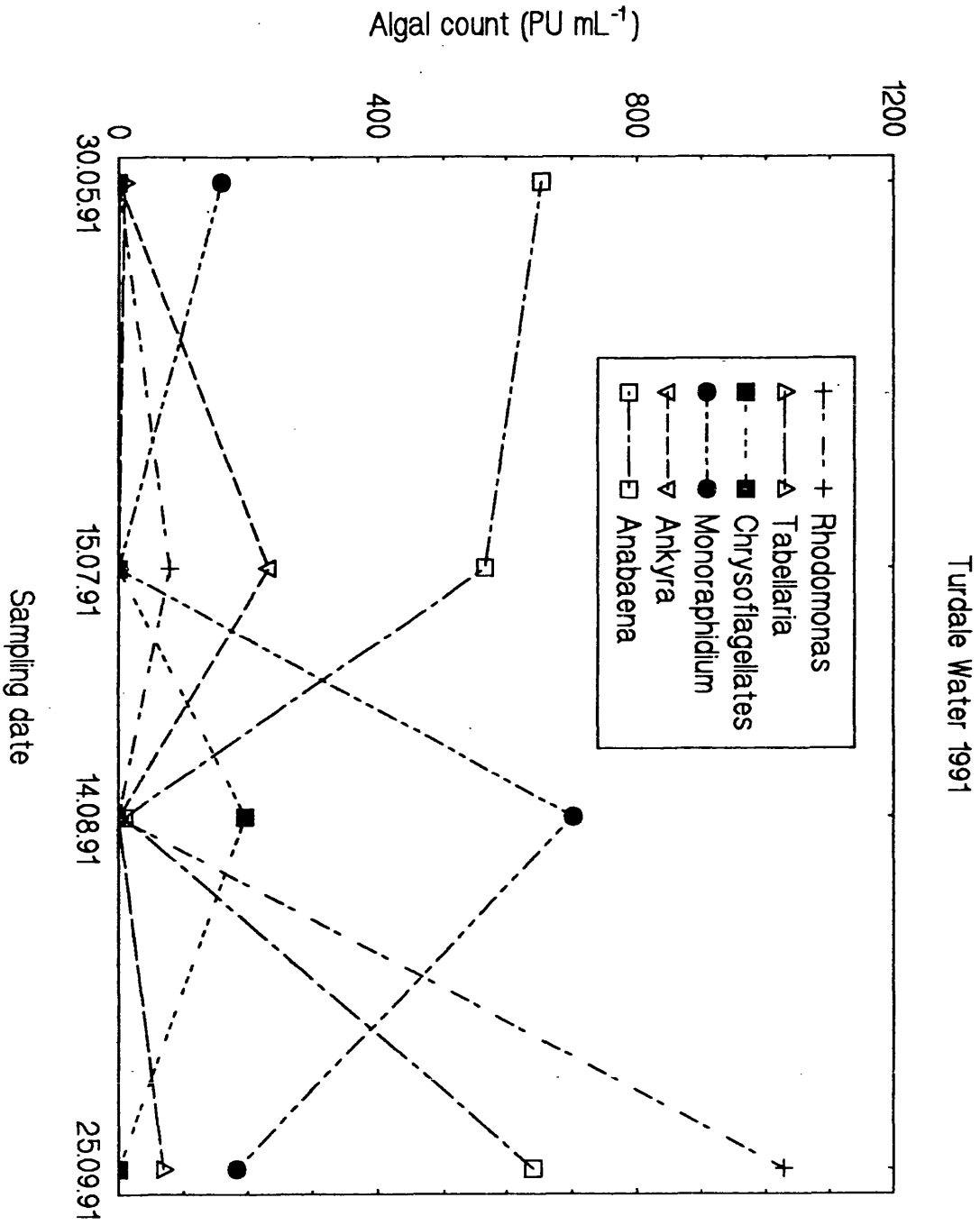


Figure 4.17 Changes in numbers of the main phytoplankton groups in Turdale Water during summer, 1991 (composite sample, n=3)



4.3.3.5.1.1 Chrysophytes, cryptophytes and diatoms

Chrysoflagellates were found in only one sample (14/08/91), at a concentration of 196 PU mL^{-1}. *Dinobryon* was observed in the 30/05/91 sample only (26 PU mL^{-1}). Diatom flora was comprised of *Melosira*, *Asterionella*, *Synedra*, *Fragilaria*, centric diatoms and *Tabellaria*. Bacillariophyceae decreased in number from May (42 PU mL^{-1}) to August (9 PU mL^{-1}), but peak count of 184 PU mL^{-1} was observed in the September sample. *Tabellaria* accounted for 69 PU mL^{-1} of this total. Cryptophytes were most numerous in the September sample. *Cryptomonas* decreased from 18 PU mL^{-1} to 3 PU mL^{-1} in the samples from 30/05/91 to 14/08/91 respectively. Maximum count was 69 PU mL^{-1}. *Rhodomonas* was undetectable in the samples from May and August, but increased to 79 PU mL^{-1} in July and 1028 PU mL^{-1} during September.

4.3.3.5.1.2 Green and blue-green algae

Anabaena was present in abundance in May (654 PU mL^{-1}), decreased in August (9 PU mL^{-1}), before numbers rose again to 640 PU mL^{-1} in September. Green algae in the algal assemblages were mostly dominated by *Monoraphidium* (2), which was undetectable during July, but maximum count was 703 PU mL^{-1} (14/08/91). This peak was concurrent with that of the chrysoflagellates. Also present in the phytoplankton were *Ankyra*, *Shroederia* and *Scenedesmus*. Generally, numbers of these algae were undetectable with the exception of one or two peak counts. *Shroederia* abundance was greatest (18 PU mL^{-1}) in May and August, *Ankyra* in July (233 PU mL^{-1}) and *Scenedesmus* (46 PU mL^{-1}) in September.

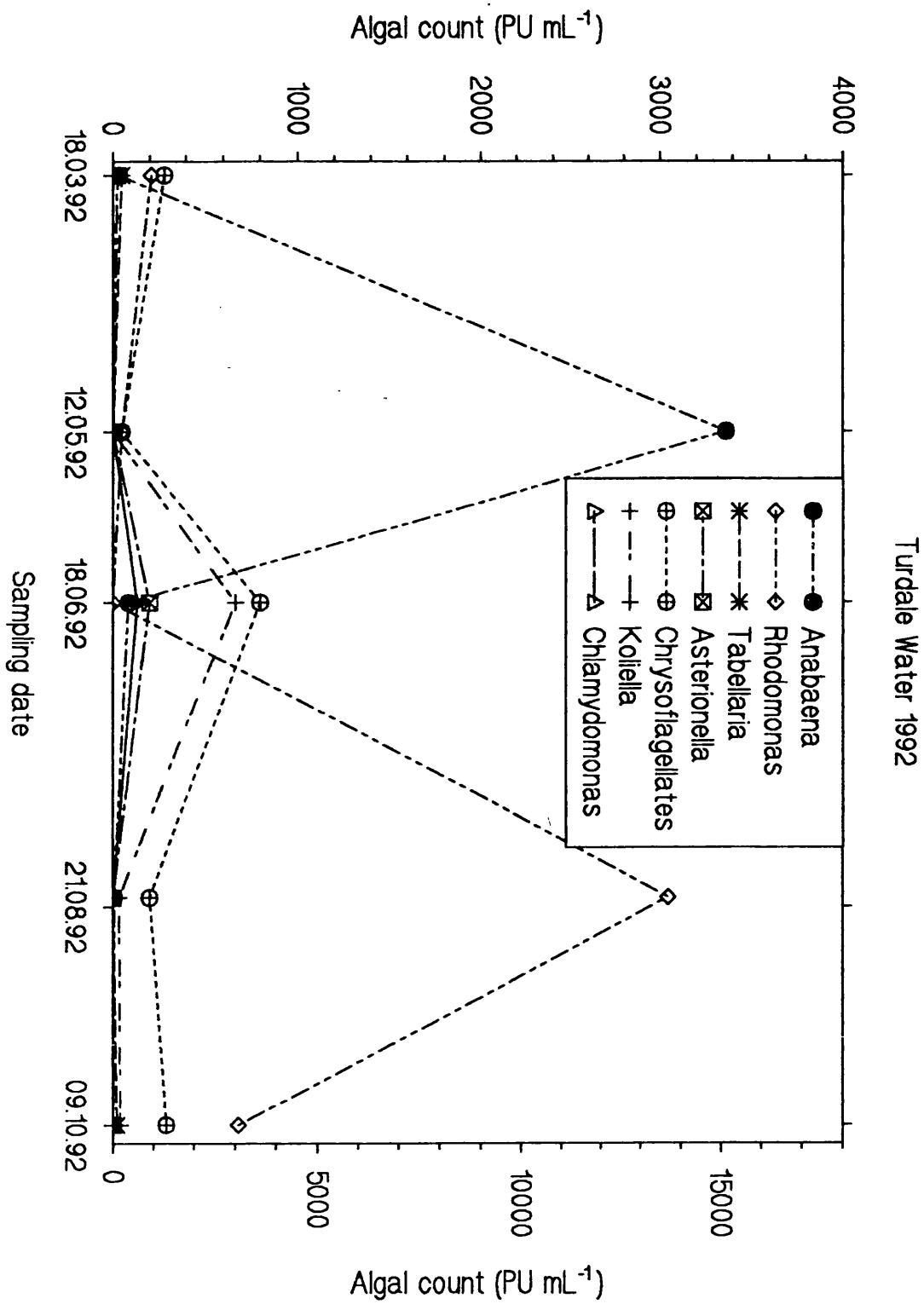
4.3.3.5.2 1992

The maximum algal count in 1992 was 15602 PU mL^{-1} and was observed in May. Lowest total phytoplankton count (1101 PU mL^{-1}) occurred in March. Changes in the abundance of the main phytoplankton taxa in Turdale Water during 1992 are described below. In addition, variations in the numbers of the most commonly observed taxa are included in Figure 4.18.

4.3.3.5.2.1 Chrysophytes, cryptophytes and diatoms

Only chrysoflagellates remained in the phytoplankton throughout 1992 sampling period. Lowest recorded number was 47 PU mL^{-1}, concurrent with peak abundance of *Anabaena*.

Figure 4.18 Changes in numbers of the main phytoplankton taxa in Turdale Water during the 1992 sampling season (composite sample, n=3)



However, in June, the maximum chrysoflagellate concentration of 803 PU mL^{-1} dominated the phytoplankton assemblage. *Dinobryon* was, however, absent from all water samples. Diatoms were most abundant in June, *Asterionella* and *Tabellaria* accounting for 201 PU mL^{-1} and 134 PU mL^{-1} respectively. However, no diatoms were observed in May or August samples. *Asterionella* was also absent from the October sample. Centric diatoms were present in March and October only. *Rhodomonas* declined in numbers from 211 PU mL^{-1} in March to undetectable levels in June. Greatest abundance, totaling 3044 PU mL^{-1}, occurred in August, with the count remaining relatively high in October (683 PU mL^{-1}). *Cryptomonas* numbers increased from below detection in earlier samples to 33 PU mL^{-1} and 59 PU mL^{-1} in August and October respectively.

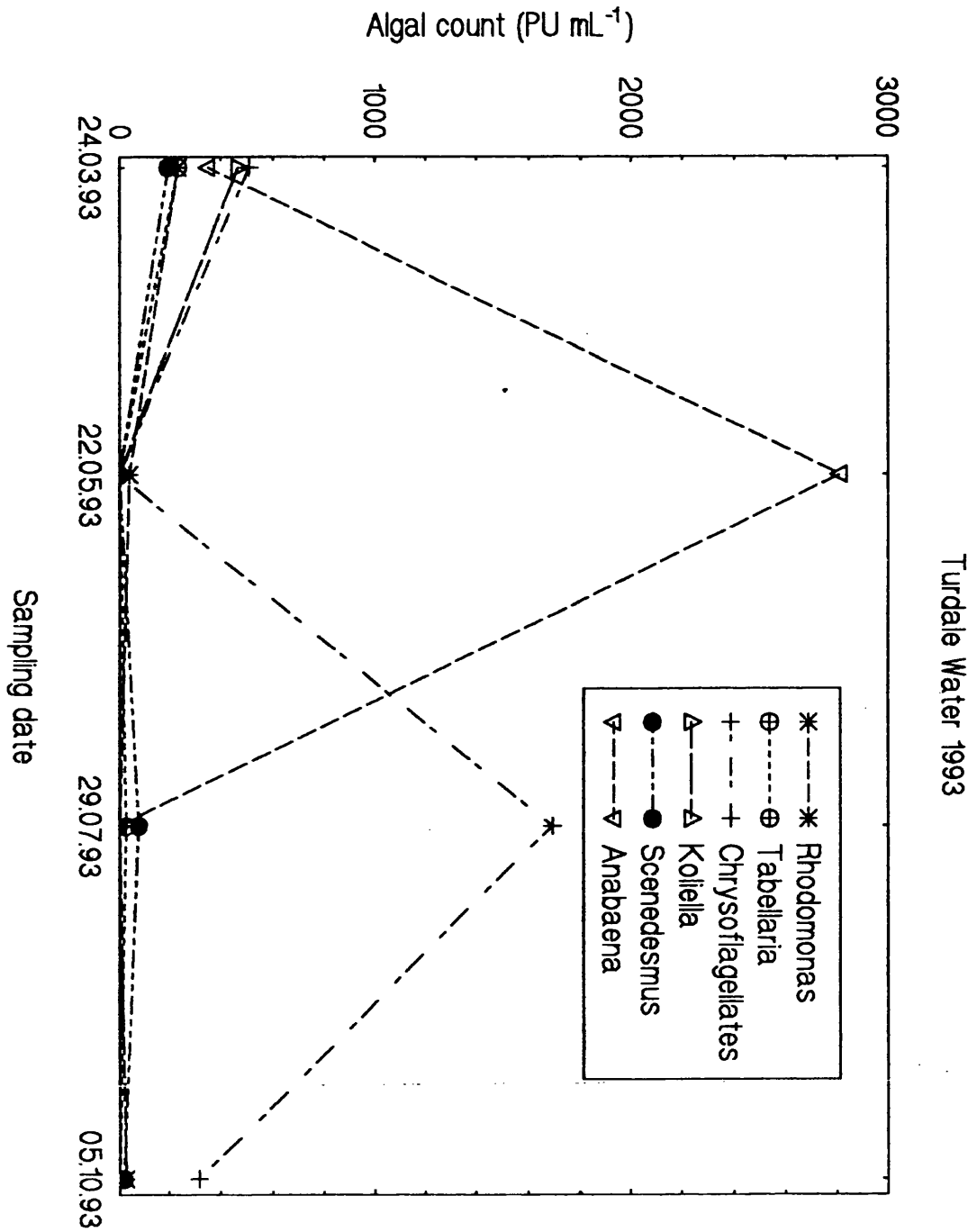
4.3.3.5.2.2 Green and blue-green algae

Anabaena was most abundant in May (15133 PU mL^{-1}), accounting for the majority of the phytoplankton present when total algal count was at its highest. The number of cyanobacteria then decreased to an undetectable level in September. Of the green algae observed, *Koliella* (2) exhibited the greatest numbers. Although absent in March, May and October, 669 PU mL^{-1} were counted in the June sample. Maximum *Chlamydomonas* concentration was also in this sample (134 PU mL^{-1}). In other samples this alga was not observed. However, unicellular green flagellates were present at a concentration of 94 PU mL^{-1} in the sample (12/05/92) containing maximum density of *Anabaena*. *Ankyra* and *Monoraphidium* were absent or present below detection levels in all samples except those of 18/03/92 and 09/10/92, where they reached 23 PU mL^{-1} and 98 PU mL^{-1}. *Scenedesmus* was not observed in samples from May or August, but occurred in the three other samples, with a maximum density of 100 PU mL^{-1} in June.

4.3.3.5.3 1993

In 1993, maximum phytoplankton density of 4490 PU mL^{-1} was observed in a sample taken in March. Algal numbers then decreased during the season to 751 PU mL^{-1} in the October sample. Changes in the numbers of the main phytoplankton taxa in Turdale Water during 1993 are described below. In addition, variations in the abundances of the most commonly observed taxa are included in Figure 4.19.

Figure 4.19 Changes in numbers of the main phytoplankton taxa in Turdale Water during the 1993 sampling season (composite sample, n=3)



4.3.3.5.3.1 Chrysophytes, cryptophytes and diatoms

Chrysoflagellates accounted for the greatest number of phytoplankton units in the March sample. However, from 508 PU mL^{-1} in March, these algae decreased to undetectable levels in May. Peak density was recorded as 1692 PU mL^{-1}, during July. In addition, *Dinobryon*, which was absent from the plankton in March, May and October, comprised 52 PU mL^{-1} in July. Highest diatom numbers occurred during March, totalling 468 PU mL^{-1}. *Tabellaria* was again the most abundant at a density of 234 PU mL^{-1}. Cryptophyceae were present in all samples in 1993. Maximum density of *Rhodomonas* was 234 PU mL^{-1} in March, but this alga was undetectable in July. *Cryptomonas* minimum concentration was 39 PU mL^{-1}, occurring concurrently with the *Rhodomonas* peak in March. Maximum abundance of 104 PU mL^{-1} was found in the July sample.

4.3.3.5.3.2 Dinoflagellates

In 1993, assemblages were different from 1991 and 1992 in that dinoflagellates appeared in the plankton in March and July. *Peridinium* was present at 156 PU mL^{-1} during March and 52 PU mL^{-1} in July, whereas *Gymnodinium* concentration was 39 PU mL^{-1} in March and 104 PU mL^{-1} in July.

4.3.3.5.3.3 Green and blue-green algae

Anabaena concentration in March was 351 PU mL^{-1}, but by May had risen to 2811 PU mL^{-1}. Thereafter, *Anabaena* though present, was not found in the count. The most commonly occurring Chlorophyceae in 1993 were *Monoraphidium*, *Scenedesmus*, *Koliella*, *Schroederia*, unicellular green algae and *Micractinium*. *Monoraphidium* numbers fell from 39 PU mL^{-1} during March to undetectable levels in May. The total then increased to 167 PU mL^{-1} in October. Similarly, *Scenedesmus* count decreased from 195 PU mL^{-1} during March to a density of < 1 PU mL^{-1} in May, before increasing to 78 PU mL^{-1} in July. The other green algae exhibited one or two peaks over the four samples, but were otherwise absent from the phytoplankton. Greatest abundance observed was 467 PU mL^{-1} for *Koliella* during March.

4.4 DISCUSSION

4.4.1 Disadvantages of algological techniques used in examination of loch phytoplankton assemblages

Although Lugol's iodine stains, preserves and facilitates sedimentation of phytoplankton, treatment of samples with this solution has disadvantages. Species which have gas vacuoles may shrink because of the collapse of these structures and fragmentation of large colonies such as those of *Microcystis*, or long filaments of, for example, *Anabaena* may occur. As a consequence, overestimates of numbers of colonies or filaments are possible, but also underestimates of sizes of aggregations and of individual cells. In addition, misidentification could potentially occur due to distortion of cells. For example, when considering the Bacillariophyceae, the form of *Asterionella* may change (Bailey-Watts, *pers. comm.* 1988) and fragile green phytoplankton (Beveridge, 1985) or Chrysophyceae, such as *Uroglena* (Margalef, 1969), may be damaged.

Owing to difficulties encountered, particularly because of the small size of many of the phytoplankton, it was necessary in certain cases to assign individuals to a category rather than to a genus *e.g.* small centric diatoms and unicellular green algae. Members of the Chrysophyceae *i.e. Ochromonas*, *Chromulina* and occasionally *Chrysochromulina* or *Dinobryon* cells outwith the lorica were all counted as chrysoflagellates. Despite a magnification of x400, features such as presence of one (*Chromulina*) or two flagellae (*Ochromonas*, *Chrysochromulina*), or a haptonema (*Chrysochromulina*), remained indistinguishable. Chrysophytes have been noted previously as being taxonomically "difficult" (Brook, 1994). Problems were also encountered with algae of similar genera, such as *Ankistrodesmus*, *Monoraphidium* and *Selenastrum*. *Monoraphidium* (1) resembled *Ankistrodesmus* whilst *Monoraphidium* (2) may have been *M. contortum*. *Selenastrum* resembled species of *Ankistrodesmus* and *Monoraphidium*. *Koliella* (2) denoted a more elongate cell than *Koliella* (1), which may have been a younger form of *Koliella* (2), prior to elongation.

Counting units rather than individual phytoplankton cells was necessary because of the difficulties involved in enumeration of cells in colonies. However, this means that filamentous algae, such as *Anabaena*, or colonial phytoplankton, such as

Aphanothece, are under-estimated relative to single celled units, such as *Rhodomonas*. Inconsistencies may also occur where number of cells per unit varies, depending on environmental conditions. For example, one colony or one or two cells of *Gomphosphaeria* could be reported as one unit.

Although chl *a* and total algal counts were found to be related to the CCA Axes, these parameters were not causative factors in phytoplankton community structure; rather they occurred as a result of algal growth (Table 4.3). The gradients of these two variables were in different directions, thus indicating that these parameters were heterogeneous. It is suggested that this occurred because units were enumerated, not cells. Therefore, in cases of high algal biomass, where colonial algae were dominant, total count was not necessarly high. Conversely, when phytoplankton productivity was low or moderate, single cell algae might account for much of the biomass and total count could be high. Despite differences in chl *a* content between algal taxa and depending on cell condition, it was concluded that chl *a* was a more effective estimate of algal productivity. Had total number of cells been counted, greater similarity would have been expected between count and chl *a*.

4.4.2 Interpretation of the CCA results

The ratio of the sum of unconstrained eigenvalues and the sum of canonical eigenvalues was relatively high (Table 4.2). A high ratio such as this indicates that a high proportion of variation between species was attributable to the environmental variables used in the analysis. The remaining variation may be related to parameters not included in the study, or random distribution of phytoplankton in a variety of water conditions. Since changes in the eigenvalues between the four axes were of low magnitude (Table 4.2), this indicated that variation in the data could not be attributed to one or two parameters only, but a complex combination of factors. As points on the biplots were the sum of positions on many environmental gradients, descriptions of positions of samples or phytoplankton scores on the biplots in terms of chemical concentration gradients are only general trends, with some environmental parameters having more impact than others. For example, as the variables TP and TAN were closely linked to the Axes, points were often placed with reference to these parameters foremost, although other factors such as TON and water hardness remained important. CCA diagrams were used as an illustrative tool, as intraset

correlations of environmental variables with Axes were indicative of trends in environmental data only (Figures 4.1a&b and 4.2a&b). The significance of the *t*-values was presumptive, as intraset correlations and canonical coefficients have greater variance than associated with normal correlations and therefore a Student *t*-test is inadequate in assessing the importance of the environmental variables (Ter Braak, 1988). However, weight was also given to the *t*-values which were more than 2.1. Values of < 2.1 are characteristic of variables which do not alone account for a consequential effect on the plant community (Ter Braak, 1988).

4.4.3 Phytoplankton occurrence in relation to environmental factors

Lochs which had been reported to have blooms or algal scums, either prior to or during the present study, had at least one sample which lay within the area of the biplot described as having increased concentrations of TP, TAN and chl *a*, but low TON concentrations (Figures 4.2a&b). These lochs were Turdale Water, Loch of Brough (Yell), Bu Water, Punds Water and Sandy Loch. (Localised phytoplankton scums observed near to the shore in Loch of Brough (Yell) and Bu Water during 1991 were constituted mainly of *Anabaena*.) Strand Loch did not appear to be of this group, but this water body is susceptible to sudden changes depending on relative contributions of freshwater and sea water to its volume. It is possible that the other lochs which had samples located in this assemblage *i.e.* Gossa Water, Loch of Snarravoe, Loch of Cliff and Loch of Brow did not develop algal blooms because a higher proportion of the TP present in the water columns of these lochs was in a less available form than in lochs which exhibited blooms or scums. In lochs with elevated levels of Ca or Mg, a high proportion of P may be bound to these divalent cations. Loch of Brow had elevated levels of Ca and Mg, Lochs of Snarravoe and Cliff each had relatively high water column concentrations of Mg, whilst Gossa had slightly higher levels of Mg in the water column than the waters of low cation concentrations (Chapter 2). In addition, Turdale, Punds and Bu Water, Sandy Loch and Loch Brough (Yell) were found to change position considerably on the TON gradient, but not on the TP or TAN rankings. It is possible that this was an important infuencing factor in bloom formation. This did not occur with either Loch of Snarravoe or Loch of Cliff, but was the case with Gossa Water and Loch of Brow. Gossa Water may therefore be at risk of developing *Anabaena* blooms in future.

Lochs which remained located at low to intermediate levels in all three of the the TP, TAN and TON rankings, such as Loch of Ustaness, Arthur's Loch and Helliers Water are unlikely to promote excessive phytoplankton biomass, assuming either all three parameters remain low, so that P and N both limit growth, or TON increases *i.e.* water chemistry becoming more like P limited lochs on the left of the biplot (Figures 4.2a&b). However, should P increase in these waters, firstly *Aphanothece* and *Oscillatoria* might be favoured and with further increasing P supply, growth of *Anabaena* could become a problem.

The area of the biplot associated with low nutrient levels was also linked to elevated Ca, Mg and chl *a* concentrations. Low P availability in a number of these lochs may be linked to relatively high concentrations of divalent cations in the water and probably also in the sediment, with P binding together with Ca and Mg. Since elevated chl *a* levels were also linked, it is suggested that inorganic N compounds were present in low concentrations as they were incorporated into the phytoplankton, *i.e.* nutrients were assimilated as they became available. Blue-green algae in this sector of the biplot may have been influenced by the increased pH and hence the increased proportion of C present in the water column as bicarbonate.

Lochs which had samples positioned in the biplot area linked with high TON, low TAN and low TP, such as Loch of Kettlester, Skutes and Roer Water, are unlikely to promote high phytoplankton biomass in their present state (Figure 4.2a&b). However, should P concentration increase within the water column, it is possible that algae such as *Gomphosphaeria* may become a nuisance, it being associated with higher TON concentrations. Further P enrichment might then shift water column conditions to high TP and low TON concentrations, as TON would be utilised in primary production once P was no longer limiting growth of the algal population.

4.4.4 Physical, chemical and biological effects on phytoplankton populations and biomass

4.4.4.1 Specific growth requirements

Since the commencement of this work, Sandy Loch, the Lerwick water supply, has exhibited excessive growth of cyanobacteria. A bloom was found in August, 1992 (although algal numbers appeared relatively low, owing to the enumeration of units

rather than cells) (Figure 4.15). Phytoplankton in the samples were mostly *Anabaena*. *Oscillatoria* and *Coelosphaerium* were also present. By October, 1992, dominance had shifted to *Gomphosphaeria* species, although *Anabaena* remained relatively common (Figure 4.15). Prior to this bloom occurring, an area of catchment had been fertilised for the purpose of growing fodder crops for sheep. Previous blooms in Turdale Water and Punds Water were also identified as being mainly *Anabaena*. The reasons for blue-green algae, and in particular, *Anabaena* dominance in certain Shetland waters rather than cryptomonads or chrysophytes is probably related to the specific physiological requirements of these algal groups. Increased competetive ability for one environmental resource may be associated with less efficient harvesting of another relative to the other phytoplankton groups present (Tilman *et al.*, 1986). In the present study, cyanobacteria were not successful when TP, TAN and TON were all at elevated concentrations in combination, whereas certain genera of green phytoplankton were linked with these conditions, perhaps as a consequence of TON uptake rates superior to those of other genera.

4.4.4.1.1 Availability of phosphorus to phytoplankton

The growth strategies of green and blue-green algae have been reported to be more suited to high P levels. At high P levels, cyanophytes are effective in sequestering, storing and partitioning nutrients into growth, whereas although chrysophytes store and utilise P for efficient growth, efficacy of uptake is inferior compared to that of blue-green algae (Sandgren, 1988). Conversely, under P-limiting conditions, chrysophytes often dominate, only diatoms such as *Asterionella* and small fast growing green algae such as *Scenedesmus* and *Chlamydomonas* species being capable of outcompeting them (Sandgren, 1988). However, intermittently higher P concentrations do not favour diatoms as they cannot store nutrients, unlike *e.g.* cyanophytes which have the faculty of luxury nutrient uptake, *i.e.* the capacity to take up nutrients in excess of immediate growth requirements at times when external nutrient supply is high. Dominance therefore passes from diatoms to other algal groups under these circumstances.

In the present study, chrysoflagellates were most numerous at low to intermediate TP levels. *Asterionella*, *Chlamydomonas* and *Scenedesmus* were all associated with higher TP levels. However, of the blue-green algae observed, only *Anabaena* was found to

be particularly highly ranked on the CCA TP gradient, the other cyanobacteria occupying low to intermediate positions on the TP scale (Table 4.4). This indicates that a range of growth requirements exist within the cyanobacteria, in terms of P. The positions of the blue-green algae on the TP gradient are also consistent with the work of Jensen *et al.* (1994); in shallow Danish lakes, green algae were observed as fast growing and capable of outcompeting other phytoplankton at high nutrient levels. Green algae, rather than cyanobacteria, were associated with high TP concentrations in the water column (Jensen *et al.*, 1994).

Of the cyanobacteria observed, *Oscillatoria* was ranked second most highly on the CCA TP gradient (Table 4.4). *Oscillatoria redekei* has been found to survive varying P loadings to a water body due to its polyphosphate kinase activity. It has the ability to take up polyphosphates during daylight for subsequent utilisation following degradation in the dark or whilst external P supply is limiting (Hickel, 1988). This may explain occurrences of high biomass of *Oscillatoria* in waters of low nutrient status in the literature. The position of *Oscillatoria* in the biplot (Figure 4.1a&b), in the same region as *Synedra* suggests that phytoplankton in this genus are efficient at P uptake. From a literature review, Sommer (1988) concluded that of six diatom species considered, *Synedra* was most competitive for P. Diatoms in the present study were associated with intermediate to high TP concentrations in the water column.

Veldhuis *et al.* (1987) examined the availability of P to *Phaeocystis pouchetii* (Haptophyceae) in the North Sea. Alkaline phosphatase activity (APA) was found to be high in areas where DRP concentration was depleted below 0.02 μmol.dm^{-3} (0.6 μg P L^{-1}). Though supply of P to the algae resulting from this occurred at a variable rate, uptake rate was comparable to that associated with DRP. In areas where nutrients were not at limiting levels, enzymatically hydrolysable P was not a significant P source. This alga is therefore suited to growth conditions of intermittent P enrichment, being able to capitalise on anthropogenic P inputs, but also to survive when DRP is at limiting concentrations. Therefore, freshwater members of the Class Haptophyceae, such as *Chrysochromulina*, or members of the Class Chrysophyceae (*e.g.* of the Orders *Ochromonadales* and *Chromulinales*), may also operate this strategy and dominate in such environments of variable DRP supply. The Bacillariophyceae are also included in the Chrysophyta and may operate a similar

strategy, as experimentation with *Cyclotella* dominated communities revealed that APA decreased when P was added to the ambient water (Stewart and Wetzel, 1982).

From a review of the available literature on chrysophyte nutrition, Sandgren (1988) concludes that during P limitation in alkaline waters, stimulation of significant alkaline phosphatase activity does not occur in this algal group. However, acid phosphatases are produced by several species in response to low P concentrations in acid waters, where they can utilise organophosphates *e.g.* glycerophosphate or glucose phosphate (Lehman, 1976). Dominance by chrysophytes would therefore not be expected in alkaline waters unless P supply was not limiting. In the present study chrysoflagellates were the dominant phytoplankton group in a range of waters including, for example, Loch of Tingwall, which is an alkaline and relatively hard water body (Chapter 2). In a shallow hypertrophic lake, Hjarbæk Fjord in Denmark, decline of the spring maximum of small centric diatoms could not be attributed to nutrient depletion and predation by zooplankton was also an unlikely cause due to relatively small numbers (Olrik and Nauwerck, 1993). However, *cf. Ochromonas* was observed engulfing diatoms and its numbers increased concurrently with diatom decline (Olrik and Nauwerck, 1993). Sandgren (1988) reported that of those chrysophytes examined, the majority could actively ingest bacteria and algae. Exceptions were *Mallomonas* and *Synura*. Nutrient requirements of chrysophytes are therefore not restricted by the availability of simple chemical forms within the water column, but can be met through phagotrophy. *Mallomonas* and *Synura* were noteably rare or absent in the phytoplankton assemblages observed in the present study, whereas other chrysoflagellates, including *Ochromonas*, were widespread in their occurrence and often present in great numbers. Phagotrophy would explain their presence in less acid waters of relatively low nutrient status, such as Loch of Tingwall.

Common species of dinoflagellates form blooms during summer in temperate lakes. During autumn, when stratification has ended, encystment occurs, with lipid used as the long term energy source (Pollingher, 1988). Dinoflagellate cysts in sediment can store P in their cells until resuspension under suitable growth conditions. Although dinoflagellate nutrient affinities and specific growth rates are relatively low, long generation time and the ability for luxury uptake of nutrients and motility within the

water column mean that these phytoplankton have an advantageous life-strategy in waters subject to extreme nutrient shortage (Pollingher, 1988). *Peridinium* from Lake Kinneret has been reported to grow in culture on ATP, G-6-P and glycerophosphate (Serruya and Berman, 1975). These factors explain dinoflagellate presence in waters associated with low to intermediate TP, TON and TAN concentrations. In terms of P dynamics within a waterbody, dominance of dinoflagellates allows slowing of P cycling, as a consequence of the long generation times of these algae.

Cryptophytes sequester P using alkaline phosphatases. This allows them to obtain P from dissolved humic complexes. However, enzyme activity does not stop when an additional P source is provided (Stewart and Wetzel, 1982). Phytoplankton such as *Anabaena* might therefore obtain a competitive advantage through superior uptake of introduced P in circumstances where the natural phytoplankton population are adapted to lower P availability and therefore do not compete for the same P source.

4.4.4.1.2 Phytoplankton strategies for fulfilling nitrogen requirements

Data collected during five years of studies at Lake St. George, Ontario indicated no correlation between percentage of cyanobacteria and TN:TP ratio. However, at NO_3 concentrations of $>$ 100 μg N L^{-1}, blue-green algae were never abundant. Furthermore, it was found that when NO_3:TP $>$ 5:1, cyanophyte blooms were not seen to occur (McQueen and Lean, 1987). Blue-green algae such as *Anabaena* and *Aphanizomenon* have the ability to grow in low N:P ratio conditions through heterocystous fixation of atmospheric N. Heterocysts are generally formed in response to low supplies of combined forms of N such as TAN and TON, through differentiation of normal vegetative cells (Fay, 1983). In the present study, *Anabaena* was associated with high TAN concentrations (Table 4.4), which might indicate superior uptake of TAN, but not TON. *Anabaena* is possibly unable to compete for TON, being in some way inferior in its uptake or utilisation of this resource compared to, for example, green algae, so making effective uptake of TAN or N fixation necessary at low TON concentrations. In contrast, *Gomphosphaeria*, *Coelosphaerium*, *Merismopedia* and *Chroococcus* were all associated with low TP and TAN concentrations and increased TON levels (Table 4.4). These algae cannot fix N. *Aphanothece* is similar to *Microcystis* and therefore probably does not fix N. It is suggested that *Aphanothece* can grow efficiently at relatively low to intermediate

levels of nutrients, or is efficient at nutrient storage. It is possible that cyanobacteria which are successful at higher TON and lower TAN concentrations may be efficient in their uptake TON, but not TAN. Some species of *Lyngbya* and *Oscillatoria* fix N, although this occurs within normal vegetative cell structure, rather than within heterocysts. Both *Lyngbya* and *Oscillatoria* were associated with low TON concentrations, but increasing TP and TAN concentrations.

In summary, as with P, a range of growth strategies exists within the cyanobacteria, with respect to N uptake, thereby explaining the range of positions of blue-green algae on the CCA TAN and TON gradients (Figures 4.1a&b).

Tilman *et al.* (1986) state that it is likely that diatoms are inferior to blue-green algae in terms of competition for N. However, although *Anabaena* was ranked highly on the CCA TAN gradient, small centric diatoms were at the top of this scale. Chrysophytes require a relatively high ratio of N:P, higher biomass occurring in lakes with a TN:TP ratio between 30:1 and 60:1 (Sandgren, 1988). Nevertheless, dominance by chrysophytes could occur in waters with low concentrations of TAN and TON if available P concentration is extremely low, *i.e.* TON levels would be high relative to P concentrtions. This would explain the occurrence of chrysoflagellates in the present study at low to intermediate TP, TAN and TON concentrations.

Chrysophytes can use either TAN or TON as their N source, though this may be species dependent (Lehman, 1976). *Ochromonas* can utilise amino acids, urea and secrete urease (Lui and Roels, 1970). Since chrysoflagellates can engulf other algae, this ensures an N source, even under low water N concentrations. This explains dominance by this phytoplankton group in many of the lochs in the present study which exhibited low water concentrations of inorganic N. In contrast, Viera and Klaveness (1986; in Klaveness, 1988) found cryptophyte *Cryptomonas cf. tetrapyrenoidosa* to have poor versatility in use of organic N sources in comparison to four other phytoplankton species examined. As a consequence this alga is presumably reliant upon inorganic N sources and would not be numerous if these were in short supply. Cryptophytes in the present study tended to exhibit peak abundances at times which did not coincide with greatest total algal counts, thereby

suggesting their growth was possible when other phytoplankton peaks collapsed because they could take advantage of the newly available nutrients.

Dinoflagellates in Shetland lochs were associated with lower concentrations of TP, TAN and TON. Slow growth rate of larger dinoflagellates and their association with nutrient-depleted waters is indicative of a K-selection strategy (Reynolds, 1984b). According to Reynolds (1984a) the preferred source of water N for phytoplankton uptake is TAN rather than TON. However, in monomictic Lake Kinneret in Israel, it was found that when water NH_4^+ concentration was low (< 1 μg-at N L^{-1}) and levels of NO_3^- were high, phytoplankton sequestered N from NO_3^- (Berman *et al.*, 1984). This occurred during the annual dinoflagellate bloom (February to May), perhaps indicating that dinoflagellates are more suited to conditions of low TAN than other algal groups. Nitrate reductase activity was found between March and May in *Peridinium cinctum* (Berman *et al.*, 1984), indicating that other groups may be outcompeted by dinoflagellates when TAN concentration is low. In culture, *Ceratium hirundinella* has been found to prefer $NaNO_3$ and urea to TAN or TON (Pollingher, 1988). It is likely that assimilation of N from TON or organic N sources by dinoflagellates will be followed by eventual availability of TAN in the water column through excretion, death and decay processes. A different phytoplankton group might then be expected to dominate. However, it is possible that a group such as the dinoflagellates which use nitrate reductase activity could dominate in low N environments, rather than nitrogen fixing cyanophytes, provided an adequate N substrate was present.

4.4.4.1.3 Other chemical determinands of phytoplankton growth

When there are no chemical restraints, in terms of N and P availability, then the ability of an alga to take up other elements may become important in determining species dominance. Si is of particular importance to diatoms and certain chrysophytes. Sommer (1988) considers that only Si limitation prevents diatoms from outcompeting blue-green or green algae in P limiting situations. However, measurement of Si was not undertaken in the present study.

Chrysophytes may be common in dystrophic lochs because the high organic content of the water results in complexation of Fe, which is a particularly important limiting

trace element for chrysophytes. Chelation of Fe in the water results in its increased availability to phytoplankton which cannot sequester it in ionic form. In contrast, *Anabaena* can exist in water regardless of its chelated Fe status, as *Anabaena* has the ability to use its own extracellular chelators. Low oxygen conditions are tolerated by prokaryotic phytoplankton and perhaps preferred (Fay, 1983). Nitrogen fixation requires oxygen exclusion from heterocysts and this is more easily attained should extracellular conditions be low in oxygen. In contrast, because of the oxygen consuming activities associated with cell division, dinoflagellates have a preference for well-oxygenated conditions in the water column (Pollingher, 1988). As Shetland waters were well-oxygenated low oxygen concentrations were not prerequisites for excessive algal growth in the present study.

The most common bloom-forming armoured dinoflagellates, *Ceratium*, *Peridinium*, and *Peridiniopsis* have a preference for hard water, with a high calcium concentration (Pollingher, 1988). Dinoflagellates in Shetland lochs were found to be ranked at intermediate to high pH, Ca and Mg concentrations on the CCA scales (Table 4.5). Dinoflagellates exhibit a wide pH tolerance range, although growth decreases at pH < 6 and species may be extremely particular in their specific requirements (Pollingher, 1988). Highest numbers and growth rates have been recorded at pH $>$ 8 (Lindstrom, 1984). This is consistent with dinoflagellates in the present study being located at intermediate to high positions on the CCA pH gradient (Table 4.5).

Preference of higher pH values in cyanobacteria is well documented (Shapiro, 1990). However, this may be related to the effects of pH on the form of dissolved inorganic C present in the water column (Chapter 1), rather than as a direct result of H^+ concentration. In harder, more alkaline waters, such as those towards the lower section of the biplot, concentration of free CO_2 may be important in its effect on cyanophyte positions within the biplot (Figures 4.1a&b) According to Shapiro (1990), blue-green algae have the ability to utilise HCO_3^-, so that in alkaline waters, free CO_2 limitation favours these algae above diatoms and green algae. Occurrence of *Cylindrospermum*, *Anabaena*, *Coelosphaerium*, *Chroococcus* and *Aphanothece* at higher pH levels on the CCA pH gradient, may be explained by the pH/CO_2 hypothesis. However, as green algae, diatoms and chrysophytes were also represented in high positions on the pH ranking, this suggests that at least some of the

phytoplankton belonging to these groups may either scavenge particularly effectively for CO_2, or utilise HCO_3^- in alkaline conditions. In dinoflagellates, specific photosynthetic carbon uptake is low in comparison with other algae (although low P:C ratios are required by *Peridinium*) (Pollingher, 1988). Possibly this low requirement means that low CO_2 concentrations in alkaline waters are adequate for growth, without HCO_3^- uptake.

4.4.4.2 Physical influences on phytoplankton dominance

Cyanobacteria may be unable to outcompete eukaryotic plankton, such as diatoms, despite presence of high nutrient concentrations (Steinberg and Hartmann, 1988). Nutrient status alone may not account for presence or absence of cyanophyte blooms. Physical factors, such as the availability of PAR, temperature of the water column and turbulence within the water column, may all have effects on development of algal biomass and phytoplankton community structure.

4.4.4.2.1 Light climate of the water column

Availability of light to algal assemblages may effect phytoplankton nutrient uptake. Phosphate additions to *Cyclotella* dominated algal assemblages have been found to depress alkaline phosphatase activity under high or low light conditions (Stewart and Wetzel, 1982). However, uptake rates for both NH_4^- and NO_3^- by phytoplankton populations are affected by light intensity and therefore fluctuate diurnally, partly in response to changing light levels, but also in relation to biomass and the physiological state of phytoplankton cells and ambient concentrations of N (Berman *et al.*, 1984).

Phytoplankton tolerate a range of light conditions, with certain algal groups showing adaptations to conditions of low PAR availability. Dinoflagellates prefer a plentiful light supply and self shading is low in populations of armoured dinoflagellates (Pollingher, 1988), presumably as a result of the large size of individuals within the population. However, dinoflagellates may tolerate a range of conditions. For example, *Peridinium* can survive in darkness for 7-9 days (Pollingher, 1988). Cryptomonads are capable of growing in light regimes typical of those found in the dystrophic lochs of Shetland. However, *Anabaena* also has this ability as cyanophytes can harvest light using compounds other than chlorophyll, called phycobiliproteins (Fay, 1983), energy then passing from these compounds to chlorophyll. Cyanophytes also have their

photosynthetic metabolism saturated at relatively low light intensities. Consequently, although another algal type may grow better at higher light intensities, blue-green phytoplankton can flourish in lower light and then shade other types.

In dystrophic lakes, water colour alone is possibly sufficient to favour growth of cyanophytes. Suspension of particulates through turbulence will also limit available light. Both high water colour and increased turbidity because of wind mixing exist in the Shetland lochs studied. However, Mill Pond, despite its dark colour supported *Scenedesmus* rather than blue-green populations, perhaps because this water body is so shallow that development of cyanobacterial populations in a deeper, darker layer is not possible and the green algae have adequate light for growth at the surface of the water body only.

In situations where water column transparency is high, it remains possible for blue-green algae to be more successful than other phytoplankton groups. For example, *Oscillatoria agardhii* cannot outgrow *Scenedesmus protruberans* except at low P concentrations and the maximum growth rate of occurs at lower light intensity than that of *S. protruberans* (Mur *et al.*, 1978). In phytoplankton growth experiments involving different light levels, *O. agardhii* dominated at low light intensity, but was inhibited at high light intensity. However, although *S. protruberans* grew quickly to steady state density under higher light levels, the increased *S. protruberans* population caused shading within the water column, so allowing efficient growth of *O. agardhii*. The volume of water available for growth of *S. protruberans* then became too small to support the *S. protruberans* population (Mur *et al.*, 1978).

A potential for excessive blue-green growth therefore exists, not only in lochs of low water clarity, but in water bodies where water column conditions allow sufficient growth of green algae to inhibit light penetration to a level where cyanophyte development is possible. This will depend on such factors as nutrient concentrations, intensity of initial light source, particulate content and colour of the water.

4.4.4.2.2 Water column turbulence

During periods of water column stability, loss rates of dinoflagellates through sinking processes are low because they can maintain themselves at their preferred depth

within the lake. Although turbulence is useful in minimising sinking loss in non-motile phytoplankton such as diatoms, dinoflagellates find water mixing stressful as it becomes difficult to maintain position at a particular depth (Pollingher, 1988). Water column stability is of great importance to cyanophyte dominance. In calm conditions blue-greens will have an advantage over non motile eukaryotic phytoplankton *e.g.* diatoms. Non motile phytoplankton sink if the rate of mixing is inferior to the rate of phytoplankton descent through the water column (Reynolds, 1973a), but buoyancy regulation occurs in cyanophytes. Gas vacuole formation ensures that blue-green algae such as *Anabaena* can maintain themselves at the most suitable depth in terms of light and nutrients.

Storm events may cause simultaneous mixing and outflow effects, *i.e.* phytoplankton may be flushed from the lake system. If stratification has occurred and nutrient concentration in deeper water is relatively high in comparison to the potentially nutrient depleted epilimnion, then increased wind velocity can result in these nutrients becoming available throughout the water column. Phytoplankton with strategies for survival in low nutrient environments *i.e.* slow-growing K-selected species can then be replaced by r-selected species, *i.e.* small, rapidly growing algal types. If there is a simultaneous rainfall event accounting for a considerable inflow of water to the lake, or if precipitation alone occurs, then the dominant algal population in the epilimnion or surface waters may decrease significantly due to losses through the lake outflow. Jacobsen and Simonsen (1993) believed losses from the epilimnion through outflow was the likely cause of a decline in *Aphanizomenon* biomass following a summer bloom in Lake Gødstrup, Denmark. Although this storm event may not have resulted in complete destruction of water column stratification and was therefore followed by re-establishment of the *Aphanizomenon* population, storms in late August allowed complete mixing, mechanical stress on the blue-green colonies, increased nutrients, a nine-fold increase in diversity and dominance by cryptomonads. Lochs in Shetland stratify weakly and infrequently, or not at all (Chapter 2). However, disturbance events may prevent the development of the potential biomass of phytoplankton, result in wash out of algal communities and in the development of cryptophyte populations. The latter may occur after resuspension of nutrients from sediment sources, or nutrient availability through decline of the previously developing phytoplankton assemblage.

In sediments, algae with exposed chloroplasts can be viable for many years (Cronberg, 1982). However, although *e.g. Mallomonas eoa* (Cronberg, 1982) and *Melosira* have the ability to survive on sediment surfaces (Lund, 1954), *Asterionella* and *Fragilaria* do not have such a survival mechanism (Reynolds, 1973a). Akinete formation through differentiation of normal vegetative cells in cyanophytes such as *Anabaena* means that vegetative spores may lie dormant in sediment for years, even in anoxic conditions until appropriate conditions prevail. Formation of akinetes therefore not only allows overwintering, but also long term survival (Reynolds, 1973a). In shallow lochs such as those in Shetland, akinetes would be frequently resuspended through wind mixing, thereby allowing advantage to be taken should increased nutrient loading from the catchment occur.

4.4.4.2.3 Temperature of the water column

Higher water temperatures may allow blue-green algae to become dominant through either preference of eukaryotic phytoplankton for lower water temperatures or suitability of greater water temperatures for growth of cyanophytes. Diatoms bloom in spring, but are then outcompeted by prokaryotes as water temperature increases. Although formation of a thermocline may maintain a diatom population in an advantageous position in terms of wind-induced circulation (Reynolds, 1973a), exponential increase of *Microcystis aeruginosa* has been associated with onset of water column stratification and water temperatures over 15°C (Reynolds, 1973b). Examination of data from Lake St. George, Ontario revealed that blue-green blooms were never observed when water temperature was < 21°C (McQueen and Lean, 1987). In the present study, CCA analysis indicated that cyanobacteria were associated with increased temperatures, with the exception of *Gomphosphaeria*. This suggests that mid winter blooms of most blue-greens are unlikely, but *Gomphosphaeria* could grow excessively at any time of year. Although many of the Shetland lochs were found to be low in inorganic N during the summer months of 1991, this may not necessarily be the case during winter. In moderately productive loch systems, it is possible for TON levels to have a wide range from summer to winter. During summer, phytoplankton growth and perhaps sediment oxygen demand account for low TON concentrations in the water column, but after summer growth has collapsed, TON is again released to the system. As *Gomphosphaeria* is associated with lower temperatures and increased TON and TP, a bloom could result.

4.4.5 Changes in phytoplankton community structure of the five study lochs over time

Phytoplankton community structure is influenced throughout the year by successional changes in dominance along nutrient ratio gradients and as a result of periodicity, which is caused by physical changes in the environment ***e.g.*** differences in light and temperature (Reynolds, 1984a;1993). The information on the Shetland study lochs is not continuous, ***i.e.*** the record of succession or periodicity during summers from 1991 to 1993 is incomplete (Figures 4.3-4.19). However, it is useful to compare information on fluctuations in phytoplankton numbers with that in published literature, in order to attempt to ascertain whether phytoplankton in Shetland lochs behave typically for temperate lake systems. The PEG Model of phytoplankton succession (Sommer *et al.*, 1986) is a standardised sequence of twenty four events in the annual succession of plankton in standing freshwaters. It states that at the end of winter, small fast-growing algae become successful. Cryptophytes and small centric diatoms are likely to be observed at this time. In the five lochs of the present study, cryptophytes did not reach peak abundance until slightly later in the year (or succession,*i.e.* after the enhancement of diatom biomass) and although centric diatoms were observed, much of the phytoplankton biomass in spring was in the form of pennate diatoms or filaments of the centric diatom *Melosira*. However, Turdale and Helliers Water, Lochs of Gonfirth and Tingwall and Sandy Loch all behaved as expected from the literature in terms of development of spring diatom increases. Chrysoflagellate numbers tended to be highest at or near to the same time as the cryptomonads in the five Shetland lochs studied, with the exception of Turdale Water which exhibited *Anabaena* blooms in early summer (May/June)(Figures 4.17-4.19). In Turdale Water, diatoms and chrysoflagellates were much less important as a proportion of the phytoplankton community than in other lochs, even in spring.

After the first stage of algal growth, the PEG Model assumes zooplankton development results in losses of phytoplankton through predation. Consequently, a decrease in algal biomass occurs, resulting in a "clear-water" period and nutrient increase within the water column. As Shetland is situated at approximately 60°N, spring growth occurs later than would be expected further south, so that this sequence of events is initiated later in the year. It is possible that in the Shetland lochs surveyed, chrysoflagellates engulf small algae, such as small diatoms and

cryptomonads. The chrysoflagellates therefore become abundant in spring or early summer, so that zooplankton numbers peak later, through feeding on chrysoflagellates, *i.e.* there may be an extra step in the food chain. At times when cryptomonads and chrysoflagellates were abundant, grazing pressure by zooplankton is not likely to have been great (Bailey-Watts and Duncan, 1981a).

After the initial zooplankton peak, the PEG Model assumes that zooplankton numbers decrease due to lack of food and fish predation. A diverse phytoplankton assemblage then develops. Dominance by edible cryptophytes and inedible colonial green algae occurs first, so removing DRP from the water column. In the Shetland lochs studied, colonial green algae were never particularly important. However, elongate unicellular forms were significant in all five lochs. In Sandy Loch, *Koliella* and *Monoraphidium* were most numerous in May, at which time cryptomonads were also numerous, rather than in summer as suggested by the PEG Model. In Loch of Tingwall, elongate green forms again were the most important of this group, but summer phytoplankton tended to be dominated by cryptomonads and chrysoflagellates. The most important green algae in Loch of Gonfirth (*Selenastrum*, *Monoraphidium* and *Oocystis*) collectively exhibited highest numbers during August, thereby showing a similarity with the PEG Model.

In the PEG Model, after dominance of cryptomonads and green algae, grazing pressure and nutrient limitation then restrict primary production. P competition results in dominance passing from green algae to diatoms. Summer increases in diatom numbers were noted in Sandy Loch (*Cyclotella*, *Fragilaria* and small centric diatoms) and Turdale Water (*Tabellaria* and centric diatoms). Subsequently, decreasing Si levels allow dinoflagellates or blue-green algae to become dominant within the phytoplankton assemblage. N-fixing, or effective TAN scavenging cyanobacteria then become advantaged through decreasing availability of TON. However, in P-limited lochs such as Gonfirth where there is a supply of inorganic N, it is obviously far less likely that N-fixing cyanobacteria form a high proportion of the total phytoplankton biomass. Blue-green algae which were numerically important in Loch of Gonfirth were *Merismopedia* and *Gomphosphaeria* which do not fix N and *Aphanothece* which, owing to its similarity to *Microcystis* is assumed not to be an N-fixer. In addition, the CCA analysis showed that increased TP is more important than water TON and TAN

levels as blue-green algae as a group are suited to both high and low water TON and TAN concentrations. Lochs low in TP are unlikely to be dominated by cyanobacteria, although they may be present in the phytoplankton. In Helliers Water, which was low in TP and inorganic nitrogen, blue-green algae were represented by *Aphanothece*, *Merismopedia*, *Gomphosphaeria*, *Chroococcus* and *Lyngbya*, but none of these were ever abundant, regardless of time of year (Figures 4.6-4.8). The loch in which dinoflagellates were most important was Helliers Water. In this water body, peak numbers of *Peridinium* were found in July 1991, June, 1992 and May, 1993. The phytoplankton assemblages in this loch therefore were not consistent with the PEG Model.

In the PEG Model, small zooplankton of lower mortality rates and greater reproduction rates replace the larger species which are affected more adversely by fish predation and presence of inedible algae. Diversity of phytoplankton increases and zooplankton biomass undulates throughout the summer season. At the end of summer, physical factors of increasing mixing depth and decreasing availability of light results in decreased phytoplankton biomass, followed by an increased of algae adapted to these conditions *e.g.* large unicellular or filamentous forms and diatoms. These are relatively inedible, but there may also be concurrent development of a community of more edible small algae. An autumn zooplankton bloom is thus encouraged. Lack of light finally results in the minimum winter algal concentration and zooplankton biomass crashes as a result of this in combination with low water temperature. All five lochs exhibited increases in diatom numbers later in the sampling seasons *i.e.* during September or October.

In Loch of Tingwall in 1992 and 1993, of *Melosira*, *Synedra*, *Asterionella* and small centric diatoms which were found in the March algal community, only *Asterionella* appeared to remain in the phytoplankton assemblage until May. The exception was in the North Basin in 1993 (Figure 4.11), when *Synedra* instead was observed in May. During 1992, dominance amongst the diatoms present in Sandy Loch passed from *Melosira* in March to *Cyclotella* in May (when *Asterionella* also peaked) to centric diatoms in June. *Melosira* was again numerous in March, 1993, centric diatoms also being present. Diatom dominance then passed to *Synedra* and *Asterionella* concurrently in May. Sequences of dominance within the diatom

community were also noted in late summer/autumn. Seasonal succession occurs not only between algal groups, but also between species of the same group. For example, in the small eutrophic Crose Mere (15.2 ha, 9.2 m maximum depth) in England, Reynolds (1973a) discovered an annual succession of four major diatom species, although biomass of each species peak was different in each year. *Asterionella formosa* and *Fragilaria crotonensis* achieved maxima between February and May and between July and September. *Melosira granulata* also attained maximal production during summer, whilst *Stephanodiscus astraea* characterised winter and spring phytoplankton populations, coinciding with reduced spring growth of *A. formosa* and *F. crotonensis*. During a study of Farmoor Reservoir (0.49 km^2, maximum depth 11 m) from November, 1973 to March, 1974, the following diatom succession was found (Youngman *et al.*, 1976). *A. formosa* exhibited peak numbers in January, followed by *S. astraea* in February and *S. hantzschii* in March. Greatest numbers were recorded of *A. formosa*, least of *S. astraea*. Concurrent to the diatom succession, a population increase of *Closterium peracerosum* during February and March accounted for the largest numbers of any alga counted. Diatom succession may occur in response to availability of silica as *e.g.* wall synthesis is impaired in *A. formosa* at 0.5 mg SiO_2 dm^{-1} (Boney, 1989). A species capable of growing at lower silica levels would therefore replace *A. formosa* at this concentration of silica. Succession is also driven by P limitation or the ratio of Si to P (Tilman *et al.*, 1982). In Loch of Gonfirth, no continuous succession was observed. Diatoms in Gonfirth were dominated by *Cyclotella* and small centric diatoms, but both of these tended to remain in the phytoplankton throughout the part of the year examined (Figures 4.3-4.5).

All five lochs studied had many relatively stable components of the phytoplankton, but there were also taxa which were not particularly consistent in terms of the size of the population or proportion of the algal community. The same seasonal succession may not occur each year in a water body, as it is possible for long term changes in species composition and biomass to occur. For example, during a 13 year study in Plußsee, North Germany, dominance passed from *Oscillatoria redekei* and *Aphanizomenon gracile* to *Ceratium* species and *Anabaena* species, a different taxa of *Anabaena* dominating during each of six different years (Hickel, 1988). In Loch of Gonfirth, which would be expected to be the most stable algal community because

of its low nutrient status, *Merismopedia* was relatively important in 1991 samples and *Gomphosphaeria* was comparatively prominent during September 1991. However, during subsequent sampling seasons, thse taxa were low in numbers or absent from the water column. In contrast, *Chrysolykos* and *Aulomonas* were observed to be more significant in 1992 and 1993, than in 1991.

Assessment of the sizes of cells in phytoplankton assemblages may assist understanding of species succession as size affects metabolic processes *e.g.* nutrient uptake and reflects environmental controls of species success. Seasonal changes are possible in sizes of phytoplankton present in the water column. The size range of algae in the plankton can affect the way light penetrates the water. Predation of phytoplankton by zooplankton has a relationship with size range of algae present *e.g.* *Cyclops* may be associated with populations of predominantly small species, whereas a *Daphnia* dominated community may be indicative of presence of larger phytoplankton species. Phytoplankton sinking rate is related to cell, filament or colony size. During quiescent water column conditions, smaller algae remain in the photic zone for a longer period than larger ones when species are neither motile nor buoyant. Studies of *O. redekei* reveal that mean filament length can differ substantially from lake to lake, suggesting that filament length is partly genetically controlled (Gibson, 1975). Seasonal polymorphism in *O. redekei* filaments in Lough Neagh, Northern Ireland, results in minimum length during the period of lowest water turbulence and viscosity, but highest temperatures. Vacuolate cells were found to take 66 days to leave the photic zone. Little advantage would be gained through cyclomorphosis for the purpose of an extended period of suspension, since rate of sinking is extremely slow. It was concluded that filament size might be related to nutrient availability, inferior growth conditions resulting in shorter filaments (Gibson, 1975). A greater relative surface area is available for nutrient uptake when filament or colony size is smaller. In four of the five lochs studied, chrysoflagellates were dominant. These yellow-brown algae were small in addition to having motility, suggesting their size was related to nutrient shortage. In contrast, green algae *Monoraphidium* and *Koliella* often made up a significant proportion of the total phytoplankton numbers in the five lochs studied, perhaps as a result of more turbulent water columns and greater nutrient availability, since these taxa are not motile and are elongate in form. Elongate forms of phytoplankton are also less easily engulfed

or eaten.

Although there was conformity with the literature in certain aspects of successional and periodic changes in phytoplankton community structure within the five study lochs, such as spring and autumn diatom increases, divergences from the PEG Model were also noted. Phytoplankton communities in Loch of Gonfirth and Helliers Water remained diverse throughout the study periods. Succession was less marked than in the other three lochs. For example, diatoms were observed in the algal assemblage during all sampling visits. Low nutrient status may therefore mean that water bodies are less likely to conform to all the stages in the PEG Model, or exhibit changes within the phytoplankton asssemblages which are less marked than would be expected from the Model. Lack of conformity of Shetland water bodies to the PEG Model may also be related to the high occurrence of water column mixing, even during the summer months. If it is assumed that phytoplankton communities develop towards a state of equilibrium, then interference with this process at intervals shorter than the time required to reach equilibrium are disturbances (Reynolds, 1993). Disturbances of intermediate frequency, *i.e.* approximately three to eight days, result in greater phytoplankton diversity (Reynolds, 1993). The relative importance of intermediate disturbances is greatest in spring and during summer and autumn equilibrium phases (Padisðk, 1993).

In shallow water bodies, such as those in Shetland, not only is there the annual cycle of great physical changes in light, temperature and extent of mixing, but also intermediate changes in the water environment superimposed upon the former by such processes as wind stress, cloud formation and precipitation (Eloranta, 1993). From examination of the published literature on phytoplankton seasonal changes, in lakes which stratify, the "clear water" stage is often associated with the onset of stratification (Sommer *et al.*, 1986). However, in non-stratifying water bodies, this phenomenon either does not occur or is of extremely short duration. In shallow lakes, phytoplankton are exposed to disturbances throughout the summer. Mixing of the water column continues to occur in summer. In a comparison of two lakes of eutrophic status in Latvia, Trifonova (1993) observed greater diversity throughout the summer in the shallower system (Lake Lobardzu) than in the stratifying lake (Lake Rudusku). Because of disturbances in the shallow lake, establishment of dominance

and low diversity associated periods of autogenic succession was interrupted by periods when biomass decreased and diversity increased. In the stratifying system, blue-greens and dinoflagellates became dominant for long periods, a consequent decrease in diversity occurring as a result of competitive exclusion (Trifonova, 1993). Sommer (1993) noted a comparable response in two lakes of similar nutrient status in northern Germany. Phytoplankton was found to be N-limited (and diatoms Si-limited) in both lakes. In the lake with the more stable water column (Plußsee), maximum algal biomass was close to the carrying capacity of the water column environment, whereas in the lake which had significant changes in mixing depth each week (Behler See), disturbance resulted in suppression of possible maximum biomass. In addition, under stable water column conditions, phytoplankton diversity decreased after algal biomass had developed to > 5% of the carrying capacity of the water body.

In Shetland lochs, great biomass of individual taxa may not develop as frequently as would be expected under conditions of higher water column stability. Despite elevated numbers of algae in spring in the lochs studied, phytoplankton numbers did not exhibit such high values during summer. Exceptions to this trend were found in samples from Turdale Water during September, 1991, Sandy Loch in August 1992 and Loch of Tingwall South Basin in June/July 1991, 1992 and 1993. Increased availability of nutrients at these times perhaps allowed dominance of individual taxa (cryptomonads, *Anabaena* and chrysoflagellates respectively), but that peak biomass was supressed. Decline of *Aphanizomenon* blooms and increased diversity after disturbance events have been documented in a shallow Danish lake (Jacobsen and Simonsen, 1993). Biomass decreased after heavy rainfall and destruction of stratification, K-selected *Aphanizomenon* (slow growing) was replaced by fast-growing r-selected species of cryptomonads.

4.5 CONCLUSIONS

As noted by Brook (1994), presence of green algae and cyanobacteria in lakes was not in itself an indicator of nutrient enrichment. Blue-green algae, such as *Gomphosphaeria* and *Merismopedia*, were observed in water bodies of low trophic status. Similarly, green algae, such as desmids, *Monoraphidium/Ankistrodesmus* and *Oocystis* were present in low nutrient waters. Chrysoflagellates were widespread in

Shetland lochs. These algae often dominate in Scottish lochs (Brook, 1964; Bailey-Watts and Duncan, 1981a). A range of phytoplankton assemblages were observed in the lochs surveyed and CCA analysis revealed that the distribution of phytoplankton was associated with many environmental factors.

Of these parameters, TP was found to be most important. Green algae were found to be linked with high TP levels, but *Anabaena* was the only blue-green genus of phytoplankton ranked highly on the TP gradient. Other cyanobacteria exhibited a range of preferences. From published literature, it was evident that cyanobacteria have a variety of adaptations which may give them a competetive advantage in certain circumstances, such as the ability to use HCO_3^- and grow in conditions of low light intensity. The environmental variables measured which appeared to positively influence growth of *Anabaena* were increased TP, increased TAN and low TON concentrations in the loch water column.

Changes in phytoplankton community structure with time demonstrated similarities with those expected in temperate lake systems, such as the occurrence of the spring diatom increase. Deviations from the model may be partly attributable to the individual status of each loch (*e.g.* in low and high nutrient waters, the spring diatom increase was not as marked and in waters where TON remained elevated throughout summer, N-fixing cyanobacteria did not develop a high biomass), disturbance effects and the infrequent nature of the sampling programme.

CHAPTER 5: AQUATIC MACROPHYTES OF SHETLAND LOCHS

5.1 INTRODUCTION

Aquatic macrophytes release oxygen necessary to maintain aerobic conditions within the water column, provide shelter for fish and invertebrates, consolidate littoral sediments and banks of running and standing waters. Macrophytes provide a food source for vertebrates both directly and through organisms existing on them. Fish may spawn on plant substrates and birds find nesting and feeding sites within plant communities. These primary producers may also be regarded as aesthetically pleasing (Seagrave, 1988). The aforementioned factors are extremely important in Shetland, as aesthetic quality, fishing and ornithological pursuits are of importance to both the local population and tourists who contribute to the economy of the area. However, if macrophyte growth becomes excessive, problems such as flooding, silting, encroachment, and difficulties for boat access can occur. As with excessive phytoplankton growth, pH and oxygen regimes may be dramatically altered, both diurnally, as a result of macrophyte respiration (DO uptake, CO_2 release) and photosynthesis (CO_2 fixation, DO release through photolysis of water) and through decay of dead plant matter. It is possible for the pH of a water body to increase by 3 units in one day due to the physiological processes of plants (Riemer, 1984), *i.e.* net production of CO_2 in darkness and CO_2 uptake in daylight.

Macrophyte distribution both within and between water bodies is determined by many factors. The influence of interspecific competition between naturally coexisting species of submerged plants is typically insignificant in comparison with the effects of spatial heterogeneity or differential utilisation of abiotic resources. The availability of growth factors and the ability of different plants to take advantage of resources promote species diversity in these communities (Chambers and Prepas, 1990). From extensive field study and information from Murray and Pullar (1910), Spence (1967) concluded that macrophyte cover of the littoral zone of large loch basins rarely occupies more than 5% of the total water surface area, although brown mud substrates in deeper water may locally support 80% plant cover.

Physical characteristics of water bodies, such as latitude, altitude and area of the loch, are important influences on plant growth. The larger the area of a water body, the

more likely it is that there will be a richness of species, simply because in a smaller area there is less probability that a diversity of habitats will present itself. For example, local enrichment may occur in a predominantly oligotrophic loch, or sheltered areas may present opportunities for plant growth protected from strong wave action (Rørslett, 1991). Altitude and latitude are factors which act upon plant growth in a similar manner. Generally, as these increase, species diversity decreases due to the effects of water temperature and duration of daylight. In Shetland, the high latitude results in a limited growing season, which in turn leads to lower potential plant diversity.

However, variety of macrophyte flora may occur in association with moderate stress (such as organic enrichment), herbivory and disturbance levels (Grime, 1979). Lakes with water levels which fluctuate by 1-3 m yr^{-1} have been found to support more species of plants than those with fluctuations of a lesser or greater degree (Rørslett, 1991). This could be of particular importance in Shetland where low summer rainfall and the shallowness of many lochs can combine to cause significant changes in depth. In addition, twenty one standing waters are used for abstraction of drinking water, so that at times of low rainfall, there can be a considerable decrease in water depth, before further rainfall replaces the water removed for the potable supply.

Chemical characteristics of a water body are the overriding factor determining species richness, abundance and biomass (Rørslett, 1991). Many submerged macrophytes may be confined to waters of specific chemical composition, or be associated with particular conditions (Table 5.1), although others may appear to have an almost ubiquitous distribution. Chloride levels in lochs of the Shetland Islands are higher than would be expected in standing freshwaters in Scotland, as a result of marine influence (wind-borne sea spray), so reducing the likelihood of water conductivity being correlated with plant distribution. In contrast, alkalinity in the same sites has been recorded as being lower on average than other Scottish lochs (Spence, 1967).

Alkaline waters are not only cation rich, but also act as sinks for CO_2 and HCO_3^- ions, the former being supplied mostly by either air or oxidising/reducing conditions in loch sediments (Spence, 1967).

Table 5.1 Plants associated with different general water characteristics (Spence, 1967)

Rich waters

Metal ions, various
Alkalinity ≥ 1.2 meq HCO_3 L^{-1}

Ceratophyllum demersum
Chara papillosa
Cinclidotus fontinaloides
Myriophyllum spicatum
Potamogeton lucens

Poor waters

Alkalinity < 0.4 meq HCO_3 L^{-1}

Elatine hexandra
Eleogiton fluitans
Isoetes lacustris
Subularia aquatica
Ranunculus flammula
Juncus bulbosus
Lobelia dortmanna
Sphagnum subsecondum

Rich and moderately rich, often slightly saline waters

Alkalinity ≥ 0.74 meq HCO_3 L^{-1}

Potamogeton filiformis
Potamogeton pectinatus

Alkalinity ≥ 0.4 meq HCO_3 L^{-1}

Potamogeton praelongus

As some plants require presence of either CO_2 or HCO_3^- for photosynthesis (for example, *Fontinalis antipyretica* can only use free CO_2 and not HCO_3^-) plentiful supply of both CO_2 and HCO_3^- will mean growth limitation will probably not occur due to lack of carbon. Certain plants are confined to calcareous lochs (*Chara*, *Potamogeton* and *Ceratophyllum* species), or to non-calcareous lochs with high pH (*Myriophyllum* species). A third group of plants are restricted to slightly saline waters of low alkalinity and pH slightly above neutral. *Potamogeton praelongus*, *Potamogeton pectinatus* and *Potamogeton filiformis* grow in all three types of these high electrolyte waters containing quantities of HCO_3^- (Spence, 1967).

A more extensive macrophyte classification involving 1124 fresh and brackish water sites in Britain was developed by Palmer (1989) and Palmer *et al.* (1992), conducting a TWINSPAN analysis of the Nature Conservancy Council (NCC) plant survey information, as used by Rodwell in the National Vegetation Classification (NVC) (1991). Several plant groupings were found (Table 5.2). However, plant groups were related only to a limited number of environmental parameters *i.e.* water pH, conductivity and alkalinity (Palmer, 1989; Palmer *et al.*, 1992). Many other water chemical variables could be important in limiting plant types to particular groups. Where P concentrations were quoted in the classification of Palmer (1989) and Palmer *et al.* (1992), the limit of detection was 20 μg P L^{-1}, so detailed information on this parameter was absent for lower categories of trophic state (*i.e.* ultra oligotrophic, oligotrophic and less nutrient rich mesotrophic lake types). Water conductivity may be slightly misleading as a predictor, for elevated concentrations of ions occur in Shetland lochs in wind blown areas proximate to the sea. A strong correlation between conductivity and trophic state may not therefore exist in the classically understood sense. Use of macrophytes as indicators of trophic status is dependent upon a clear relationship existing between P and N concentrations in the water column and the species of plants which grow under different conditions of P and N availability in standing freshwaters.

Table 5.2 **Classification of standing waters (Palmer, 1989; Palmer *et al.*, 1992)**

Group	Characteristic plants	pH	Conductivity ($\mu S\ cm^{-1}$)	Alkalinity ($meq\ L^{-1}$)
1	*Sphagnum* *Juncus bulbosus* *Potamogeton polygonifolius*	3.5-5.5	<200	≤0.04
2	*Juncus bulbosus* *Potamogeton polygonifolius* *Littorella uniflora* *Lobelia dortmanna* *Potamogeton natans*	5.0-7.5	<200	0-0.5
3	as Group 2 but also *Myriophyllum alterniflorum* *Isoetes lacustris* *Fontinalis antipyretica*	5.0-7.5	<200	0-0.5
4	*Myriophyllum spicatum* *Myriophyllum alteriflorum* *Potamogeton natans* *Chara* *Potamogeton praelongus* *Potamogeton filiformis*	7.0-9.0	>200	0.5-4.0
5A	*Littorella uniflora* *Myriophyllum alterniflorum* *Nitella* *Elodea canadensis* *Potamogeton* various	6.0-8.0	*	0.2-1.0
5B	*Potamogeton natans* *Nymphaea alba*	6.0-8.0	*	0.2-1.0
6	*Potamogeton pectinatus* *Ruppia* *Fucus*	8.0-9.0	>5000	
7	similar to Group 4, but lacks *Myriophyllum alterniflorum* *Juncus bulbosus*	7.5-9.5	200-1500	1.0-4.0

Table 5.2 (cont.)

Group	Characteristic plants	pH	Conductivity ($\mu S\ cm^{-1}$)	Alkalinity ($meq\ L^{-1}$)
8	*Lemna minor* *Polygonum amphibium* *Callitriche stagnalis*	7.0-8.5	200-1000	1.0-5.0
9	*Nuphar lutea* *Nymphaea alba*	6.5-8.5	200-1000	0.2-4.0
10	*Myriophyllum spicatum* *Potamogeton praelongus*	6.5-8.5	200-1000	0.5-4.0
A	*Elodea canadensis*			
B	*Chara*			

KEY:

* conductivity greater than that for Groups 2 and 3

5.1.1 Aims

Macrophytes have been used as indicators of chemical limnology (Sneddon, 1972). In shallow loch systems such as those in Shetland, it is possible for macrophytes to have significant effects on ecosystem processes. Canfield *et al.* (1984) successfully used the percentage of lake volume occupied by macrophytes to improve the efficacy of a TN/TP model for predicting water column chl *a* concentrations. Rooted aquatic vegetation may compete with phytoplankton populations for available resources. If competition exists between macrophyte and phytoplankton communities, then information on macrophyte assemblages might be of use in developing a loch water quality indicator system. This would assist in determining susceptibility of standing freshwaters to excessive phytoplankton growth *i.e.* eutrophication. It may also be possible to manage macrophyte growth for the purpose of prevention of algal bloom development. An investigation of the macrophyte communities of Shetland lochs was therefore undertaken, the aims of which are outlined below.

(a) Identify the macrophyte species present in thirty one loch sites across the Shetland Islands.

(b) Estimate biomass of macrophytes growing in each of the study waters.

(c) Investigate whether macrophyte species present in Shetland lochs could be used as indicators of water quality, including phytoplankton biomass.

(d) Using published information, consider the likely magnitude of the effects of the species present on nutrient cycling within the loch systems examined.

Although other primary producers (*e.g.* bacteria and algae attached to macrophytes, sediments and stones) are important in lacustrine environments, in terms of competition with phytoplankton for resources and in nutrient cycling, examination of these biota was outwith the scope of the present study.

5.2 MATERIALS AND METHODS

5.2.1 Construction of macrophyte species lists

Presence of macrophyte species in each loch was determined by two methods. Firstly, vegetation in shallow water was identified and recorded while wading at and around

the shoreline, or, in the case of larger water bodies, by identifying different habitat types and listing plant species found there. Secondly, grapnel hauls were undertaken in transects parallel to the shore to investigate which species were present in deeper water. During the 1993 survey, it was also possible for a SCUBA diver to view and retrieve macrophytes from the deeper waters of Lochs of Gonfirth and Tingwall, Helliers and Turdale Water. Plant samples requiring further identification were pressed and returned to the laboratory. Standard plant keys were then used to recognise taxa present (Wigginton and Graham, 1981; Haslam, Sinker and Wolseley, 1982; Polunin, 1988; Seagrave, 1988). In addition, macrophyte species identifications were confirmed by Dr. K.J. Murphy and Dr. K. Watson (Department of Botany, University of Glasgow). *Chara* and *Nitella* were not identified to species level due to difficulties in taxonomy associated with these macroalgae (Arts and Leuven, 1988).

5.2.2 Estimation of macrophyte biomass

Samples for biomass estimates were taken using the following equipment:

Lambourn sampler 25 cm x 19.5 cm (1991, 1993)
Lambourn sampler 30 cm x 30.5 cm (1992)
Quadrat 50.5 cm x 50.5 cm (1992)
Quadrat 50 cm x 50 cm (1993)
Ekman grab 15 cm x 15.5 cm (1992)

Plant samples for biomass estimates were washed thoroughly in tap water before spin drying to remove excess moisture. Each sample was then weighed fresh before being oven dried at 90°C for 24 hours. Dry weights were then determined and biomass calculated for each sample.

5.2.3 TWINSPAN analysis of macrophyte data

From macrophyte lists constructed for the thirty one lochs in 1991, a two-way indicator species analysis (TWINSPAN) was carried out (Hill, 1979). This is a method of cluster analysis which operates on a divisive strategy *i.e.* all individuals begin the analysis in one group, rather than each individual starting as one group, as occurs in accumulative clustering methods. TWINSPAN carries out Correspondence Analysis (CA) on the entire data set and uses Axis 1 scores to divide site information

into two groups. Species which are highly correlated with this Axis are used as indicators; indicators for one group are positively correlated with the Axis, those for the other exhibit negative correlations with the Axis. This type of data analysis is then repeated for the new groups formed. The resulting groups of lochs were then compared (using a two-tailed Mann-Whitney U test on the Statgraphics statistical package) in terms of water mean summer pH, colour, light attenuation and concentrations of chl *a*, TP, TDP, TAN, TON, Ca, Mg, Na and K, in addition to mean macrophyte biomass and number of macrophyte species present in each loch.

5.3 RESULTS

5.3.1 Macrophyte species found in Shetland lochs (Table 5.3)

Isoetids were widespread in their distribution. *Subularia aquatica* was located in two lochs, *Isoetes lacustris* in nine, *Lobelia dortmanna* in eleven and *Littorella uniflora* in twenty three water bodies. Several *Potamogeton* species were observed *i.e. P. berchtoldii*, *P. filiformis*, *P. gramineus*, *P. natans*, *P. perfoliatus*, *P. polygonifolius* and *P. praelongus*. The most widespread of these was *P. perfoliatus*, which was observed in seventeen lochs (Table 5.3). Species of *Chara* and *Nitella* were also frequent in occurrence, these algae being located in twelve and ten water bodies respectively. Charophytes were not noted in fourteen of the thirty one lochs surveyed. *Juncus bulbosus* was common in occurrence, being observed in sixteen of the Shetland sites studied. The macrophyte which was seen in most lochs was *Myriophyllum alterniflorum*. Species of *Callitriche* which were found in the lochs were *C. hamulata*, *C. hermaphroditica*, *C. platycarpa* and *C. stagnalis*.

5.3.2 Estimates of macrophyte biomass in Shetland lochs (Table 5.4)

On a dry weight basis, biomass was found to be highly variable both within and between sites in areas of colonisation (Table 5.4). Average plant biomass estimates for each loch in 1991 ranged from 0 g m^{-2} (Loch of Brough, Yell) to 1044.9 g m^{-2} (Loch of Huesbreck). In lochs where biomass estimates were > 0 g m^{-2}, results from individual Lambourn samples ranged from 0.2 g m^{-2} for *Callitriche stagnalis* in Mill Pond and *J. bulbosus* in Roer Water, to 1289 g m^{-2} in Loch of Huesbreck for a Lambourn sample of *Chara* and *Nitella*. Although Loch of Huesbreck was productive in terms of macrophyte growth, it is suggested that biomass figures may be overestimated due to mineral encrustation of these algae.

KEY FOR TABLE 5.3
Macrophyte taxa present in the 31 lochs of the 1991 survey

Macrophyte	TWINSPAN code
Bryum pseudotriquatrum	59 BRY PSE
Callitriche hamulata	05 CAL HAM
Callitriche hermaphroditica	04 CAL HER
Callitriche platycarpa	03 CAL PLA
Callitriche stagnalis	06 CAL STA
Carex lasiocarpa	07 CAR LAS
Caltha palustris	02 CTH PAL
Chara species	08 CHA SPP
Eleocharis acicularis	11 ELE ACI
Eleocharis palustris	09 ELE PAL
Enteromorpha intestinalis	12 ENT INT
Epilobium palustre	13 EPI PAL
Equisetum fluviatile	10 EQU FLU
Eurytrichium cf praelongum	61 EUR PRA
Fontinalis antipyretica	14 FON ANT
Galium palustre	16 GAL PAL
Glyceria declinata	15 GLY DEC
Hydrocotyle vulgaris	17 HYD VUL
Iris pseudocorus	18 IRI PSE
Isoetes lacustris	19 ISO LAC
Juncus articulatus	22 JUN ART
Juncus bufonius	21 JUN BUF
Juncus bulbosus	20 JUN BUL
Lemna minor	26 LEM MIN
Littorella uniflora	25 LIT UNI
Lobelia dortmanna	24 LOB DOR
Mentha aquatica	30 MTH AQU
Menyanthes trifoliata	29 MEN TRI
Myriophyllum alterniflorum	27 MYR ALT
Myriophyllum spicatum	28 MYR SPI
Nitella species	33 NIT SPP
Nymphaea alba	31 NYM ALB
Phalaris arundinacea	35 PHA ARU
Polygonum amphibium	34 POL AMP
Potamogeton berchtoldii	44 POT BER
Potamogeton filiformis	43 POT FIL
Potamogeton gramineus	39 POT GRA
Potamogeton natans	38 POT NAT
Potamogeton pectinatus	42 POT PEC
Potamogeton perfoliatus	45 POT PER
Potamogeton polygonifolius	36 POT POL

KEY FOR TABLE 5.3 (cont.)
Macrophyte taxa present in the 31 lochs of the 1991 survey

Macrophyte	TWINSPAN code
Potamogeton praelongus	37 POT PRA
Potamogeton pusillus	40 POT PUS
Ranunculus aquatilis	48 RAN AQU
Ranunculus flammula	47 RAN FLA
Ruppia maritima	46 RUP MAR
Scapania species	49 SCA SPP
Schoenoplectus lacustris	55 SCH LAC
Scorpidium scorpioides	50 SCO SCO
Sparganium angustifolium	52 SPA ANG
Sparganium emersum	53 SPA EME
Sparganium erectum	54 SPA ERE
Subularia aquatica	51 SUB AQU
Utricularia species	57 UTR SPP
Zannichellia palustris	58 ZAN PAL

KEY FOR TABLE 5.3

Loch codes in TWINSPAN analysis

Water body	TWINSPAN number
Arthurs Loch	01
Bu Water	02
Loch of Brindister	03
Loch of Brough (Bressay)	04
Loch of Brough (Yell)	05
Loch of Brow	06
Loch of Cliff	07
Eela Water	08
Loch of Gonfirth	09
Gorda Water	10
Gossa Water	11
Helliers Water	12
Loch of Huesbreck	13
Loch of Huxter	14
Loch of Kettlester	15
Lunga Water	16
Mill Pond	17
Papil Water	18
Punds Water	19
Roer Water	20
Sand Water	21
Sandy Loch	22
Skutes Water	23
Loch of Snarravoe	24
Loch of Spiggie	25
Strand Loch	26
Loch of Tingwall	27
Turdale Water	28
Loch of Ustaness	29
Loch of Watlee	30
Whitelaw Loch	31

Table 5.3 Computer output of TWINSPAN analysis of macrophyte species present in the 31 lochs of the 1991 survey

```
     Species          Samples, relative numbers.
Rel.  True

                      12 11 3111 22  12 2212 3 11222
                     2248094115790913686153770548326

 60 POT  SPP   ----1-------------------------  11111
 28 MYR  SPI   --1--------------------------  11111
 26 LEM  MIN   1----------------------------  11111
 16 GAL  PAL   --1--------------------------  11111
 15 GLY  DEC   1-11-------------------------  11111
 11 ELE  ACI   ---1-------------------------  11111
 13 EPI  PAL   -----1---------1-------------  11110
 49 SCA  SPP   ----------------1-------------  1110
 31 NYM  ALB   ----------------1-------------  1110
 24 LOB  DOR   -1-11111---1-11-1-1----------  1110
 22 JUN  ART   -----------11-----------------  1110
 52 SPA  ANG   1-----11111-111-1--11---------1  1101
 47 RAN  FLA   ---1--111-1111111111-1-1------  1101
 20 JUN  BUL   -1-1--11-111111-1--1-111---1---  1101
  3 CAL  PLA   ---------11--------1----------  1101
 54 SPA  ERE   --------------1-1------1-------  1100
 27 MYR  ALT   1111-11111-1-1-11-1-1-1111-11--  1011
 25 LIT  UNI   -111111111-111111--11-111-111--  1011
  6 CAL  STA   1-------1-1--11--11-1------1-1-  1011
 59 BRY  PSE   -1---------1----------1--------  1010
 19 ISO  LAC   --11111----1----------11--1----  1010
 51 SUB  AQU   -----------1--------------1----  100
 45 POT  PER   -11---1111-----1-1111-1--1111--  100
 33 NIT  SPP   -11--11--1--------11-1----11---  100
 21 JUN  BUF   -----------111-1--11--1-------1  100
 61 EUR  PRA   ---------1----------1----------  011
 53 SPA  EME   ------11--1-------111----------  011
 38 POT  NAT   -----------1--1-11111-1--------  011
 14 FON  FNT   --1-11--1------11---1-111-111--  010
  2 CTH  PAL   -----1--------11---11-111------  010
 29 MEN  TRI   ----------------1-1-1----------  0011
 17 HYD  VUL   ----------------1-----1------1-  0011
  9 ELE  PAL   ---------------11-11---11--1--1  0011
 44 POT  BER   -11----1----------1-1-1---111--  00101
 39 POT  GRA   ------1----------1--------11--  00101
 10 EQU  FLU   -------1--------1-111--11111-1-  00101
  8 CHA  SPP   -1---------1------1111111--11-1  00101
  5 CAL  HAM   1-1----------------11-1-1-11-1-  00101
 37 POT  PRA   --1----------------1-11-1------  00100
 58 ZAN  PAL   ----------------------1-------1  00011
 46 RUP  MAR   -----------------------------1  00011
 40 POT  PUS   ------------------1---1----1--1  00011
 12 ENT  INT   -----------------------------1  00011
 55 SCH  LAC   -------------------1----------  00010
 48 RAN  AQU   --------------------1----------  00010
 43 POT  FIL   --------------------111--------  00010
 36 POT  POL   --------------------1----------  00010
 35 PHA  ARU   --------------------1----------  00010
 30 MTH  AQU   --------------------1----------  00010
 18 IRI  PSE   -------------------11-1--------  00010
  7 CAR  LAS   --------------------1----------  00010
  4 CAL  HER   ----------------------1--------  00010
 57 UTR  SPP   ------------------------1-------  0000
 50 SCO  SCO   -----------------------------1--  0000
 34 POL  AMP   ------------------------1---1---  0000

                     00000000000000000011111111111111
                     00000011111111111110000000000001
                     01111100000111111110000011111111
                      00111001110001111000110000001
                                              001111
```

Table 5.4 Ranges of plant biomass estimates in areas of macrophyte growth

Water body		Macrophyte biomass (g dw m^{-2}) Minimum	Maximum
Arthurs Loch		14.6	123.9
Bu Water		17.6	69.7
Loch of Brindister		44.5	68.1
Loch of Brough (Bressay)		2.9	207.8
Loch of Brough (Yell)		*	*
Loch of Brow		24.2	94.8
Loch of Cliff		13.1	98.9
Eela Water		0.6	158.2
Loch of Gonfirth	(1991)	17.2	207.8
	(1992)	9.9	592.7
	(1993)	0.9	95.8
Gorda Water		6.8	25.6
Gossa Water		8.6	300.7
Helliers Water	(1991)	35.5	130.9
	(1992)	8.3	214.2
	(1993)	9.4	166.8
Loch of Huesbreck		701.7	1289.0
Loch of Huxter		0.4	250.3
Loch of Kettlester		2.3	30.6
Lunga Water		44.9	64.6
Mill Pond		0.2	6.2
Papil Water		23.0	58.3
Punds Water		1.6	74.1
Roer Water		0.2	6.8
Sand Water		0.4	44.3
Sandy Loch		*	*
Skutes Water		12.7	57.6
Loch of Spiggie		9.0	188.5
Strand Loch		26.5	126.6
Loch of Tingwall	(1991)	6.8+	255.0
	(1992)	12.2	1154.0+
	(1993)	0.1	63.6+
Turdale Water	(1991)	11.9	90.9
	(1992)	3.9	104.5
	(1993)	0.6	74.6+
Loch of Ustaness		28.7	37.9
Loch of Watlee		10.7	143.0
Loch of Whitelaw		13.1	104.5

KEY:

* extremely low biomass for entire loch
\+ includes filamentous algae

Locally dense stands of isoetids were found to result in biomass estimates up to 300 g m^{-2} for *L. uniflora* alone (Gossa Water, Lambourn sample, 1991), 345 g m^{-2} for a stand of *L. uniflora*, *L. dortmanna* and *I. lacustris* (Loch of Gonfirth, Ekman sample, 1992) and 592 g m^{-2} for a colony of *I. lacustris* (Loch of Gonfirth, Ekman sample, 1992). Minimum recorded biomass for single species samples of *L. uniflora* and *I. lacustris* were 2.3 g m^{-2} (Loch of Kettlester, Lambourn sample, 1991) and 0.4 g m^{-2} (Loch of Huxter, Lambourn sample, 1991) respectively.

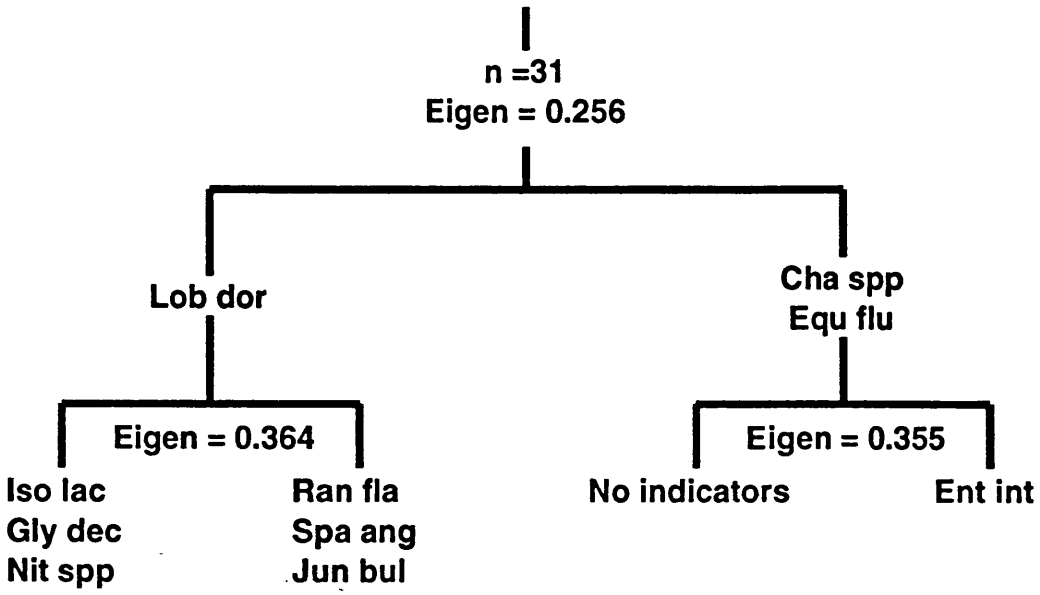
5.3.3 TWINSPAN classification of Shetland lochs (Figure 5.1)

At the first level of TWINSPAN classification, one group of eighteen lochs was categorised by presence of *L. dortmanna*. The other group of thirteen lochs was associated with presence of *Chara* spp. and *Equisetum fluviatile*. At the second level of classification, the first group was divided into a group of six lochs and one of twelve lochs. These groups were characterised according to presence of *I. lacustris*, *Glyceria declinata* and *Nitella* spp. in the former (Group 1) and *Ranunculus flammula*, *Sparganium angustifolium* and *J. bulbosus* in the latter (Group 2). The second group of the first classification level remained the same with the exclusion of Strand Loch on the basis of presence of *Enteromorpha intestinalis* in that water body (Group 3). Low Eigen values were associated with all these divisions made by TWINSPAN, indicating that the Groups were not strongly heterogeneous.

5.3.3.1 Comparisons of TWINSPAN Groups (Tables 5.5 and 5.6)

Following statistical analysis, Group 3 ($p < 0.001$) and Group 1 ($p < 0.1$) were found to have higher pH values than Group 2. Group 3 also had higher pH values than Group 1 ($p < 0.05$). In addition to the weak difference in water pH between Group 1 and Group 2, there also existed a significant difference in water Mg concentrations, greater levels being associated with Group 1 ($p < 0.05$). Mg levels in Group 2 were significantly lower than those in Group 3 ($p < 0.01$). In terms of Mg concentrations, Group 1 and Group 3 were similar, although there may have been a trend of slightly higher values in Group 3, since there was a less significant difference between Groups 2 and 1 than Groups 3 and 2.

Figure 5.1 TWINSPAN division of lochs by macrophyte species present



GROUP ONE (n = 6)	GROUP TWO (n = 12)	GROUP THREE (n = 12)	GROUP FOUR (n = 1)
Bu	Arthurs	Brough (Y)	Strand
Eela	Brindister	Brow	
Gorda	Brough (B)	Cliff	
Helliers	Gonfirth	Huesbreck	
Punds	Gossa	Huxter	
Snarravoe	Kettlester	Papil	
	Lunga	Sand	
	Mill	Sandy	
	Roer	Skutes	
	Turdale	Spiggie	
	Ustaness	Tingwall	
	Whitelaw	Watlee	

Table 5.5 **Median values of environmental parameters associated with each TWINSPAN Group of water bodies**

Environmental parameter	Group 1	Group 2	Group 3
pH	6.89	6.36	7.48
Conductivity (μS cm^{-1})	276	251	353
Light coefficient	0.350	0.649	0.354
Colour (abs 400 nm)	0.102	0.200	0.122
TP (μg P L^{-1})	18.1	9.4	16.2
TDP (μg P L^{-1})	6.6	5.3	6.8
TON (μg N L^{-1})	6.3	57.7	6.5
TAN (μg N L^{-1})	37.7	27.5	40.5
Ca (mg Ca L^{-1})	4.3	3.7	8.6
Mg (mg Mg L^{-1})	7.9	5.1	10.0
Na (mg Na L^{-1})	33.6	31.4	37.5
K (mg K L^{-1})	1.7	1.4	1.7
Chl *a* (μg chl*a* L^{-1})	4.1	2.4	5.8

Table 5.6 Comparisons of TWINSPAN groups by Mann-Whitney U-test

Parameter	Group 1 *vs* Group 2	Group 1 *vs* Group 3	Group 3 *vs* Group 2
pH	$p<0.1$	$p<0.05$	$p<0.001$
Conductivity	n.s.	n.s.	$p<0.05$
LAC	n.s.	n.s.	n.s.
Water colour	n.s.	n.s.	n.s.
TP	n.s.	n.s.	$p<0.1$
TDP	n.s.	n.s	n.s.
TAN	n.s.	n.s.	n.s.
TON	n.s.	n.s.	$p<0.1$
Na	n.s.	n.s.	n.s.
K	n.s.	n.s.	n.s.
Ca	n.s.	$p<0.05$	$p<0.01$
Mg	$p<0.05$	n.s.	$p<0.01$
Ca + Mg	n.s.	$p<0.05$	$p<0.001$
Chl*a*	n.s.	n.s.	$p<0.05$
NOS	n.s.	n.s.	n.s.
BM	n.s.	n.s.	n.s.

KEY:

NOS number of macrophyte species observed
BM macrophyte biomass estimates

Although Mg levels were different in Groups 1 and 2, a significant difference in Ca concentrations could not be detected between these Groups. However, there may have been a trend of higher Ca levels in Group 1, as a greater difference was detected between Group 3 and Group 2 than between Group 3 and Group 1 when considering this parameter.

When Ca and Mg concentrations were combined, the difference between Groups 3 and 2 became highly significant ($p < 0.001$), though the difference in Groups 1 and 3 remained similar to that for Ca concentration alone ($p < 0.05$). It is likely that the significantly higher conductivity values in Group 3 compared to Group 2 were at least partly attributable to the higher Ca and Mg concentrations in Group 3.

The concentrations of TP in Group 3 lochs were higher than those in Group 2 ($p < 0.1$); conversely TON concentrations were lower in Group 3 than in Group 2 ($p < 0.1$). Although these differences were not highly significant, chl *a* levels were also higher in Group 3 than in Group 2 ($p < 0.05$). As in the CCA analysis of phytoplankton data (Chapter 4) higher chl *a* values were associated with lochs with increased water column TP levels, but low TON concentrations.

In summary, the most important differences between TWINSPAN Groups were in pH, Ca and Mg concentrations. An increase in these parameters occurred from Group 2 to Group 1 to Group 3. As would be expected from the TWINSPAN divisions, Group 3 was the least similar of the three Groups. No differences were found between Groups on the basis of light attenuation, water colour (400 nm), number of species or biomass of macrophytes, nor water concentrations of TAN, TDP, Na and K. The median value for light attenuation in Group 2 was considerably greater than that of Groups 1 and 3, but the degree to which ranges of values overlapped meant that there was not a significant difference in this variable between Groups. Similarly, although the median value of number of macrophyte species present was highest in Group 3, there was considerable variability in the numbers found in each Group.

5.4 DISCUSSION

5.4.1 Macrophyte species present in Shetland lochs compared with those of other studies

In Loch Urigill and other lochs of the Ullapool area, submerged vegetation was found to consist of *Lobelia*, *Littorella* and *J. bulbosus* in shallow water, with *I. lacustris*, *P. praelongus* and *P. perfoliatus* occurring in deeper water (Spence and Allen, 1979). Many of the lochs in Rhum have been found to have *L. uniflora*, *L. dortmanna* and *J. bulbosus*, with *M. alterniflorum* and *I. lacustris* sometimes growing in the same lochs as these three species (Farmer, 1984). In general terms, the submerged vegetation in Shetland lochs surveyed was similar to that observed in the above studies. Also observed in Shetland were water bodies which contained species of *Chara*, *Nitella* and *Potamogeton*, as did Loch Borralie (northern Scotland) when surveyed by Spence *et al.* (1984). Plants growing in Shetland waters included nationally scarce species as defined by Bell (1991), such as *Callitriche hermaphroditica*, *P. filiformis*, *P. praelongus* and *S. aquatica*. Notably, *S. aquatica* has also been described as "apparently very rare" in Shetland (Scott and Palmer, 1987). Certain species of macrophytes recorded in Shetland have been regarded as infrequent in occurrence in the north of Scotland. *P. praelongus* and *P. filiformis* were described as rare in Sutherland (Anthony, 1976). This is compared with observations of these species in sixteen and ten percent respectively of the Shetland waters surveyed. Occurrence of *P. perfoliatus* in Sutherland has been defined as occasional (Anthony, 1976), whereas *P. perfoliatus* was noted in more than half the Shetland lochs surveyed during 1991. Similarly, this species was described as common in Shetland by Scott and Palmer (1987).

The catalogue of aquatic macrophyte species observed in the present study included many of the list for Shetland of Spence (1979), although there were macrophytes noted in the latter which were not observed in the 1991 survey. For example, *Potamogeton friesii* and *Phragmites australis* were noted by Spence (1979), but were not observed in the 1991 survey. This can be attributed to these species being scarce in Shetland (Spence, 1979). Spence (1979) also recorded *Sphagnum subsecundum* in small dark peaty pools. This species was not observed in the present study, but peaty pools were not included in the survey.

Although previously recorded in Shetland (Maitland and Lyle, 1986; Scott and Palmer, 1987), *Potamogeton rutilus* and *P. pectinatus* were not observed in the 1991 Shetland loch surveys. This is possibly due to the rapid nature of the survey of each lochs, rather than the disappearance of these species. *P. rutilus* and *P. pectinatus* are also described as being very rare (Scott and Palmer, 1987). In addition, *P. rutilus* is similar to *Potamogeton pusillus* which was found in Shetland lochs in 1991, as was *P. filiformis*, which resembles *P. pectinatus*. Therefore *P. rutilus* and *P. pectinatus* may have been overlooked. Notably absent from all Shetland water bodies surveyed was *Elodea canadensis*. This species has become a nuisance plant in many lakes, where it forms extensive beds which may result in waters becoming impenetrable to boats and a reduction in water quality. Introductions of *Elodea* have been widespread, even occurring in Orkney (Robson, 1987). Another submerged macrophyte which was not observed was *Utricularia*, which has been found in freshwater lochs of Sutherland (Bell, 1991). *Utricularia* species have been associated particularly with West Mainland (Scott and Palmer, 1987).

5.4.2 Parameters affecting macrophyte growth in Shetland Lochs

5.4.2.1 pH, Carbon, Calcium and Magnesium

Mean summer water pH, Ca and Mg concentrations were found to be the most significant factors influencing species present in Shetland lochs. The pH of natural waters broadly correlates with a number of other factors such as dissolved inorganic carbon, conductivity and macronutrients. Rørslett (1991) indicated that none of these other factors, either alone or in combination, produced such a good correlation with macrophyte species richness as pH alone. In a study of 135 Finnish lakes, most variance was accounted for by pH, though water colour also contributed significantly to the variation between the sites (Heitto, 1990).

In a comparison of two circumneutral oligotrophic lakes and two acid oligotrophic lakes in Maine, U.S.A. (Hunter *et al.*, 1986), fewer species were found in the acid waters than in the circumneutral lakes. Rørslett (1991) also observed that acid waters supported less species of macrophytes than alkaline waters. In the present study, no significant differences were found between Groups on the basis of number of macrophyte species present. However, there were no particularly acid waters included in the present study. Hunter *et al.* (1986) also found biomass measurements showed

mass of macrophyte structures per unit area in acid waters to fall within the range of biomass determinations of the macrophytes of circumneutral waters. It would therefore be expected that no difference could be detected in macrophyte biomass estimates between different loch Groups in the present study. Although species composition was affected by pH, biomass and number of species adapted for growth in the more acid conditions of Group 2 in the present study were not restricted.

Differences in species present in waters of different pH values may occur due to pH alone, or because of differences occurring in the sources of C for photosynthesis (Moss, 1980). Many plants are known to be able to utilise HCO_3^- as a C source (for example, *Ceratophyllum demersum*, *Lemna trisulca* and *Chara spp.*) and are found often in hard, HCO_3^- rich waters (Moss, 1980). Aquatic mosses and plants such as *L. dortmanna* and *I. lacustris* are generally associated with acid, soft water conditions and like *F. antipyretica*, are apparently restricted to use of free CO_2 (Moss, 1980). Since *L. dortmanna* and *Chara* spp. were the indicator species at the first division of the TWINSPAN classification in the present study, this suggested that the nature of the inorganic C source might be affecting macrophyte distribution.

Rooted and non-rooted floating leaved plants and emergent species of macrophyte carry out gaseous exchange with the atmosphere, thereby ensuring an unlimited supply of CO_2. This C source is not directly available to plants which are entirely under water. However, submerged plants have a variety of adaptations to the reduced inorganic C:

(1) lower CO_2 compensation points
(2) seasonal variability of CO_2 compensation points
(3) dark fixation of CO_2 through Crassulacean Acid Metabolism (CAM)
(4) utilisation of the lacunar system to transport respiratory CO_2 to photosynthetic C fixation sites
(5) employment of the lacunar system to transport CO_2 from rhizosphere interstitial water to photosynthetic C fixation sites

J. bulbosus, which was an indicator of the lochs in Group 2, can utilise bacterial CO_2 in the rhizosphere to assist with meeting its photosynthetic C requirement (Wetzel *et al.*, 1985), but unlike isoetid species, it uses little of this C source. *J. bulbosus* is

particularly efficient at removal of CO_2 from the water column: more efficient than *L. uniflora*. Photosynthesis of the former is saturated at lower water free CO_2 concentrations than the latter (Roelofs *et al.*, 1984). Presence of *J. bulbosus* in Group 2 lochs may be indicative of CO_2 in the water column being the main C source, as a consequence of low pH favouring C presence in this form. Plants in more acid waters than in Group 3 (pH < 5) may become CO_2 limited because of slow diffusion from the atmosphere combined with little or no HCO_3^- being present for conversion to CO_2. In addition, rates of decomposition of organic matter are slow (Wetzel *et al.*, 1985). In acidified waters, *J. bulbosus* and or *Sphagnum* spp. may subdue growth of isoetid plants (Roelofs *et al.*, 1984; Heitto, 1990). However, other species which are restricted to CO_2 as their C source, such as *P. natans* and *P. polygonifolius*, may still occur through growth of leaves at the water surface (Maberly and Spence, 1983). In the present study, since isoetids were noted, but *Sphagnum* spp. were not observed in lochs of Group 2, this confirmed that Group 2 lochs were only slightly acidic.

The primary nutrient source of Ca and Mg to submerged macrophytes is the water column rather than bottom sediments (Barko *et al.*, 1991). However, these cations are also involved with the availability of C within the water column, as at high pH they combine with CO_3^{2-} and C is therefore stored in this bound form. Contrastingly, at lower pH values, a greater proportion of C present in the water is as free CO_2. In Group 1 waters, which had *I. lacustris* as an indicator species, Mg concentrations were significantly greater than in Group 2 soft water, more acidic lochs, and there may have been a trend of slightly higher Ca concentrations in Group 1 lochs. However, Group 1 waters were relatively soft in absolute terms.

Isoetids have been associated previously with oligotrophic soft water lakes (Spence, 1964; Seddon, 1972). In addition, *Isoetes* species have been found to operate the CAM system of CO_2 fixation, accumulating C overnight in malic acid and decarboxylating this during the light period for incorporation into the Calvin Cycle (Keeley, 1982). This system is indicative of soft waters of low CO_2 concentration. Other isoetids also occurred in Group 1 waters, further indicating low concentrations of CO_2 in overlying water column as *e.g. L. dortmanna*, *L. uniflora* and *I. lacustris* can acquire C from sediment pore waters (Wium-Andersen, 1971; Søndergaard and Sand Jensen, 1979). These plants are also suited to low CO_2 concentrations through

high root biomass and high oxygen release rate from roots (Roelofs *et al.*, 1984). It is therefore suggested that CO_2 limitation may be occurring in Group 1 lochs, possibly as a result of near neutral pH. A greater proportion of available C would be as HCO_3^- in circumneutral waters than in more acid conditions.

Under the conditions of higher pH values observed in Group 3 waters, there will be proportionately less CO_2 and more HCO_3^- than in Group 1 or Group 2 lochs. This is also suggested by the fact that as isoetids were not indicators for this Group, but *P. perfoliatus*, which has the capability to use HCO_3^- as a C source was present in many of the lochs in Group 3. *P. filiformis*, which is similar in growth form to *P. pectinatus*, was present in both Loch of Spiggie and Loch of Tingwall. *P. pectinatus* can only obtain C from its shoots and in HCO_3^- form (Van Wijk, 1989). Although alkalinity was not measured in the first year of this study, it is suspected, because of the harder, more alkaline waters in Group 3, that values would increase from Group 2 to Group 1 to Group 3 lochs.

5.4.2.2 Light penetration

Although light attenuation was not a significant influence on plant species present, there may have been a tendency, as illustrated by the median values, for there to be less light available in lochs of Group 2, than in either of the other Groups. Plant species growth form is important in its influence on the ability of a plant to harvest light for photosynthesis. In experiments involving sediment with different nutrient concentrations and a range of light levels, maximum summer mean biomass of *P. praelongus*, *Vallisneria americana* and *Potamogeton robbinsii* were found to be affected by both sediment composition and light levels (Chambers and Kalff, 1987). In shallow water, erect forms tend to be limited by sediment composition rather than by light, whereas bottom-dwelling forms are light limited. Rosette forms such as *Vallisneria* show an intermediate response (Chambers and Kalff, 1987). The *I. lacustris* of Group 1 of the present study are rosette forms, which, like the *Chara* spp. of Group 3, were generally found in deeper water, consequently requiring more light than the emergent edge plant, *R. flammula*, which was an indicator of Group 2 lochs. Light limitation effects may be promoted by coloured water and loch basins of higher depth:volume ratio, *i.e.* when the surface area of a water body is small in relation its depth and consequent volume. Although Shetland lochs are not generally

of high depth:volume and no significant effect of water colour on plant species present was detected, the median value for water colour in Group 2 was greater than that for either of the remaining Groups.

5.4.2.3 Sources of nitrogen and phosphorus for plant growth

In the present study there was no significant difference between Groups in terms of number of macrophyte species present, although highest numbers were observed in lochs of Group 3, *i.e.* were associated with more alkaline pH and increased water hardness. Differences between Groups were associated most with pH and water hardness. However, Group 3 also had slightly higher TP and lower TON concentrations than Group 2. Rørslett (1991) examined species richness data for 641 northern European lake systems and concluded that species richness was greater in mesoeutrophic and eutrophic lakes than in those which were of dystrophic or oligotrophic status, the latter two categories being relatively species poor. Experimental work with *Lagurosiphon major* and *Myriophyllum triphyllum* involving eutrophic and oligotrophic sediment in an oligotrophic lake resulted in those on eutrophic sediments having twice the biomass of those grown on oligotrophic sediments. In eutrophic lake water, no consistent difference was found between plants on different sediments. This suggested that when substrate nutrient levels are low, macrophyte nutrition is mainly from shoots, whereas under conditions of enriched sediments, nutrient uptake occurs through the root system (Rattray, 1991).

Barko *et al.* (1991) state that the major source of plant N comes from benthic sediments. However, there is evidence that both sediment and water act as nutrient sources for aquatic macrophytes, though to varying degrees, depending upon plant type, richness and chemical speciation of each N source. In oligotrophic lakes, water is poorly buffered and relatively low in winter N levels compared to those of eutrophic waters. The N present in oligotrophic waters is mostly as NO_3-N (Schuurkes *et al.*, 1986). Soft water macrophyte species show NO_3^- dominated (63-73%) N utilisation, with roots as the major uptake site (83%). These plants are capable of surviving very low concentrations of N. This work was based on studies of *L. dortmanna*, *L. uniflora*, *Luronium natans* and *Echinodorus ranunculoides*. This situation may have occurred in the lochs of Group 1 in the present study, as Group 1 was characterised by isoetid plants.

Acidified systems are generally dominated by *Juncus* and *Sphagnum* communities. From experimental work involving *J. bulbosus*, *Sphagnum flexuosum* and *Drepanocladus fluitans*, it has been observed that in acid water communities, N utilisation is ammonium dominated (85-90%) with leaves as the major uptake site (71-82%). It is possible for soft water species to be rapidly saturated, not requiring N in large quantities for survival and growth. In contrast, there is a strong increase in biomass of *J. bulbosus* and *Sphagnum* with increase in N supply (Schuurkes *et al.*, 1986).

From experiments adding P, N and K to sediment, Grace (1988) concluded that N was the nutrient limiting *Typha latifolia* and *Typha domingensis*. When cultured without an external DRP source, *P. pectinatus* survived for five weeks on P stored in its tubers, whereas without either a source of TON or DIC, plants died quickly (Van Wijk, 1989). In the present study, summer water TON concentrations were relatively high in lochs of Group 2 in comparison with those of Group 3. In more acid Group 2 waters, the major N source for macrophyte growth would be expected to be TAN from the water column, thereby possibly explaining the TON pool remaining relatively large. TON uptake in Group 3 would be greater from the sediment than from the water column and water TON levels may have been low as a result of low sediment TON concentrations.

During experimental work with *Myriophyllum spicatum*, no response was found to P or K levels in enriched sediments, but a significant increase in biomass was observed with increasing substrate N supply (Anderson and Kalff, 1986). In the present study, although TON concentrations were significantly higher in Group 2 than Group 3, TP concentrations were significantly lower in Group 2 than Group 3 ($p < 0.1$ in both cases). It is therefore likely that both variables were having a relatively small effect on plant species present. P is not generally a limiting factor for macrophytes owing to their ability for P uptake from their roots. Carignan (1982) suggested a model for P uptake by submersed macrophytes. It predicts that > 50% of the supply of P to submersed aquatic macrophytes is from sediments when the water column DRP:sediment interstitial water DRP ratio is > 1:4. As water DRP concentration is often < 1.0 μg P L^{-1} in the present study, it is likely that P for macrophyte growth is mostly derived from the sediments.

The TP levels observed in Group 3 waters may have been important because of the consequent enrichment of the sediment. Experimental studies on *Egeria densa*, *Hydrilla verticillata* and *M. spicatum* demonstrated that these species are capable of deriving their P nutrition exclusively from the substrate (Barko and Smart, 1980). Furthermore, in oligotrophic Lake Hampen, Denmark, addition of P to sediment resulted in increased leaf production rate of *L. uniflora*, so causing a depletion of N in the sediment (Christiansen *et al.*, 1985). If the sediment was providing a plentiful P source, then it is possible that macrophytes of Group 3 lochs were N limited. P availability in loch bottom deposites is infuenced by the P binding sites present within the sediment (Chapter 3).In lochs of elevated water Ca and Mg concentrations, it is likely that the sediment is Ca and Mg rich, thereby having enhanced P binding capacity. Increased P content of the sediment would encourage macrophyte growth. Although sediment P was not one of the parameters measured in relation to the macrophyte studies, this variable may have an important effect on the macrophyte community. The differences in water Ca and Mg levels between loch TWINSPAN groups may have been related to sediment P binding efficiency.

5.4.3 Factors influencing macrophyte or phytoplankton dominance of lake systems

Following enrichment of a body of standing water, it is difficult to predict whether this will be expressed as macrophyte or phytoplankton dominance of primary productivity. Development of a nutrient-rich water body of low mean depth has often been associated with a loss of submerged plants and the occurrence of dense phytoplankton populations, the common explanation of this result being loss of light available to macrophytes (Balls *et al.*, 1989). Isoetids decline in numbers and mass with the onset of anthropogenic perturbation to a catchment, such as field drainage, reservoir construction, acidification and eutrophication, the latter perhaps being most important (Farmer and Spence, 1986). *L. dortmanna* and *L. uniflora* are more resilient to disturbance and therefore are found in shallow water whereas *Isoetes* may be found at greater water depth as it is a non-ruderal species. Eutrophication may lead to loss of isoetids as they are outcompeted by faster growing macrophytes, or growth is restricted due to epiphytic colonisation (Phillips *et al.*, 1978). Isoetids in the present study were indicators in Groups 1 and 2 rather than Group 3 which incorporated lochs with elevated TP levels. *S. aquatica*, *L. dortmanna* and *I. lacustris*

are all generally restricted to waters of P concentration up to 10-20 μg P L^{-1}, whereas *L. uniflora* may be found in waters of up to approximately 25 μg P L^{-1}. However, it is actually alkalinity rather than P concentration which distinguishes the growth of these four species as follows in order of increasing alkalinity of habitat: *S. aquatica*, *I. lacustris*, *L. dortmanna*, *L. uniflora* (Farmer and Spence, 1986). Relatively high alkalinity of the Shetland lochs examined in the present study (Chapter 2) could account for the fact that *S. aquatica* was observed in two lochs only, rather than its limited distribution occurring as a result of eutrophication.

A change from an aquatic system in which macrophytes are important to one in which phytoplankton dominate does not necessarily occur with increasing nutrient concentrations. In the present study, phytoplankton chl *a* concentration was found to be slightly higher in Group 3 than Group 2 ($p < 0.1$), though there was no difference between Group 1 and Group 3. It is probable that phytoplankton biomass was not generally having a significant effect on macrophyte species present. Both phytoplankton and macrophyte growth were dependent on water and sediment nutrient dynamics, with increased phytoplankton chl *a* in Group 3 likely to be associated with the higher TP levels in lochs of this Group. From the work of Chapter 3, it is possible that a change from a macrophyte to phytoplankton dominated community may be related to the P binding capacity of the loch sediment. Macrophyte communities may be encouraged in lochs where P is adsorped by the sediments. However, once binding sites become full, the sediment can no longer remove P from the overlying water and may release P to the water column. The increased P in the water column could then stimulate filamentous algae or phytoplankton growth.

Observational data on Turdale Water over the three year study period did, however, suggest a decline of macrophytes with progressive intensification of eutrophication. Macrophyte limitation in this instance was likely to be caused by a combination of phytoplankton blooms and the observed growth of filamentous algae over submerged vegetation. By 1993, the stand of *P. perfoliatus* noted in Turdale Water in 1991 had almost completely disappeared. Those plants located by diver were weighed down under filamentous algae, an observation in agreement with the work of Phillips *et al.* (1978). Turdale Water sediment is likely to have had a low P binding efficiency (Chapter 3). This combined with the high P concentrations within the water body and

its inflow waters (Chapter 2) resulted in augmentation of the algal assemblage (Chapter 4).

However, explanations of either macrophyte or algal dominance may be complicated and a holistic approach is necessary to understand the relevant processes which favour one or other plant community (Moss, 1989). Strategies for maintenance of each community type have been defined as follows (Balls *et al.*, 1989):

Aquatic plant stabilisation:

(a) luxury nutrient uptake

(b) allelopathy

(c) shedding leaves with heavy epiphyte burdens

(d) provision of shelter for large grazing communities resulting in their protection from fish and consequent consumption of phytoplankton

Phytoplankton stabilisation:

(a) early season growth allowing shading of plants

(b) easier acquisition of CO_2 especially when pH is high

(c) vulnerability of grazers to fish predation

(d) production of large inedible algae

Under conditions of low ambient water P concentrations phosphatase enzymes may be utilised by bacteria and phytoplankton to acquire P. These proteins are located bound to cells or released to the water column. Stands of littoral vegetation may combat this process through release of dissolved humic compounds which form complexes with these enzymes, thereby causing enzyme inhibition. Depending upon enzyme reaction sites and type of organic compound involved, phosphatases may be rereleased at some distance from their source, both spatially and temporally (Wetzel, 1990). However, in harder waters, divalent cations may complex with the organic compounds so rendering them unable to bind with phosphatase enzymes. Therefore, at low P concentrations planktonic algae may reach greater biomass than possible in soft waters, this being assisted if alkalinity is also high, as phytoplankton are efficient users of HCO_3^- (Maberly and Spence, 1983). It is possible that Loch of Huesbreck is such a water body, as it exhibited high macrophyte biomass, but also low water TP concentration and chl *a* levels which were higher than expected for the water TP and

DRP values (Chapter 2).

Although water colour was not found to be significantly different between TWINSPAN Groups, there were examples of coloured Shetland lochs where few macrophytes were present and cyanophyte biomass became excessive. This occurred in both Sandy Loch and Loch of Brough (Yell). Mill Pond also supported little macrophyte growth, but dense communities of planktonic green algae were observed in this water body. Many factors may cause growth difficulties to submerged plants in humic lakes.

(1) Complexation of nutrient elements with organic matter may result in their non-availability (Sikora and Keeney, 1983).

(2) Anaerobic decomposition in highly organic sediments can result in production of phytotoxins.

(3) Light limitation occurs as a consequence of high water colour, phytoplankton dominance being likely as a result.

(4) Light limitation may also result from phytoplankton growth as algae can remain in the surface waters to utilise available light.

(5) Slow release of phosphate from humus-iron complexes results in prevention of acute P limitation of the phytoplankton in dystrophic lochs (Jones, 1992b).

In some highly coloured Shetland lochs, few macrophytes occurred and phytoplankton were the successful primary producers. This situation was notable in both Sandy Loch and Loch of Brough (Yell). It is therefore likely in these cases that initial ambient conditions are not suitable for colonisation by rooted plants, but can support algal growth in the water column, rather than macrophytes disappearing as a consequence of phytoplankton growth.

The zooplankton grazing community affects phytoplankton numbers, size and community structure. This in turn could influence macrophyte vegetation present. During enrichment experiments on the Norfolk Broads, a complex relationship was found between fish stock and dominant zooplankton (Irvine *et al.*, 1989, Table 5.7). This example illustrates the importance of fish survival in determination of type of predation system dominating in a water body because of its influence on the grazing community present.

Table 5.7 **Fish stock-zooplankton populations in the Norfolk Broads (Irvine *et al.*, 1989)**

Stock (g m^{-2})	Dominant zooplankton type
0.5-1	*Daphnia*
18.1	*Eudiaptomus gracilis*
22.8-29.1	*Bosmina longirosrtis*
	cyclopoid copepods

5.4.4 Classification of lochs incorporating macrophyte communities

Attempts to classify water bodies using plant communities must take fully into account the influence of underlying physical, chemical and biological processes upon growth of vegetation. The TWINSPAN classification of the present work failed to exhibit many highly significant differences between Groups, owing to complex interactions of these parameters, chance distribution of plant species and probability of different conditions occurring within the same loch system. For example, Loch of Gonfirth was an oligotrophic loch by water chemistry classification (Chapter 2), but had an area of mineral sediment within it (Chapter 3).

The National Vegetation Classification (NVC) (Rodwell, 1991) acknowledges that many different assemblages of aquatic plants may be present within a water body. The NVC allows description of lakes with respect to macrophyte communities rather than the individual species present. Information from NCC survey sites throughout Britain, though with a bias toward Scotland (over 50% of NCC macrophyte data is from Scottish sites), allowed characterisation of twenty four aquatic communities. Many of these have sub-communities, making a total of thirty eight community types from both lotic and lentic water environments. However, for water management purposes, it would be more useful to have a system which classified entire water bodies and a different approach is taken by other authors in attempts to categorise lakes using plant species present.

From a study of twenty eight water bodies in The Netherlands, Arts and Leuwen (1988) were able to divide macrophytes into five groups, each characteristic of a different type of water body:

(a) *J. bulbosus*, *Sphagnum* spp., nymphaeids, species poor

(b) isoetids

(c) isoetids with a number of other species (soft waters)

(d) absence of a group of species such as *Echinodorus repens*, *Eleocharis acicularis*, *I. lacustris* and *L. dortmanna* which are mostly confined to groups (c) and (e); *F. antipyretica* is almost restricted to (d)

(e) presence of *Hydrocharis morsus-ranae* and to a lesser degree, *Riccia fluitans*, *P. pusillus*, *Stratiotes aloides*; group includes species frequently growing in hard, circumneutral or alkaline waters.

Nitella and *Chara* were not included in this classification due to uncertainties of taxonomic status and difficulties of identification.

The categories of TWINSPAN division produced by Palmer (1989) are shown in Table 5.2. The second Group had characteristic plants of *J. bulbosus* and *L. dortmanna* and therefore was similar to Group 2 of the present study. The third category of categorisation was similar to the second, but had additional characteristic species, including *I. lacustris*, suggesting a coincidence with Group 1 of this study. *Chara* spp. were the indicators of Group 3 lochs of the present study. Water bodies in this Group also incorporated *Potamogeton* species and *M. alterniflorum*. Consequently, it is suggested that this division was similar to the fourth group of Palmer (1989). As Strand Loch was under marine influence and was characterised by *Enteromorpha*, this Loch may be likened to those of Group 6 of Palmer (1989).

It is suggested that both classification systems were restricted in their usefulness, as a consequence of limited available data. The categorisation of Palmer (1989) was confined by few environmental variables, whereas the present study was restricted to a small number of sites and therefore fewer divisions were feasible. It is possible that if more lochs had been involved in this study, TP and TON concentrations may have been illustrated as being more important than they were using only thirty one water bodies. However, the two studies were alike in suggesting a gradation in water pH and ionic content between Groups.

From results of the present study, it is suggested that oligotrophic, dystrophic and nutrient enriched lochs where phytoplankton population or epiphytic algae have become dominant may possess similar macrophyte communities as expressions of low diversity can result from different forms of limitation of primary production. A humic loch, Mill Pond, was in the same TWINSPAN group as Roer Water and Loch of Ustaness, which were waters of low P concentration. Turdale Water was found to be in Group 2 of the TWINSPAN classification of the present study *i.e.* the same category as oligotrophic and dystrophic lochs stated above. Chemical and chl *a* data shows this water body to be highly eutrophic, therefore illustrating that the TWINSPAN classification is not necessarily a good indicator of trophic status and likelihood of excessive phytoplankton growth.

It appears that the indicator value of aquatic macrophytes for nutrient enrichment is limited because both sediment and water characteristics affect macrophyte vegetation. Nutrient dynamics in freshwater systems are complex. As a result, causal relationships are difficult to establish without detailed study. Use of macrophytes as indicators is further complicated by the variable response time which elapses between a water enrichment event and eventual macrophyte response (Kelly and Whitton, 1994). Relationships between macrophytes, environmental variables and appropriate procedures which would be common to all water bodies would therefore be difficult to establish (Kelly and Whitton, 1994).

Results of the present study indicate a classification system based primarily on pH and natural cation richness, associated with increased hardness, alkalinity, or Ca and Mg concentrations and probably inorganic C sources, rather than P and N levels which are involved with anthropogenic eutrophication and problems of phytoplankton biomass. Water pH was significantly different between Groups 1 and 3, Groups 2 and 3 and Groups 1 and 2. This is consistent with the water Ca and Mg concentrations of the different Groups, as waters are generally less acid when hardness is greater. If pH increase had been due to increased phytoplankton growth through artificial eutrophication, then a consistent relationship might be expected between chl *a* and classification Group. Phytoplankton chl *a* was however, only slightly significantly different between Groups 2 and 3.

5.4.5 Importance of macrophyte vegetation in freshwater lakes

Macrophyte stands in freshwater lakes may have important effects on water flow, nutrient cycling and water temperature. In macrophyte stands where water circulation is limited, temperature gradient from water surface to bottom may be greatly affected. Retardation of water flow occurs in macrophyte stands (Carpenter and Lodge, 1986). This in turn may have important effects on cycling of nutrients. It is possible that it could result in much of the autumnal P losses from plants being retained within the vegetation area until uptake in spring, the colonised area operating as a semi-closed cell within the loch system. In the littoral *Equisetum* belt of oligotrophic Lake Paajarvi (southern Finland), total primary production and respiration indicated high internal C, N and P cycling during summer, with P requirements of *Equisetum*

growth being 2-4 times greater than that present in the surrounding water. The amount of P available from decay and excretion products could not compensate for this deficit. P content of the annual production of the *Equisetum* accounted for 2.3% of the mean annual P loading of the lake and 5.3% of mean total P storage within the water column (Sarvala *et al.*, 1982). The influence of submersed plants on lacustrine nutrient cycling can be great, as the littoral zone is the most productive part of the lake system (Sarvala *et al.*, 1982; Wetzel, 1990). As P nutritional requirements may be met entirely from the sediment, this may allow substrate P to become available in the water column through secretion or decay of plant material. P may be mobilised mainly as DRP and N mostly as TAN (Kistritz, 1978). Since P is generally the limiting nutrient for freshwater phytoplankton, this could result in increased algal biomass. It is possible that macrophytes are actually competitively excluded from aquatic systems having P concentrations high enough to allow significant uptake by leaves (Barko and Smart, 1980).

In temperate eutrophic lakes, seasonal variation in nutrients contained within macrophyte tissue may be great because of the life forms of plant species which tend to colonise sediment under these conditions. Photosynthetic structures of species of submerged elodeids die back in autumn, turions and rhizomes surviving to allow redevelopment of the plant stand the following spring (Wetzel, 1964; in Sand-Jensen and Søndergaard, 1979). However, in soft water lakes of low productivity, such as water bodies included in TWINSPAN Groups 1 and 2 of this study, in which macrophyte communities are dominated by isoetids, rooted plants may have a relatively small seasonal effect on the water nutrient chemistry. For example, *L. uniflora* in Lake Kalgaard (Denmark) has been found to vary little in its biomass throughout the year, possibly as a result of its evergreen nature (Sand-Jensen and Søndergaard, 1979). Christiansen *et al.* (1985) suggest that rather than P loss occurring from *L. uniflora* leaves as they age, translocation to younger tissue takes place. Consequently, lochs in the present study in which isoetids are the dominant form of macrophyte, such as Loch of Gonfirth, will be affected relatively little by P dynamics of the rooted vegetation. Generally Groups 1 and 2 had locally dense areas of isoetid colonisation, but other plant growth forms such as *Potamogeton*s were more important in Group 3. Group 3 lochs would therefore be expected to experience a greater effect on water nutrient chemistry from the macrophyte stands present.

In the present study, loch macrophyte biomass estimates were highly variable and no difference could be detected between TWINSPAN Groups on this basis. It is possible, even in nutrient poor acid conditions, for locally high biomass to occur. In acidified systems (pH < 4.5), biomass of *J. bulbosus* and or *Sphagnum* spp. may be prolific, associated with raised concentrations of N (with TAN as the major source) and increased CO_2 levels in sediment and water column (Roelofs *et al.*, 1984). Biomass of *J. bulbosus* in Group 2 lochs was not great and infrequently occurred in isolation, often being found with *L. uniflora*. This is probably due to conditions not being acid enough to promote greater *J. bulbosus* growth at the expense of other macrophyte species. Mean midsummer biomass of *L. uniflora* and *I. lacustris* in oligotrophic Lake Kalgaard, Denmark were found to be 112 g organic dry weight m^{-2} and 66 g organic dry weight m^{-2} respectively, where organic dry weight represents loss on ignition (Sand-Jensen and Søndergaard, 1979). The organic fraction of plant material constitutes the great majority of the total dry weight. In the present study, single species biomass samples ranged from 2.3 g dry weight m^{-2} to 300 g dry weight m^{-2} for *L. uniflora* and 0.4 g dry weight m^{-2} to 592 g dry weight m^{-2} for *I. lacustris*.

From analyses of plant material from the Scottish freshwaters of Forfar Loch (polytrophic), Balgavies Loch (eutrophic) and Loch of the Lowes (mesotrophic), a relationship was found to exist between enrichment of the environment of plant growth and the nutrient content of the macrophyte biomass. This relationship was stronger when considering P than N (Ho, 1979). Plants examined from these lochs were *Juncus effusus*, *Iris pseudocorus*, *Carex rostrata*, *Glyceria maxima*, *Nuphar lutea*, *Polygonum amphibium* and *Schoenoplectus lacustris*. From a variety of tissues examined a range of P, N and C contents were found in plant material from each loch (Table 5.8).

Table 5.8 **P, N & C content of plant material in three Scottish Lochs (Ho, 1979)**

Water body	P (mg g^{-1})	N (mg g^{-1})	C (mg g^{-1})
Forfar Loch	3.12-5.90	6.91-34.24	450-502
Balgavies Loch	1.39-4.67	7.52-40.78	452-490
Loch of the Lowes	1.02-1.38	8.22-15.95	468-490

KEY:
P and N reported as of dry weight, C content as ash-free dry weight

During sediment enrichment experiments, by Christiansen *et al.* (1985), tissue P concentration in *L. uniflora* was found to increase with increasing P additions in leaf, stem and root structures. Additions of TAN and TON, in a 1:3, TAN:TON ratio, resulted in greater N content of leaves and shoots, but did not affect leaf production. Average tissue concentrations of P and N in *L. uniflora* were 0.28% (estimated critical tissue concentration) and 3.29% respectively. Critical tissue concentration of *P. pectinatus* has been found to be only 0.15%, but this plant also takes up P in excess to immediate requirements at high external DRP concentrations (Van Wijk, 1989).

Allenby (1981) found that there was no correlation between water DRP concentration and P content of the following aquatic macrophytes: *Lemna minor*, *Elodea canadensis*, *Potamogeton crispus*, *P. pectinatus*, *Ceratophyllum demersum*, *Scirpus tabernaemontani*. This may have been because macrophytes are generally dependent upon sediment, rather than water, as a P source (although it is also possible for DRP concentration to be influenced by plant uptake).

In water washed plants, P ranged from 0.68% per plant of *S. tabernaemontani*, to 2.56% per plant of *E. canadensis*. Total kjeldahl N (TKN) of water washed material was determined in *L. minor*, *L. gibba*, *P. crispus*, *P. pectinatus* and *C. demersum*. Mean TKN expressed on a per plant basis ranged from 2.4% in *P. pectinatus* to 4.3% of *L. gibba* (Allenby, 1980). Concentrations of P in plant tissues varies and critical P concentrations for submerged macrophytes differ, depending upon species (Christiansen *et al.*, 1985) and generally, the more enriched a loch system, the greater the concentration of nutrients in plant structures through luxury uptake. Plants associated with enriched systems are more likely to lose nutrients to the water column than those of nutrient poor situations. As a consequence, deterioration of water quality through macrophyte growth is likely to be faster than in an oligotrophic system. However, during studies of *Typha latifolia* and *Typha domingensis*, sediment was affected by these species as follows: TAN was reduced by 90-95 %, K was depleted by 35-55%, but P remained at the same concentration as uncolonised sediment because of N limitation (Grace, 1988). Consequently, regardless of P concentration available for macrophyte growth, if another factor is limiting, the effects of macrophyte stands on P dynamics in the loch system are decreased. For

example, water depth effects prevent macrophytes utilising increased nutrient supply, as a consequence of lower light availability in deeper water (Chambers and Kalff, 1985; Anderson and Kalff, 1986) and because the degree of aeration of the sediment surrounding the macrophyte root system may be depth dependent in certain species (Grace, 1988).

When oxygen leakage from vascular macrophytes occurs in reduced sediments, P becomes bound to Fe, so decreasing concentrations of Fe and P in sediment interstitial waters and resulting in arrest of P release from sediment sources to the water column. Potential for aeration of roots and rhizosphere varies depending on plant species. For example, sediment redox potential is increased by *T. domingensis* at medium depths, but unaffected by *T. latifolia*, regardless of water depth (Grace, 1988). Oxidation of sediment in oligotrophic lakes by rosette forms decreases the rate of P cycling (Jaynes and Carpenter, 1986). However, in eutrophic systems, rate of oxygen release is slower owing to the different plant life forms present under these conditions and sediment oxygen deficit is greater, so that the effect of macrophyte growth is inadequate to improve sediment conditions (Sand-Jensen *et al.*, 1982; Carpenter *et al.*, 1983). Again, those lochs in the present study with a high proportion of total macrophyte biomass as isoetid species, such as *L. uniflora*, are likely to be less affected by P flux from the macrophyte colonisation zone. Generally this applies to lochs of Group 1 and Group 2 where, though there may be other growth forms, such as *Potamogeton* species, plants of rosette-like structure nevertheless comprise much of the total biomass. Sediment of lochs of Group 3, such as that in Lochs of Tingwall and Spiggie, is likely to be affected less by oxidation via macrophytes, as much of total macrophyte biomass is present as non-rosette forms.

5.5 CONCLUSIONS

Macrophyte species present in Shetland Island lochs were typical of those observed elsewhere in Scotland, in lowland areas under maritime influence, in water bodies situated on fertile and non-fertile geology.

Between TWINSPAN Groups of lochs in this study, there was no significant difference in macrophyte biomass estimates from areas of vegetation colonisation. As total area and volume of macrophyte colonisation in each water body were not

determined, it is not possible to conclude whether these variables would have been valuable as indicators of phytoplankton growth.

In terms of water quality, macrophyte species present in the Shetland lochs surveyed were found to be influenced most by pH, Ca and Mg concentrations. The classification system of Shetland lochs by TWINSPAN division was therefore indicative of different water pH values, CO_2/HCO_3^- levels, hardness and alkalinity.

Group 3 TP levels were elevated compared to those of Group 2 and TON concentrations were low in the former. These conditions may be indicative of a similar situation in the sediment. Therefore, particularly in lochs with higher TP concentrations, macrophytes may be N rather than P limited.
Macrophytes may not be competing for the same nutrient sources as phytoplankton. Phytoplankton can obtain nutrients from loch bottom deposits, either from the sediment surface, or from the loch water when sediment nutrients have become available to the water column. Macrophytes can assimilate nutrients directly from the water column. However, phytoplankton nutrition is typically taken directly from the water column, whilst sediments are the major source of P and N for macrophytes. Phytoplankton growth in freshwater systems is normally P limited, although N levels may influence species composition. Typically, aquatic macrophytes obtain their P requirement from sediment sources and may become N limited.

Owing to within Group variation, there was no consistent relationship between chl *a* concentrations and TWINSPAN Group. Chl *a* levels in Group 3 lochs were only slightly elevated in comparison with Group 2 lochs. It was concluded that macrophyte species present would not be an effective indicator of water column conditions likely to support excessive phytoplankton growth.

In oligotrophic water bodies, macrophyte growth is likely to have relatively little effect on nutrient cycling within the lake system. However, in enriched systems, it is more probable that macrophyte vegetation accounts for an important proportion of the total lake nutrient budget, through increased uptake with increased availability and die-back of eutrophic growth forms.

CHAPTER 6: CHARACTERISTICS OF SHETLAND SOILS WITH REGARD TO THEIR PHOSPHORUS BINDING PROPERTIES

6.1 INTRODUCTION

6.1.1 Aims

The purpose of this section of the study was to investigate whether it was possible that when land is treated with fertiliser, as occurs during reseeding operations, fertiliser nutrients may be transported to the water drainage system and consequently cause enrichment of standing freshwaters. Both N and P are important in primary production in freshwaters. It is possible for N to restrict algal production and the concentration of N in relation to P influences which genera of algae are likely to dominate the phytoplankton community. However, P is generally the limiting nutrient for phytoplankton in freshwater systems.

The aims of this section of work were therefore as follows.

(a) From published information consider briefly the effects of reseeding procedures on soils in terms of drainage, N transformations and soil pH.

(b) Conduct a study of a range of soils from the catchment areas of the lochs studied in 1991, in order to determine the basic soil characteristics of pH, water and organic content.

(c) Collect soils from the study watersheds of the period 1992 to 1993 and determine:

(i) soil characteristics as specified in (b) above

(ii) present water soluble molybdate-reactive P content, *i.e.* that which might be lost to the drainage system through soil water flow

(iii) the capacity of soils for sorption of added P.

(d) relate water soluble P content and P uptake capacity to the simple soil variables of pH, water and organic content determined in the soils from the study drainage basins of the period 1992 to 1993.

(e) formulate a soil P loss risk assessment for Shetland soils, based on easily measurable soil parameters of pH, water and organic content.

6.1.2 Effects of pre-fertilisation management practices on catchment soils

6.1.2.1 The influence of field drainage on catchment water flow patterns

The greatest impact of drainage is on the route of water loss. During waterlogging, infiltration of precipitation to the soil is slow and restricted to shallow depth. Water

leaves either by surface runoff or near surface flow, whereas introduction of drainage enhances soil macroporosity and incident precipitation can then travel through the soil and leave rapidly through the drainage system (Armstrong and Garwood, 1991). In areas of clay loam soil, although drainage lowers the water table and reduces duration of water logging, its effects in terms of total loss of water from a soil or on peak flow are relatively small (Armstrong and Garwood, 1991).

In a study by Knight *et al.* (1972), water was traced through peat and found to move in a distinct layer. A general flow of ground water was found which was independent to that associated with flow to the drainage ditches. Different drainage conditions will affect distribution of water movement. Water movement through peat is dependent on hydraulic gradients which are generally related to hydraulic conductivity. However, although it was possible to link downward movement to drainage conditions, lateral movement is much more complex and may be inexplicable in terms of surface topography or hydraulic gradient. Local configurations within peat may therefore significantly affect water movement (Knight *et al.*, 1972).

Ground water movement affects the distribution of vegetation. Benefits of water movement may include removal of toxic waste products of breakdown of organic matter, such as CO_2, sulphides and ethylene as well as transport of oxygen from the soil surface (Knight *et al.*, 1972). Water movement can also transfer nutrients to plant roots (Knight *et al.*, 1972). It has been suggested that growth of *Pinus contorta* (lodgepole pine) is improved through drainage on deep peat, due to the increase of water movement within the soil, rather than from consequences of reduction of water content (Boggie and Miller, 1976), although experimental work on blanket bog in Scotland found that increased N availability to *Pinus contorta* following lowering of the water table was a result of deeper rooting depth (Williams and Wheatley, 1988)

6.1.2.2 Effects of field drainage on nitrogen transformations in soils

Drainage results in aeration of the soil, thereby causing changes in the chemical form in which nutrients are present. Decay processes are facilitated by oxygenation, with a general increase in microbial biomass developing with improved aeration (Williams and Wheatley, 1988). Because N mineralization in peat is slow, availability of N for plant growth is limited despite the fact that peat may contain large amounts of organic

N (Dickson and Savill, 1974; in Williams and Wheatley, 1988). Biological activity of microorganisms involved in N cycling may be affected considerably by increasing soil aeration and plant growth (Williams and Wheatley, 1988). Increased mineralization of organic matter may occur as a result of soil aeration. Numbers of aerobic and anaerobic ammonifying bacteria in oligotrophic deep peat in Scotland have been found to increase following lowering of the water table from 0 cm to 50 cm, 80-90 % of the ammonifiers occurring in the upper 20 cm of the soil profile (Williams and Wheatley, 1988). Mineral N present mostly as ammonium decreased rapidly with depth below 20 cm. NO_3-N was present in trace amounts only, probably due to low abundance of ammonium oxidising (nitrifying) bacteria in this soil. Bacteria capable of transforming nitrate to nitrite, *i.e.* nitrate reducers were also present mostly in the first 20-30 cm of profile, though in considerably smaller numbers than the ammonifiers (Williams and Wheatley, 1988).

Effects of microorganisms on N cycling are likely to depend upon several factors. High acidity, poor aeration and restricted ammonium supply are likely to limit growth in oligotrophic peats, although other higher pH and more mineral rich peats may have greater N availability. The nitrogen content of mineral soils generally falls within the range 0.1-0.5 %, whilst that of organic soils is typically 0.5-1.5 % (Allen *et al.*, 1974).

During operation of a pump drainage scheme in England, lowering of the water table through pumping resulted in discharge of nutrients from the peat in the watershed (Heathwaite, 1991). In the water of the drainage ditch examined, solute peaks were noted in the following order: SO_4-S, NH_4-N, Ca+Mg + NO_3-N. It follows that natural seasonal variations in the water table, such as the lowering of the water table in summer, after the increased water level of winter and spring, could result in nutrient releases. In addition, when soils are drained initially in preparation for fertiliser treatment, a nutrient flux to a loch might occur. The nature of the nutrient load would depend on soil type and there are differences between peats in terms of their natural nutrient pools. Drainage increases bulk density and decreases hydraulic conductivity in peat. The characteristics of the soil hydraulic conductivity affect the volume of peat influenced by drainage. In base-rich, fen peats, removal of nutrients from peat through drainage is high. The low hydraulic conductivities generally

present in amorphous peats result in relatively low nutrient removal when drainage is implemented, whereas in fibrous peats, where hydraulic conductivity is greater, a larger volume of peat contributes to nutrient loss (Burke, 1975).

6.1.2.3 Adjustment of pH in soils

The soil pH which is required for agricultural purposes is approximately pH 6.5 (pH 6.0 for grass (I.D. Pulford, University of Glasgow, *pers. comm.*, 1995)). In order to improve land for pasture it is therefore generally necessary to increase the pH of the soil. This may be achieved by the addition of lime ($Ca(OH)_2$) or ground limestone ($CaCO_3$). The lime requirement of a soil is dependent on the pH of the soil, but also the total exchangeable hydrogen content. This means that when lime is first added to the soil, neutralisation of the free H^+ ions in the soil solution occurs, but ionization of H^+ from the unsaturated exchange complex continues. All exchangeable H^+ must be neutralised and replaced by metal cations before pH can be adjusted to pH 6.5. (Etherington, 1982). Lime requirement will therefore depend on soil type. Sandy soil needs relatively little lime because of its low CEC, whereas acid soils with a high organic content would require more. CEC in clayey soils is extremely high, so an acid soil with a significant clay content would be much more difficult to neutralise.

6.1.3 Fate of fertiliser nutrients in soils

Many factors influence what happens to fertiliser nutrients in soils: soil class, rainfall, fertiliser type, together with method and time of application all have a variable effect on fate. After fertilisation of soil, N is lost to drainage water or runoff. The inorganic form in which N is mainly found when this occurs appears to vary. In temperate regions, mineralization of N from soil reserves and plant remains through microbial action accounts for more N loss than is possible through crop uptake during some periods of the year. Loss of nitrate to drainage water is therefore inevitable. Though losses from grassland are probably less substantial than from crop land, nitrate is released from organic matter in spring through increased rate of mineralisation, and much may be lost through leaching of decomposition products in winter, due to increased precipitation and slow plant growth. After fertiliser applications of N (50 kg N ha^{-1}), P (50 kg P ha^{-1}) and K (100 kg K ha^{-1}) to blanket bog, under drained and undrained conditions (Burke, 1975), peak inorganic N concentrations in drain outflow and surface runoff occurred immediately after soil treatment. Surface runoff exhibited

a nitrate concentration of > 3 mg N L^{-1} and an TAN level of 20 mg N L^{-1}. In contrast, drainage outflow water had > 5 mg N L^{-1} of both NO_3^- and TAN. The increased level of P in fertilised soils has been associated with limited N mineralisation rates. After treatment of free-draining peat with NPK additions (Malcolm *et al.*, 1977), TAN loss was observed to be three times greater from peat treated with 200-400 kg P ha^{-1}, than from that with an addition of only 4.4 kg P ha^{-1}.

The fate of P additions to soils is influenced by soil pH, ash content, CEC (buffering capacity), phosphate sorption index, iron (Fe) and aluminium (Al) content. All affect P retention, CEC playing a crucial role (Cuttle, 1983) as it affects availability of cations for binding with the anion PO_4^{3-}. Both sorption and desorption of P in soils are influenced positively by nutrient and electrolyte concentration, the period of reaction and temperature (Barrow, 1983). Increasing temperature results in increased sorption and conversely, desorption (Barrow, 1979). The amount of P adsorbed by soil generally increases with concentration of P in solution, although this relationship is complex and heavily dependent upon pH. Presence of a more concentrated background electrolyte solution of other elements elevates sorption processes (Barrow *et al.*, 1980). Although P adsorption is dependent upon many parameters, through formation of relatively insoluble complexes, it is not easily lost from soil once sorbed. A longer period of uptake allows P to become more firmly bound and therefore difficult to desorb, although if the rate of P sorption has been high, desorption will occur more readily.

Local variations in soil structure may be significant influences on fates of fertiliser nutrients through their influence on pore water flow rates (Heathwaite, 1991). Occurrence and extent of preferential flow in larger water filled soil pores depends on the hydraulic conductivity of all other pore sizes in the soil and on density of rainfall. Degree of equilibration between soil zones of greater or lesser water mobility varies with the relative volume of these zones and the rates at which solute equilibrates with leaching water within a given area of low hydraulic conductivity (Barraclough *et al.*, 1983).

6.1.4 Indices of P sorption in soils

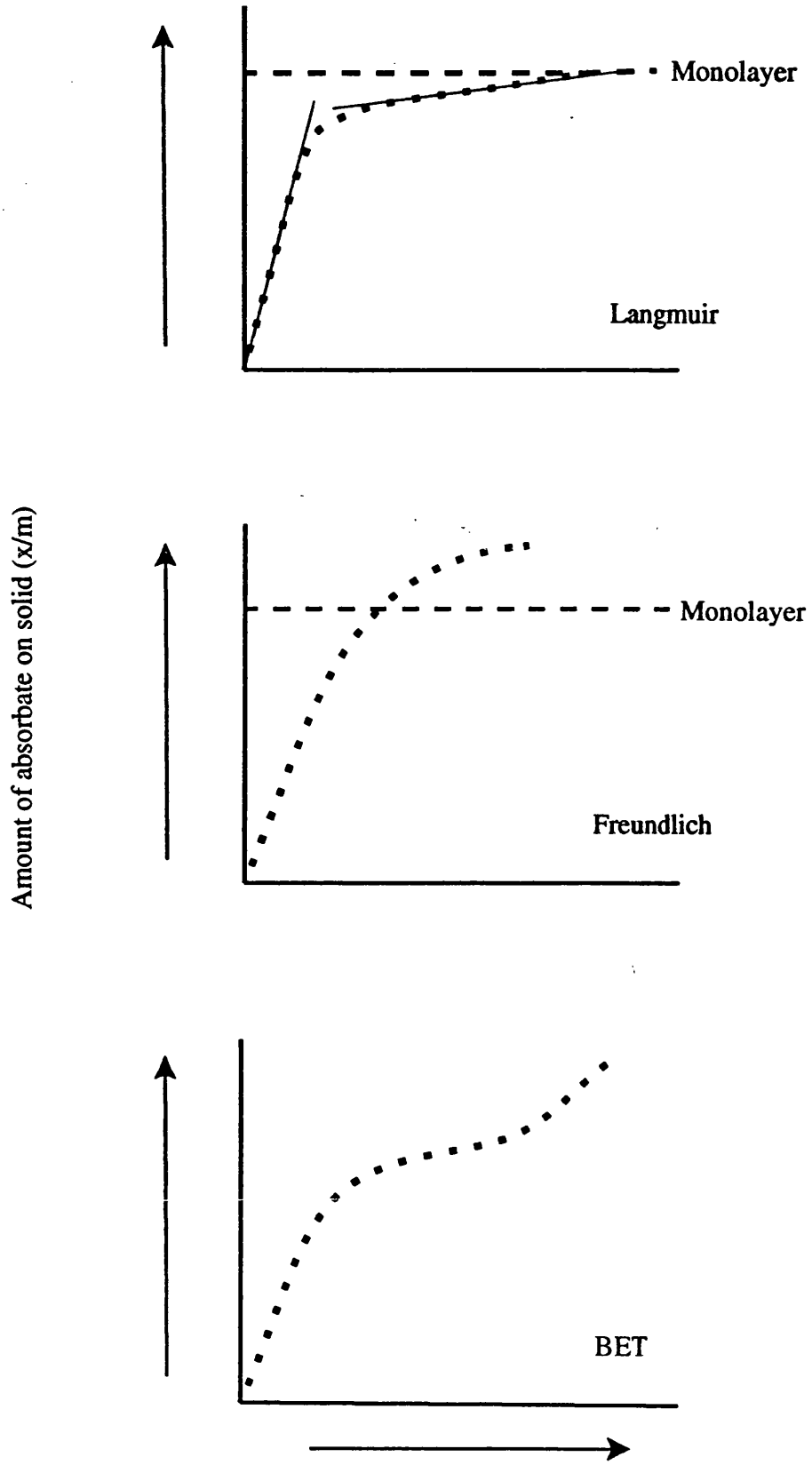
P in soil may be classified as P in solution, solid bound labile P, or solid bound non

labile P (Hartikainen, 1991). Since the fate of labile inorganic phosphate in soils is dependent upon sorption and desorption mechanisms, characterisation of soils in terms of these processes is useful for prediction of their behaviour during fertilisation. A soil sorption index may also take into account Quantity (Q) and Intensity (I), parameters which have been used in studies of plant P uptake (Bache and Williams, 1971). I is the P concentration in equilibrium solution and Q is the amount of labile P available when solution concentration is changed, *i.e.* it is equated with P sorbed plus P already sorbed in the field.

P uptake onto soil particles is dependent on quantity of adsorption sites and P affinity of the sites. P in solution moves onto vacant adsorption sites until an equilibrium is reached, between solution and solids. Conversely, when P is removed from soil solution through leaching or plant growth, P moves from its binding sites into solution to dynamic equilibrium. Intensity and quantity of labile P and the equilibrium buffering capacity of a soil are related to the P adsorption capacity of the soil and additions of P which have been made to the soil (Holford and Mattingly, 1976a). Changes in Q and I occur between soils, depending on the slope of the sorption isotherm which shows the buffering capacity of a soil in relation to P addition (Bache and Williams, 1971; Holford and Mattingly, 1976a).

Adsorption isotherms show the amount of adsorbate as a function of the equilibrium concentration of the added solution and are commonly used to quantitatively illustrate solute adsorption by solids at constant temperature and pressure. The P buffering capacity of a soil is the relationship between the concentration of P in soil solution and the amount of adsorbed P. These parameters are known as intensive and extensive respectively. The shape of the isotherm in adsorption studies is dependent on the affinity of the soil for the adsorbate. There are three equations which are generally used in describing data from adsorption tests: Langmuir, Freundlich and Brunauer-Emmett-Teller (BET) equations (Figure 6.1) (Bohn *et al.*, 1989). According to Bohn *et al.* (1989), the shape of the Langmuir adsorption curve is well established when considering P uptake by soil. The form of the curve is such that it can be divided into two distinct straight lines.

Figure 6.1 Three characteristic forms of adsorption test results



There may be two types of uptake sites of different binding strength and adsorption maxima or two separate processes of uptake on similar sites (Bohn *et al.*, 1989). It is thought that high energy and low energy P adsorption surfaces exist (Bohn *et al.*, 1989; Holford and Mattingly, 1976b).

For most soils, sorption continues to increase slowly with increasing P concentration and time, but an obvious end-point of maximum adsorption is difficult to ascertain. The sorption maximum determined experimentally is generally greater than, though may be proportional to, that calculated from tangents to Langmuir isotherms (Bache and Williams, 1971). Maximum buffer capacity has been recommended as a P sorption index by Holford and Mattingly (1976a). Isotherm slopes should be compared at the same equilibrium concentration, since uptake varies with concentration (Bache and Williams, 1971). Several P concentrations of addition are required to produce data for an isotherm, but the simplest way of comparing soils is through addition of a single P concentration. Isotherm slopes of different soils may intersect, so that whilst sorption of P at a particular concentration may be the same for various soils, P uptake rate is actually different. However, this is considered only to occur at low equilibrium concentrations, due to differences in the initial amount of exchangeable P present in different soils. At low concentrations, varying actual concentration due to this differing residual may be taken into account by plotting mass P sorped/eqilibrium concentration or log equilibrium concentration (Bache and Williams, 1971).

Tangents to Langmuir isotherms, mass of adsorbate/log equilibrium P concentration, mass of P sorped at a single equilibrium P concentration or a single P addition concentration are all well correlated with isotherm slope. However, single addition P concentration is the most convenient way of examining soil P uptake characteristics when there are many soils to examine in a limited time period.

6.2 MATERIALS AND METHODS

6.2.1 Site locations and field methods

In October 1991, sites at which samples of soil were taken were chosen from catchments of twelve of the thirty one lochs surveyed in order to encompass a range of soil types (Table 6.1). In October 1992 up to seven soil sampling pits were created in each of the five chosen catchments.

Table 6.1 Map grid references of soil sampling sites of the 1991 soil survey

Site	Grid reference	Site	Grid reference
Arthurs 1	HU272565	Huxter	HU556619
Arthurs 2	HU272565		
Brough 1 (Yell)	HP531027	Lunga	HU230532
Brow 1A	HU385162	Spiggie 1A	HU375175
Brow 1B	HU385162	Spiggie 1B	HU376174
		Spiggie 2	HU366160
Bu 1	HU548619		
Bu 2	HU549621		
Cliff 1	HP605138	Tingwall 1	HU422433
Cliff 2	HP600102	Tingwall 2	HU413427
Helliers 1	HP611051	Turdale 1	HU307532
Huesbreck 1	HU388139	Turdale 2	HU307533

KEY TO FIGURE 6.2 (overleaf)

Letter codes

Deep blanket peat	A
Peaty gleys, peat; some peaty podzols and peaty rankers	B
Peaty gleys, peaty podzols, peaty rankers	C
Peat, peaty gleys, peaty podzols	D
Magnesian gleys, some brown magensian soils	E
Magnesian gleys, some magnesian soils	F
Peaty gleys, peat, some peaty rankers and peaty podzols	G
Alpine soils; some rankers, subalpine soils and peat	H
Basin and valley peat	I
Brown forest soils; some brown rankers and non calcareous gleys	J
Peaty gleys, peaty podzols and peaty rankers	K
Peaty gleys, peaty podzols and some peat	L
Peaty podzols, peaty rankers	M
Blanket peat; some peaty gleys	P
Peat with some peaty gleys, peaty podzols and peaty rankers	R
Peaty gleys, peat; some peaty podzols and peaty rankers	S
Deep blanket peat	T
Peaty gleys, non calcareous gleys; some peat, peaty podzols and rankers	U

Number Codes

Numbers refer to sampling sites in text and tables

Shading/symbol

Sampling site ■

Loch surface 

Other standing waters 

Source: Data from MISR (1985)

Figure 6.2 Soil sampling sites in Shetland catchments, 1992

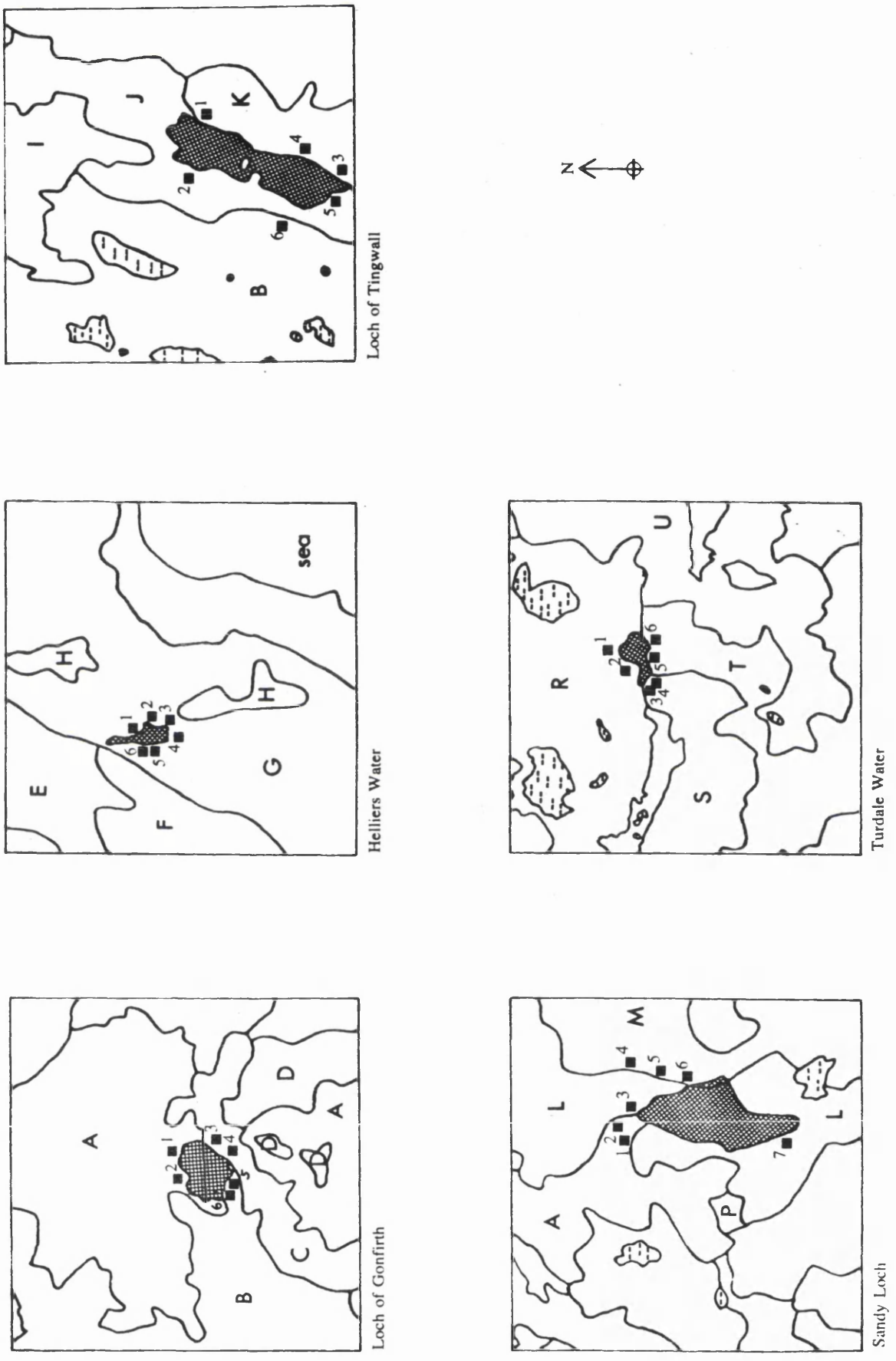


Figure 6.2 illustrates the positions of soil sampling sites within each of the catchment areas examined in 1992. At each site a pit was excavated in order that soil horizons be identified, depth of each horizon measured and samples of soil obtained. Soil was stored in polyethylene bags and remained refrigerated until further analysis on return to the laboratory.

6.2.2 Determination of pH, water and organic contents of soils

In the laboratory, soils were spread out on plastic sheeting and air dried at temperatures not exceeding 30°C. Lumps of soil were broken up to assist drying. Sieving was undertaken after the soil was dry and removal of the majority of stones and vegetation complete. A mortar and pestle were used to grind soil, taking care not to break down stones, prior to passage through a 2 mm mesh. The sieved samples were stored in glass jars.

Percentage water content (%WC) of each soil was determined by weighing 10 g air dry soil on a (type) balance before and after oven drying overnight at 110°C. Percentage loss on ignition (%LOI) of these samples was calculated after they had been reweighed. Vitreous basins containing these subsamples of soil were placed in a muffle furnace and heated at 500°C for 6 hours. After cooling in a desiccator, samples were reweighed on the same balance. Both %WC and %LOI were calculated as a percentage of oven dry soil weight. This method of calculating %WC can result in values in excess of 100%. For example, when an air dry soil sample weighing 10.0 g contains 4.7 g soil and 5.3 g water, the %WC is calculated as 112.8%, rather than 53%.

pH measurement was carried out using air dry soil. 10 g of soil was weighed into a beaker and 25 mL distilled water added. The mixture was stirred intermittently by hand for 15 minutes using a glass rod. The resulting paste was then agitated and the pH probe inserted. The pH was determined after 30 seconds to allow the Corning Model 5 Meter reading to stabilise.

6.2.3 Phosphorus adsorption studies

Of the soils sampled in 1992, five were chosen on the basis of field description, pH, water content and %LOI to give a range of soil types. 1 g of each soil was weighed

into a screw-capped glass bottle. Standard solutions of KH_2PO_4 were made up in 0.01 M $CaCl_2$ solution. These eleven solutions contained standards at 10 mg P L^{-1} intervals within the range 0-100 mg P L^{-1}. Each soil was treated with 25 mL of each solution. The bottles were then shaken continuously on an end-over-end shaker for 18 hours, before soil-solution mixtures were filtered through Whatman Nº1 filter papers. Filtrate was collected in polyethylene bottles and stored frozen until analysis. Procedure blanks were obtained by passing 0.01 M $CaCl_2$ through the above schedule. After dilution to within the standard range, P was determined as molybdate reactive P, using the techniques described in Chapter 2. Spectrophotometric determinations were carried out using a 1cm cell pathlength.

From results of the above investigation, P solution concentrations of 0, 20 and 100 mg P L^{-1} were chosen as treatments for the remaining soil types. Soils which had already received fertiliser additions in the field were given the control treatment of 0.01 M $CaCl_2$ only, in order to estimate P losses, resulting from their previous fertilisation in the field. Procedures were undertaken as described above.

6.2.3.1 Relationships between soil P retention and pH, %LOI and %WC

Linear regression analysis was carried out in order to ascertain whether significant relationships existed between each of the parameters of pH, %WC and %LOI (as independent variables) and each of water soluble P content and adsorption at the different treatment levels (as dependent variables).

6.3 RESULTS

6.3.1 Characteristics of soils collected in 1991

Results of the determinations of pH, %WC and %LOI of soils sampled in 1991 are presented in Table 6.2.

6.3.1.1 The range of pH in Shetland soils

Soils collected from twelve of the thirty one loch drainage basins showed a wide pH range from acidic to slightly acidic conditions (of more than 3.00 pH units). Peat from the catchment of Loch of Brough (Yell) had the lowest pH at pH 3.69. Soils in the catchments of three other lochs had pH levels of $\leq$ 4.00.

Table 6.2 **Characteristics of catchment soils sampled during the 1991 soil survey**

Site	Horizon	Depth (cm)	pH	%WC	%LOI
Arthurs 24/10/91					
1	O	0-8	4.57	14.0	32.4
2	O	0-15	5.09	2.1	8.0
Brough (Y) 25/10/91					
1	P	0-29	3.69	29.5	91.2
Brow 27/10/91					
1A	O/A	0-6	4.96	n.d.	n.d.
1A	B_w	6-16	4.81	3.6	17.2
1B	O	0-20	4.81	5.5	28.2
Bu 26/10/91					
1	O	0-16	4.87	73.8	90.4
1	Bh/E	16-20	4.32	3.2	36.8
2	O	0-26	4.30	29.3	94.4
Cliff 25/10/91					
1	O	0-20	4.25	4.4	25.1
1	E	20-23	5.02	1.7	5.3
1	E/Bs	23-34	4.97	2.3	6.5
1	Bs1	34-44	5.45	1.0	2.8
1	Bh	44-48	5.20	1.3	3.3
1	Bs2/C	>48	5.51	2.9	5.8
2	A	0-11	5.10	13.1	67.9
2	B1g	11-26	5.34	10.5	24.0
2	B2g	26-38	5.82	1.8	3.2

Table 6.2(cont.)

Site	Horizon	Depth (cm)	pH	%WC	%LOI
Helliers 25/10/91					
1	A	0-8	4.35	12.2	32.5
1	B	8-16	4.67	4.0	20.5
Huesbreck 27/10/91					
1	Ap	0-18	6.56	1.1	7.0
1	B_w1	18-27	5.80	0.3	1.3
1	B_w2	>27	6.90	0.1	0.9
Huxter 26/10/91					
1	P	0-20	3.99	34.3	96.8
Lunga 24/10/91					
1	P	0-9	4.08	12.0	96.8
1	P	0-10	4.50	19.7	86.1
Spiggie 27/10/91					
1A	A	0-28	5.40	9.0	13.7
1B	E	5-14	4.98	3.2	16.3
2	O	0-10	4.18	9.6	85.9
Tingwall 27/10/91					
1	O	0-15	3.98	11.0	95.2
1	Bg	>15	3.79	8.5	93.9
2	A	0-12	5.40	5.4	15.6
2	B_w1	12-39	5.59	6.7	9.5
2	B_w2	39-79	5.86	4.0	7.1
2	C	>79	5.00	2.7	6.3

Table 6.2(cont.)

Site	Horizon	Depth (cm)	pH	%WC	%LOI
Turdale 24/10/91					
1	O	0-23	4.19	11.5	95.7
1	B	>23	4.00	13.0	95.8
2	O	0-15	3.95	12.7	97.0
2	B2	15-40	4.00	11.9	97.0

These samples were taken from Loch of Huxter peat, Tingwall Site 1 (O and Bg horizons), Turdale Site 1 (B horizon) and Turdale Site 2 (O and B2 horizons). Soils from watersheds of Lochs of Cliff, Spiggie, Brow, Tingwall, Turdale Water, Helliers Water, Lunga Water, Bu Water and Arthur's Loch all fell into the range pH 4.08 to pH 5.00, these values referring to Lunga Water surface peat and Loch of Tingwall Site 2, C horizon respectively. Drainage basins of Lochs of Cliff, Spiggie, Tingwall and Arthur's Loch also incorporated soils within the range pH 5.02 (Cliff Site 1, E horizon) to pH 5.86 (Tingwall Site 2, B_w2 horizon). Of the nine different horizons sampled at Loch of Cliff, seven were in this category. Loch of Huesbreck soil from the B_w1 horizon with a pH of 5.80 also came within this range and the most alkaline soils collected were obtained from this catchment. pH levels of 6.56 and pH 6.90 were recorded in soil of the Ap and B_w2 horizons respectively.

6.3.1.2 Water content of catchment soils

Soil from Bu Water Site 1 had a %WC in the O horizon soil of 73.8%. This was in excess of all other soil %WC observed, the next highest being Loch of Huxter peat with a %WC of 34.3%. Also notably high were %WCs of 29.5% and 29.3% for Brough (Yell) peat and Bu Water Site 2, O horizon respectively. Other soils which were found to have %WC > 10% were collected from the following loch catchments:- Arthur's, Cliff, Helliers, Lunga and Tingwall. Soils with the lowest %WCs were from the drainage basins of Lochs of Huesbreck, Spiggie, Brow, Tingwall, Cliff, Helliers Water, Bu Water and Arthur's Loch. These watersheds incorporated soils with %WC < 10%. Least moisture was found in samples from Loch of Huesbreck catchment, horizons B_w1 and B_w2 having water contents of 0.3% and 0.1% respectively.

6.3.1.3 Organic content of drainage basin soils

The maximum recorded %LOI of the samples taken was for Turdale Site 2. Organic matter constituted 97% of both O and B2 horizons. Of thirty eight determinations, thirteen soil samples were found to have %LOI of > 80%. Included in this category were soils from the following catchments: Lochs of Huxter, Brough (Yell), Spiggie, Tingwall, Lunga Water, Bu Water and Turdale Water. Those exhibiting > 80% %LOI were mostly O horizons or peats; all peat samples contained > 80% organic matter. Conversely, %LOI of seventeen samples was < 20%. These less organic soil

samples were taken from the drainage basins of Lochs of Cliff, Spiggie, Brow, Tingwall, Huesbreck and Arthur's Loch. Least organic was the soil from Loch of Huesbreck, the B_w1 and B_w2 horizons exhibiting 1.3% and 0.9% %LOI respectively. Soil horizons taken from Bu Water and Helliers Water, Lochs of Brow and Cliff and Arthur's Loch were found to have %LOI figures intermediate between highly organic and mineral soils. Loch of Cliff Site 2, A horizon showed the highest organic content of these soils (67.9%), whereas Helliers Water Site 1, B horizon was only slightly organic in comparison (20.5%).

The characteristics of %WC, %LOI and pH were found to vary both with depth in individual soil profiles, diversity occurring between horizons and within catchment areas. For example, although watersheds of Lochs of Cliff, Spiggie and Tingwall incorporate a large proportion of mineral soils, relatively wet, organic, acid soils are also present within these drainage basins.

6.3.2 Characteristics of soils collected in 1992

Results of pH, %WC and %LOI determinations in soil samples obtained from the 5 catchments of the 1992-1993 section of this study are presented in Table 6.3.

6.3.2.1 Loch of Gonfirth

The pH of soils collected in the Loch of Gonfirth catchment area ranged from pH 3.85 in soil taken from 24-52 cm depth at Site 6, to pH 4.91 in soil from site 1, 0-20 cm. Generally, soils were characterised as being highly organic. With the exceptions of Sites 3 and 4, all %LOI determinations were >90%, greatest organic content of 97.5% being present in soil from Site 2, 20-50 cm. %LOI of soil from sites 3 (0-31 cm) and 4 (0-33 cm) was 65.5% and 54.1% respectively. %WC was greatest in soil from Site 1 (20-50 cm), 86.6% being recorded, although only 11.6% of the soil sample from Site 6 (24-52 cm) was found to be water.

6.3.2.2 Helliers Water

The pH of soil from Helliers Water catchment area was generally higher than pH of soils from Loch of Gonfirth drainage basin. Maximum pH recorded was pH 5.81 (Site 5, 22-23 cm), minimum pH 4.48 (Site 3, 0-8.5 cm).

Table 6.3 Characteristics of catchment soils surveyed in October 1992

Loch of Gonfirth 12/10/92

Site	Depth (cm)	pH	%WC	%LOI
1U	0-20	4.91	18.4	95.6
1L	20-50	4.00	86.8	94.7
2U	0-20	4.65	50.1	97.2
2L	20-50	3.82	35.3	97.5
3	0-31	4.40	22.8	65.5
4	0-33	4.73	14.4	54.1
5U	0-25	4.72	13.6	96.6
5L	25-46	4.00	56.5	97.0
6U	0-24	4.06	14.4	96.7
6L	24-52	3.85	11.6	97.4

Helliers Water 10/10/92

Site	Depth (cm)	pH	%WC	%LOI
1	0-19	5.28	23.3	36.2
2	0-20	4.91	7.0	30.4
3U	0-8.5	4.48	42.5	94.5
3L	8.5-18.5	4.56	32.4	56.5
4U	0-7	4.85	16.5	80.5
4L	7-16	4.63	9.8	38.6
5U	0-22	5.35	24.2	37.3
5L	22-23	5.81	1.2	3.1
6U	0-15	5.21	5.7	17.3
6L	15-22	5.42	0.6	2.3

Sandy Loch 14/10/92

Site	Depth (cm)	pH	%WC	%LOI
1U	0-20	3.80	14.3	92.7
1L	20-50	4.17	21.2	96.7
2U	0-20	4.50	20.7	96.9
2L	20-50	4.25	20.5	97.6
3U	0-20	3.98	86.1	84.9
3L	20-50	4.16	49.3	86.0
4	0-10	6.15	7.8	43.4
5U	0-10	4.05	29.5	83.0
5L	10-26	3.80	189.4	97.3
6U	0-21	4.25	6.4	49.5
6L	21-30	4.56	3.2	26.5
7U	0-12	5.25	2.1	10.6
7L	12-29	5.03	2.8	12.2

Table 6.3(cont.)

Loch of Tingwall 14/10/92

Site	Depth (cm)	pH	%WC	%LOI
1U	0-14	4.02	19.2	91.9
1L	14-34	4.18	139.8	90.4
2	0-15	5.88	5.3	13.3
3	0-20	5.36	4.2	15.4
4U	0-8	4.90	3.8	26.2
4L	8-21	5.00	2.8	17.9
5	0-14	5.25	2.5	8.9
6U	0-10	5.29	3.1	15.5
6M	10-19	5.20	2.3	9.1
6L	19-50	5.34	3.1	9.1

Turdale Water 12/10/92

Site	Depth (cm)	pH	%WC	%LOI
1U	0-10	4.56	19.7	93.9
1L	10-20	4.45	14.7	97.4
2U	0-10	4.58	16.8	93.9
2L	10-17	4.80	105.8	55.1
3U	0-9	4.02	15.7	96.4
3L	9-50	4.62	29.0	97.5
4U	0-10	4.14	44.6	97.7
4L	10-50	4.40	20.7	97.1
5U	0-10	4.35	16.0	97.3
5L	10-50	4.80	15.8	97.7
6U	0-20	3.80	35.3	95.4
6L	20-50	3.84	125.5	96.4

Organic content of Helliers Water soils was usually less than that of Gonfirth soils. %LOI ranged from 2.3% at Site 6, 15-22 cm, to 94.5% for soil from Site 3, 0-8.5 cm. A %LOI of 2.3% was the lowest value recorded in any soil tested in 1992. %WC varied between 0.6% in soil from Site 6 (15-22 cm) to 42.5% in the wettest soil from Site 3 (0-8.5 cm).

6.3.2.3 Loch of Tingwall

Results of pH determinations showed a range of pH 4.02-5.36 in soil from the east side of Loch of Tingwall drainage basin and a gradation from pH 5.20-5.88 on the west side. Lowest recorded pH was pH 4.02 in soil from site 1 (0-14 cm) and the maximum of pH 5.88 was found in Site 2 (0-15 cm) soil. Least organic soil was collected at Site 6, where %LOI was 9.1% for soil samples between 10-19 cm and 19-50 cm depth. In contrast, soil from Site 1 (0-14 cm) contained 91.9% organic matter. %LOI was greater in soil samples taken from the eastern part of the catchment area. Relatively low moisture content was found in all Tingwall soils examined, excluding soil from Site 1, 14-34 cm depth, of which 139.8% was water with respect to oven dry weight. All other samples had %WCs of between 2.3% (Site 6, 10-19 cm) and 19.2% (Site 1, 0-14 cm).

6.3.2.4 Sandy Loch

Soils collected at Sandy Loch showed a range of pH values from pH 3.80 in samples from Site 1 (0-20 cm) and Site 5 (10-26 cm) to pH 6.15 in top-soil taken at Site 4. Maximum pH recorded for an unimproved soil was pH 4.56 for soil from Site 6 (21-30 cm). Organic content was > 80% in all samples of unimproved soil except that from Site 6. %LOI in the deeper soil of this site was 26.5%, rising to 49.5% in the surface soil. Greatest %LOI found in the Sandy Loch watershed was 97.6% in Site 2 (20-50 cm) soil. %WC of soils from this catchment was found to range from 2.1% in previously improved soil (Site 7, 0-12 cm) to 189.4% of soil oven dry weight in soil from Site 5 (10-26 cm). The latter was the greatest recorded %WC of the 1992 survey.

6.3.2.5 Turdale Water

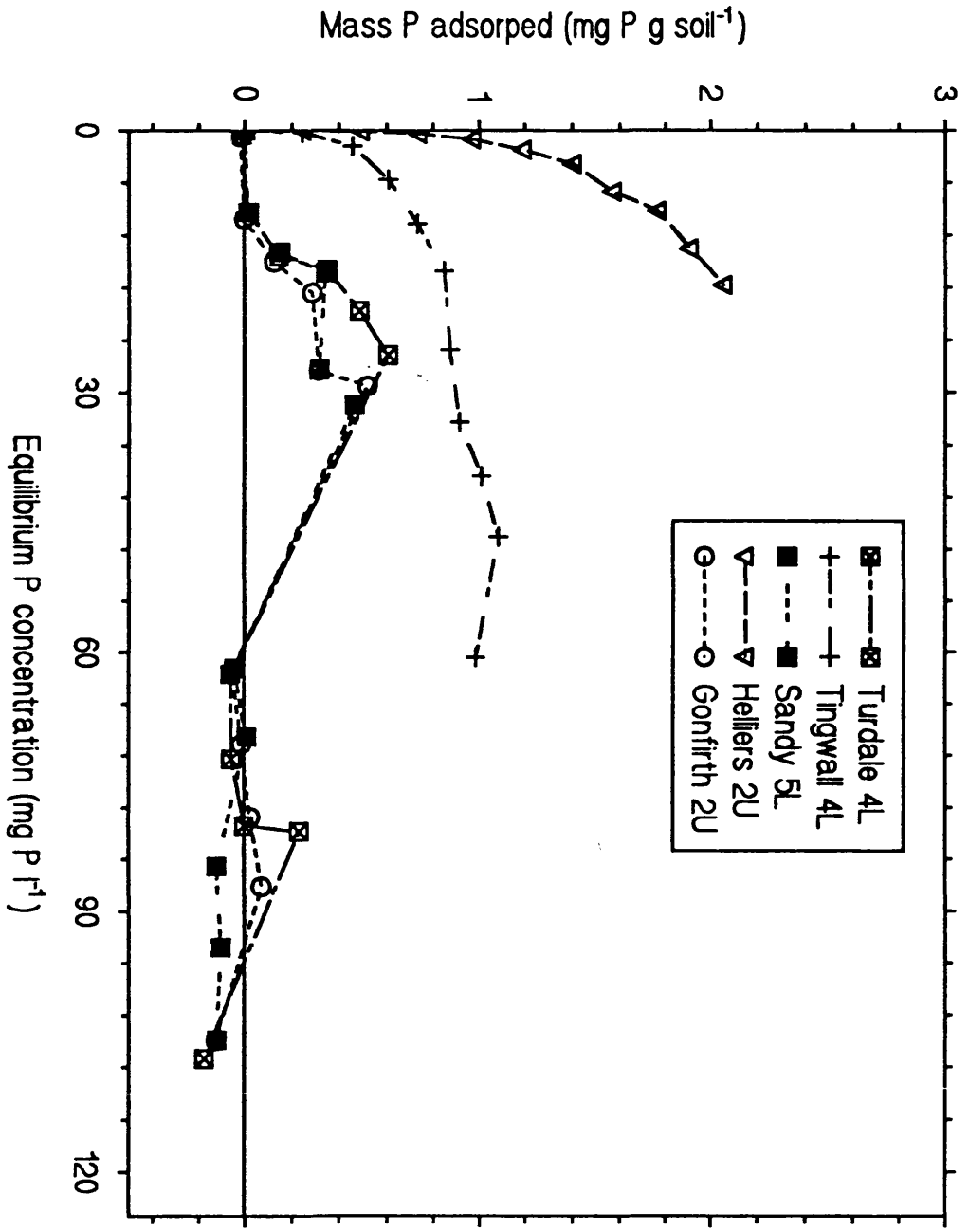
Soil taken from Site 6 (0-20 cm) was at pH 3.80, the most acidic in the 1992 survey.

Maximum pH 4.62 was determined for Site 3 (9-50 cm) soil. Turdale soils may be compared to those of the Loch of Gonfirth drainage basin as pH was found to remain below pH 5.00 in both cases. The range of pH values in Turdale Water catchment soils was more acid than that of any of the other four loch catchment areas. %LOI was consistently high, all samples except that of Site 2, 10-17 cm (55.1%) containing > 90% organic matter. Greatest %LOI was determined in soils from Sites 4 (0-10 cm) and 5 (10-50 cm). At 97.7% this was the maximum percentage of organic matter found in soils examined in 1992. Maximum %WC of Turdale soils was 125.5% in soil from Site 6 (20-50 cm). Moisture also accounted for 105.8% of Site 2 (10-17 cm) soil on an oven dry basis. In the remaining soils %WC was within the range 14.7-44.6% in soil from Sites 1 (10-20 cm) and 4 (0-10 cm) respectively.

6.3.3 Soil phosphorus adsorption isotherms of test samples from each of the five survey watersheds

P adsorption isotherms for the five soils treated with solutions of 0 mg P L^{-1} to 100 mg P L^{-1} are illustrated in Figure 6.3. Additions of P to soil from Helliers Water catchment area (Site 2) resulted in increased adsorption of P with increased addition. P uptake was more efficient in this soil than the other test soils. Soil from Loch of Tingwall drainage area (Site 4L) also showed increasing uptake of P with increased concentration of P in the experimental solution, although maximum P retention occurred at a treatment level of 90 mg P L^{-1}, rather than there being a continual upward trend in P adsorption, as observed with soil from Helliers Water catchment area. Uptake of P by this soil was nevertheless more efficient than that of any of the remaining three soils. Soil samples from the watersheds of Sandy Loch (Site 5L), Turdale Loch (Site 4L) and Loch of Gonfirth (Site 2U) exhibited little or no trend in adsorptive capacity at the different treatment levels. At lower concentrations of P addition ($\leq$ 50 mg P L^{-1}), retention of P by these three soils followed similar rates of increase, but at subsequent higher treatment levels ($\geq$ 60 mg P L^{-1}) P adsorption failed to follow an upward relationship with increased additions of P. In summary, the two more mineral soils were relatively efficient in their adsorption of P, whilst the organic soils tested were comparatively inefficient.

Figure 6.3 **Adsorption isotherms derived for the soils of the five study catchments, 1992**



Only two of these five test soils released water soluble P when the treatment P concentration was 0 mg P L^{-1}. Turdale Site 4L soil desorption was 0.01 mg P g $soil^{-1}$ and that of Gonfirth Site 2U was 0.02 mg P g $soil^{-1}$.

6.3.4 Phosphorus retention capacity of soils collected in 1992

Means of adsorption and desorption of P by soils collected in 1992 are presented in Table 6.4.

6.3.4.1 Loch of Gonfirth

In contrast to other Gonfirth soils tested, soil samples from Sites 1L and 3U did not release any water soluble P. Retention of P increased as P concentration of the treatment increased in soils from Sites 1U and 3U. However, adsorption of P was poor in all soils tested, with the exception of that from Site 3U. In terms of P uptake, the latter was comparable with soils from the Helliers Water catchment area.

6.3.4.2 Helliers Water

Water soluble P content was undetectable in all soils examined. Highest P accumulation at both addition levels occurred in experiments involving the sample from Site 2U. Least efficient in retention of P was soil from Site 3U, which was comparable with soils from the Sandy Loch catchment area. All remaining soils were relatively efficient at P uptake, although efficacy of P retention in the soils was greater when the P addition was 20 mg P L^{-1}, rather than at 100 mg P L^{-1}.

6.3.4.3 Loch of Tingwall

Release of water soluble P was recorded for only one Tingwall soil sample of those examined. This soil also showed poorest adsorption capacity in 20 mg P L^{-1} and 100 mg P L^{-1} treatments in comparison with the other three soils tested in these P solutions. Generally, amount of P adsorped increased as P in the added solution increased, though efficacy of uptake was greater in 20 mg P L^{-1} than in 100 mg P L^{-1} solution. Soils from Sites 3 and 4 were relatively efficient in retention of P, being comparable with those of the Helliers Water catchment area in this respect.

Table 6.4 Mean adsorption and desorption of phosphorus by catchment soils obtained during 1992 survey (mg P g soil^{-1})

Catchment	Soil sample site									
Treatment										
Gonfirth	**1U**	**1L**	**2U**	**2L**	**3U**	**5U**	**5L**			
0	-0.02	0.00	-0.02	-0.04	0.00	-0.03	-0.01			
20	+0.12	+0.07	+0.12	+0.05	+0.41	+0.08	+0.08			
100	+0.30	+0.04	-0.13	-0.29	+1.21	-0.05	+0.02			
Tingwall	**1U**	**1L**	**2**	**3**	**4U**	**4L**	**5**	**6U**	**6M**	**6L**
0	-0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	+0.02	+0.17		+0.41	+0.47	+0.45				
100	+0.06	+0.27		+0.40	+0.58	+0.98				
Helliers	**2U**	**3U**	**3L**	**5U**	**5L**	**6U**	**6L**			
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00			
20	+0.50	+0.09	+0.35	+0.49	+0.31	+0.35	+0.24			
100	+2.06	+0.03	+0.69	+1.73	+0.29	+0.64	+0.21			

Table 6.4(cont.)

Sandy	**1U**	**1L**	**3U**	**3L**	**4U**	**5U**	**5L**	**7U**	**7L**
0	-0.03	-0.03	0.00	0.00	0.00	-0.03	0.00	0.00	0.00
20	+0.03	+0.02	+0.04	+0.11	+0.06		+0.15		
100	-0.04	-0.16	+0.08	+0.14	-0.01		-0.12		

Turdale	**1U**	**1L**	**2U**	**2L**	**4U**	**4L**	**6U**	**6L**
0	-0.04	-0.07	-0.02	0.00	-0.03	-0.01	-0.04	-0.01
20	-0.04	-0.05	+0.22	+0.48	+0.02	+0.14	+0.01	-0.01
100	-0.22	-0.15	+0.48	+1.82	-0.16	-0.18	-0.09	+0.06

Treatments of 0, 20 and 100 mg P L^{-1}, as described in Section 6.2.3, correspond to 0, 0.5 and 2.5 mg P g $soil^{-1}$.

KEY:

\+ net adsorption of P
\- net desorption of P

6.3.4.4 Sandy Loch

Soil samples from Sites 1U, 1L and 5U released 0.03 mg P g soil^{-1} water soluble P when treated with 0 mg P solution. All other soils studied (from Sites 3U, 3L, 4, 5L, 7U and 7L) retained their associated P within their structure when treated with P free solution. Adsorption of P by soils from the Sandy Loch catchment area was inefficient. Soils from Sites 3L and 4U exhibited increased retention of P with increased concentration of P in the treatment solution. Nonetheless, the actual percentage of P added to the soil which was retained was low (3.2-22.0%) and in both soils, the proportion of treatment P retained was lower at the higher treatment level.

6.3.4.5 Turdale Water

Generally, soils from the Turdale Water catchment area exhibited poor P uptake in the treatments given. There were two soil samples which did not retain P in any of the three treatment media. Samples from Site 1 released water soluble P regardless of ambient P solution concentration. In contrast, soil from Site 2 adsorped more P as P concentration of the treatment increased. In addition, unlike the other soils from this drainage area, soil from Site 2L released no water soluble P in P free solution. Results from this soil were comparable with the more efficient soils of the Helliers Water watershed, discussed above.

6.3.5 Relationships of soil pH, %WC and %LOI with soil phosphorus adsorption capacity

Linear regression analysis revealed that there was no relationship between %WC and water soluble P release from the soils. Neither was %WC related to P adsorption at either of the treatment P concentrations. Conversely, significant relationships were found between %LOI and P adsorption/release by soils in the three treatment media (Table 6.5).

All three relationships were significant at $p < 0.001$, but the regression of %LOI with soil P adsorption in 20 mg P L^{-1} solution was most significant. The correlation coefficient of this linear equation was -0.77 and the standard error of the estimate 0.11 (Table 6.5).

Table 6.5 Relationships between LOI and P adsorption in catchment soils receiving different P treatments

Treatment (mg P L^{-1})	Relationship	$p<$	r	se	R^2(%)	F
0	y = 0.0003x - 0.0054	0.001	0.60	0.014	36.3	22.2
20	y = -0.0041x + 0.47	0.001	-0.77	0.110	59.3	45.0
100	y = -0.01x + 1.1	0.001	-0.56	0.510	31.6	14.3

where:

x is the %LOI of the soil
y is expressed in mg P g $soil^{-1}$
p is the significance level
r is the correlation coefficient
se is the standard error of the estimate
R^2 is the percentage variability in y explained by x
F is the F value

Table 6.6 Relationships between pH and P adsorption in catchment soils receiving different P treatments

Treatment (mg P L^{-1})	Relationship	$p<$	r	se	R^2(%)	F
0	y = -0.013x + 0.07	0.01	-0.47	0.015	22.0	11.0
20	y = 0.16x - 0.54	0.01	0.54	0.15	29.3	12.8
100	y = 0.39x - 1.45	0.05	0.39	0.57	15.3	5.6

where:

x is the soil sample pH

Correlation coefficient of the regression of %LOI *vs* water soluble P released was 0.6, whilst the standard error of the estimate was the lowest of the three linear equations at 0.014 (Table 6.5). Least significant was the regression of %LOI *vs* P adsorption in 100 mg P L^{-1} solution. This relationship had a correlation coefficient of only -0.56 and had the greatest standard error of 0.51 associated with it (Table 6.5). It should be noted that despite the significance of these relationships, there is a high degree of scatter around the regression slope, but also that P adsorption was always low when %LOI > 80%.

Following linear regression analysis, significant equations were also observed between pH and soil P release/adsorption in different treatments (Table 6.6). These relationships were found to be significant at $p < 0.01$, $p < 0.01$ and $p < 0.05$ respectively and are therefore not as significant as the regressions of %LOI and P adsorption/release rates (Table 6.6).

Standard error of the estimate ranged from 0.015 for the pH *vs* P release equation to 0.57 for the relationship between pH and P adsorption in 100 mg P L^{-1} solution. The latter also had the lowest correlation coefficient of 0.39 compared to the highest for these pH dependent equations of 0.54 associated with P adsorption in 20 mg P L^{-1} solution (Table 6.6). As with the %LOI *vs* P adsorption relationships, although significant, the pH *vs* P adsorption regression slope had a high degree of scatter around it. However, it is evident that soils with pH around pH 4.00 are poor in their P uptake capacity.

6.4 DISCUSSION

6.4.1 Relevance of field and laboratory procedures of soil characterisation

6.4.1.1 Measurement of %WC, %LOI and pH

Both %WC and %LOI were calculated as a percentage of soil oven dry weight, rather than as a proportion of air dry soil weight. %LOI is relevant only when considered in terms of the weight of the soil alone, as soil water is not a significant source of organic matter. Calculating %WC as a percentage of oven dry soil weight allows it to be expressed in a comparable way to %LOI, *i.e.* water and organic matter are regarded as discrete from the mineral constituents of the soil matrix. Whereas the

mass of mineral components of a soil may be relatively constant, the amount of organic matter and water present may vary considerably. Results of %WC and %LOI are, therefore, expressed using the more consistent technique of the two discussed.

Direct measurement of soil pH in the field would give more accurate data on conditions at a sampling site at the time of survey. However, use of air dried soil for this purpose is more manageable and has become standard procedure (Jackson, 1958). Different soil:water ratios are used in pH determinations and $CaCl_2$ or KCl solutions may be used instead of water, where relatively large variations in soil salt content exist. Generally, the more dilute a soil sample, the higher soil pH becomes. The increase in soil pH from 'sticky point' to a 1:10 soil suspension is commonly in the range 0.2-0.5 pH units, although it may be $\geq$ 1 pH unit when dealing with neutral or alkaline soils (Jackson, 1958). This means that pH values determined from soil suspensions tend to be over-estimates of actual conditions. Using a low soil to water ratio such as 1:2.5 utilised in the present study ensured relatively little change, whilst providing enough water to saturate peaty samples. Although a 1:1 ratio may be used (Jackson, 1958), this would not have fulfilled the latter requirement.

6.4.1.2 Applicability of a laboratory based approach to estimation of soil fertiliser nutrient losses

Although laboratory experiments involving nutrient additions to air dry soil are technically very different to field approaches to studying fertiliser losses, Rõmkens and Nelson (1974) found good agreement between results obtained from both approaches. Work with Russell sil soil suggested that DRP in runoff can be estimated through 'overnight equilibration of 0.5 g of soil with a 25 ml aliquot of 0.1 *N* NaCl'. However applicability of this estimation technique to other soil types was not investigated. Sharpley *et al.* (1977) found mean concentration of dissolved inorganic P from surface runoff events from Tokomaru silt loam (fragiaqualf) under permanent pasture to be correlated with inorganic P extracted using 0.1 M NaCl. Soil was treated in four different ways in the field experiments: undrained, unfertilised; drained, unfertilised; drained, fertilised; undrained, fertilised. Despite large variations in observed runoff P concentrations, the linear relationships obtained for each of the first three treatment pairings were similar. However, there was a considerable difference in regression slope for the undrained, fertilised soil. The relationship

between extractable inorganic P and runoff concentration was more complex when soil from different depths was studied. Considerable variation in soil adsorption capacity may occur between sites, but also within sites. This variability is largely because of differences in quantities of Fe oxides present in the soil (Holford and Mattingly, 1976b).

A proportion of P adsorbed becomes non-labile and non-exchangeable, this occurring more with time (Holford and Mattingly, 1976a). It is impossible to measure the exact quantity of P in equilibrium with the soil solution due to slow continuous exchange and effects of experimental variables such as soil:solution ratio, rate of shaking the suspension (Bache and Williams, 1971). When examining effects of time on water-extractable P content of mineral surface soils, Sharpley (1982) found it to be linearly related to P addition, irrespective of time after application, although the slope of the relationship decreased logarithmically with time (*i.e.* as time passes less P is water extractable), thereby making prediction of extractable P impossible by a simple exponential equation. However, percentage clay content and P sorption capacity of the soil were found to be good predicters of extractable P during the first two weeks after fertilisation.

Results of P enrichment experiments in the present study are therefore representative of quantity of P potentially leachable directly after fertiliser addition at each treatment level. Since no pH control was carried out in the experimental work, adsorption of P occurred at a pH related to initial soil pH and pH of added solution. In previous work of this nature, P sorbed/log equilibrium concentration at pH 6.5 in limed soil differed by only 3% from that of the same soil unlimed at pH 4.3 (Bache and Williams, 1971). The unbuffered approach was therefore chosen and was easily applicable to both calcareous and acid soils, but in more acidic soils adsorption figures may have been underestimated if pH were to be raised to recommended levels in the field.

6.4.1.3 Suitability of experimental P solution concentrations

Langmuir isotherms have been efficient in description of P adsorption from solutions of $< 10^{-3}$ M P (Holford and Mattingly, 1976b). Bache and Williams (1971) found that isotherm slopes for different soils at 10^{-4} M P were closely correlated with those

plotted using 10^{-3} M P and 10^{-5} M P. These concentrations correspond to the lower end of the range of solutions employed in the present study (10^{-3} M P corresponds to 31 mg P L^{-1}). Use of considerably higher P concentrations than this in the present work possibly accounts for isotherm shape not corresponding to the classical Langmuir form when P solutions were added to soils from Tingwall Site 4L, Sandy Site 5L, Helliers Site 2U and Gonfirth Site 2U (Figure 6.3). After soil P saturation point is reached, the relationship between P adsorped and equilibrium P solution concentration is no longer comparable with that at lower concentrations.

6.4.2 Water soluble P in soils

The quantities of TP in mineral and organic soils are generally within the ranges 0.02-0.2% and 0.01-0.2%, respectively (Allen *et al.*, 1974). In the present study, there was a tendency for organic soils to release soluble molybdate reactive P (DRP). As the plant matter in these soils is broken down, P mineralisation occurs. However, there are few binding sites for this P within the soil, or in the soil solution, so a portion of TP remains in soluble reactive form. The more mineral soils did not release P in this water soluble molybdate reactive form. It is likely that this was due to the superior adsorptive capacity of these soils, although the commonest forms of inorganic P in soils all have low solubility, so that dissolved P is generally restricted to concentrations up to 0.01-1.0 mg P L^{-1} (Etherington, 1982). In more mineral soils, fertiliser applications of water soluble phosphates may be precipitated in forms which are only slightly water soluble. This results in soil water having a low P concentration, therefore allowing little P to reach plant roots through movement of water through the soil. Plant uptake of fertiliser P is consequently dependent on P diffusion rate and proximity of root systems to P residues. The action of water soluble phosphate alone is slow. The result is that in one growing season, only a fraction of P added to the soil as fertiliser is actually taken up by plant roots.

6.4.3 Factors influencing P sorption capacity of soils

6.4.3.1 Effect of previous fertiliser applications on P adsorption

Investigations of P accumulation in 16 Finnish mineral soils have been carried out by Hartikainen (1989). Crops were mostly cereals, but peas and grass were also grown. Following seven years of cultivation, losses of NH_4F- extractable (Al bound) and NaOH-extractable (Fe bound) P from clay soils which had not received fertiliser

applications ranged from 22-69 kg P ha^{-1} (2-17 %). Losses of these P fractions from coarser soils were within the range 8-140 kg P ha^{-1} (2-17%).

H_2SO_4-extractable (Ca bound) P from 16 - 34 kg P ha^{-1} was lost from seven of the soils. In soils where P as superphosphate had been added at a rate of 30 or 60 kg P ha^{-1} yr^{-1} (210 and 420 kg P ha^{-1} total loadings respectively), Al-P and Fe-P increased in twelve of the sixteen soils. In four soils, no significant difference was found before and after P additions. The percentages of the total loadings of 210 kg P ha^{-1} which were found in these P fractions were within the range 11-83 %, whilst the corresponding range for a total loading of 420 kg P ha^{-1} was 11-88 %.

At higher fertiliser loadings, P was found proportionately more in NH_4F-extractable than in NaOH-extractable forms. However, Ca-P was found to increase in three soils only. It is suggested that Ca compounds may have been broken down by NH_4F earlier in the extraction procedure. This presumably might also account for the increase in NH_4F-extractable P.

Results of the present study showed previously fertilised grassland in the catchment of Loch of Tingwall to be retaining P as water soluble P was undetectable. The same occurred with soil from Sandy Loch Sites 7U and 7L, which were in an old area of reseeded land. All these soils followed the general pattern of low organic content and pH > 5.00. However, soils collected from reseeded areas in Turdale Water catchment area, *i.e.* Sites 1U, 1L and 2U, were found to release water soluble P. Soils from these three sites were highly organic, whereas in soil from Site 2L, %LOI was only 55.1% and pH was slightly greater than that of the other three samples (all were pH < 5.00) No release was recorded from soil at Site 2L.

P treatment of a soil reduces its P sorption capacity. When a soil has been previously fertilised in the field, the mass of P adsorbed by the soil at any solution equilibrium P concentration is less than it would be, had no earlier P addition occurred, *i.e.* isotherm slope is lower (Barrow, 1974). However, when initial exchangeable P present is taken into account, the pretreated soil exhibits the same isotherm characteristics as the same soil which has received no earlier P addition (Bache and Williams, 1971). The decrease in isotherm slope, as a result of earlier fertiliser

additions, indicates a reduction in the P buffering capacity of the soil (Barrow, 1974). Field trials have confirmed that greater loss occurs if previous fertilisation has taken place (Burke, 1975). However, reduction in P buffering capacity is not linearly related to the size of previous P application, as low P addition concentrations result in a proportionately greater effect than higher levels (Barrow, 1974). Presumably this occurs due to the finite number of P binding sites.

It is thought that with time following a P addition, either (a) P leaves the original adsorption sites to form crystals or to locate in less accessible places within the soil matrix or (b) P becomes more tightly bound or occluded in some way. Because the sorption curve has been found to change both position and slope this is indicative that at least a proportion of the P which becomes non-isotopically exchangeable continues to occupy adsorption sites (Barrow, 1974). This means that in soils where water soluble P was not detectable, assuming that it was not previously removed by water flow, P is occupying binding sites and therefore potential for uptake of P in any future fertiliser addition has been reduced. This indicates that not only is there a risk of P leaching from highly organic and acid soil, when P is added, but also from more mineral soils of higher pH which have previously received a fertiliser dressing.

6.4.3.2 The influence of soil type on P retention

In studies of the land use in the catchment area of the Loch of Harray in Orkney (Sinclair *et al.*, 1992), annual loss of P_2O_5 in water from fertilised grassland was approximately 3% of that applied in fertiliser at the lowest treatment rate and < 1% at a treatment rate of > 40 kg P ha^{-1}. However, agricultural land in this catchment area incorporated mineral soils. In the present study, soils high in organic matter have been found to be inferior to more mineral soils in terms of P uptake capacity. This is in agreement with previous studies of P retention in peaty soils. In their natural, undrained, unfertilised state, peat bogs are generally nutrient sinks, inputs exceeding losses to drainage (Malcolm and Cuttle, 1983). However, Burke (1975) investigated losses of NPK from blanket bog after fertiliser additions of N (50 kg N ha^{-1}), P (50 kg P ha^{-1}) and K (100 kg K ha^{-1}) under drained and undrained conditions. Losses of fertiliser P occurred through drainage water and surface runoff, peak P loss occurring in surface runoff immediately after fertilisation at the rates quoted above. Peak concentrations of P in drain outflow and surface runoff were > 10 and > 25 mg P

L^{-1} respectively.

Therefore, although loss of P was not great when related to amount added and peak discharge of nutrients was of short duration, a pulse of nutrients at the concentrations given might be significant to a water body where nutrients are limiting. Shetland loch water DRP, for example, is often found to be <1 μg P L^{-1} (Chapter 2). When examining results from the present study, it is important to consider that even in situations where increased P supply results in increased P uptake, adsorption does not necessarily account for all P introduced. For example, soil from Tingwall Site 4L adsorbed 0.45 mg P g $soil^{-1}$ at the 20 mg P L^{-1} treatment level, but this leaves 50 μg P g $soil^{-1}$ (10% of added P) free in solution. In a field situation, provision of P in excess of P sorption capacity of the soil could result in the remainder leaching into the drainage system, regardless of the P adsorption efficiency of that soil.

6.4.3.3 Effects of magnitude of P addition on soil P uptake

Larger applications of fertiliser result in increased losses from blanket peat bog (Burke, 1975). This is in agreement with experimental results of the present study as can be seen from Figure 6.3 and Table 6.4. P retention was shown to rise as P addition concentration increased up to the 50 mg P L^{-1} treatment, after which, P assimilation was poor. The results of the present study indicated that the greatest P losses occurred from peaty soils which had been treated with high P additions. This is consistent with the findings of Malcolm *et al.* (1977). In experimental work on effects of fertilizer on *Picea sitchensis* (Sitka spruce), ground mineral phosphate was mixed through free-draining *Calluna-Sphagnum* peat at a rate of 375 kg P ha^{-1} followed by surface addition of 232 kg P ha^{-1}; or 190 kg P ha^{-1} followed by a further 190 kg P ha^{-1}. N was added as formalized casein (either 238 kg N ha^{-1} alone or plus a subsequent equal addition) and K as K sulphate (total addition of 411-556 kg K ha^{-1}). Magnesian limestone was used to raise pH from 3.2 to 4.7 (1:2.5 v:v in $CaCl_2$). The P was found to be highly mobile, leaching rapidly in the first few weeks after fertilisation, whilst P found in leachate water was found to be 60% and 25% of the original additions of 375 kg P ha^{-1} and 190 kg P ha^{-1}, respectively. Greater P loss occurred in more heavily fertilised peat and through high rainfall.

6.4.3.4 Mechanisms of phosphorus binding in soils

P in soil may be incorporated in Fe phosphate or occluded phosphate surrounded by

a coating of Fe oxide. Under anaerobic conditions such as occur during waterlogging, Fe may become soluble as Fe^{2+}, may form organoferrous compounds, or precipitate as FeS, $FeCO_3$ or $Fe(OH)_2$. This allows Fe bound P to become available in the soil solution. Fe^{2+} may also be produced in normal, neutral or alkaline soils if the redox potential falls, though this is dependent upon soil type. Reducing conditions also allow Fe^{2+} to occupy cation exchange sites (Etherington, 1982). P availability in these situations is therefore dependent upon redox conditions. However, in acid soils, Fe will be more soluble, regardless of redox (Etherington, 1982). Fe^{3+} in aerobic soils is soluble below pH 3.0 (I.D. Pulford, University of Glasgow, *pers. comm.*, 1995). Fe deficiency is therefore generally characteristic of well drained calcareous soils. High accumulation of Al- and Fe-bound P has been found in very acid mineral soil (pH 4.2 in $CaCl_2$) high in oxalate-soluble Fe treated with fertiliser (Hartikainen, 1989). Ionic interactions of P in soils are pH dependent. At low pH, Fe and Al combine with orthophosphate ions, whereas at neutral to alkaline pH, bonding occurs between Ca and P. In mineral soils, P can be sorped rapidly by soil components (Sharpley, 1982).

However, acid organic soils may be low in Fe and Al content (Cuttle, 1983). As seen from the results of the present study, poor P sorption capacity occurred in soils high in organic matter in the P retention experiments. An inadequate supply of Fe and Al binding sites would explain this result. The relationship found between P retention and pH may be due to the higher solubility of Fe in acid soil conditions. This would also explain the relationship between pH and low P retention capacity observed in the present study and would have important implications in a field situation if soil pH was not raised sufficiently to promote improved P uptake. Soil from Turdale Site 1 (1992) was the only soil which released P regardless of P treatment applied. This may have been partly because pH remained at approximately pH 4.5, rather than being at pH 6.5 as recommended for fertiliser operations. Turdale Water catchment area is situated on limestone of the Walls Formation, but peat formation has invalidated the potential advantage of such a Ca-rich drainage basin.

Elevated P adsorption capacity was exhibited by one soil of those examined in the Turdale Water catchment area (Table 6.4). Soil 2L had a considerably lower organic matter content than the other Turdale catchment soils. In addition it had the highest

pH value of the Turdale Water soils studied (Table 6.3). This soil was likely to constitute a mineral horizon where soluble inorganic matter leached from the oragnic soil above accumulated. Fe may have been present in an oxidised state and therefore may have bound with P, thereby explaining the relatively efficient P adsorption capacity of this soil.

Soil Sites 2, 5 and 6 in the west of Loch of Tingwall catchment area were efficient at retaining P, water soluble P being undetectable. This is probably as a result of pedogenesis from calcareous bedrock. It is likely that in these soils of pH > 5.0 and low organic content, P is binding to Ca. To the east side of the catchment, P uptake may be dependent upon Fe content.

In soil of the Leslie Association on Unst and Fetlar, pedogenesis is from serpentinite, meaning that soil is rich in bases, especially Mg, but also in Fe, Ni and Cr. Although soil maps do not indicate the presence of such soil within the Helliers Water catchment area (Table 6.7), it is suggested that a proportion of the watershed incorporates base rich soil, as loch water column Mg concentrations have been shown to be high, though those of Ca have not. For example, it may be that the Alpine soils in the Helliers Water drainage basin are Mg rich, as the term "Alpine" may refer to mode of soil formation rather than describing the soil properties (Table 6.8). Alternatively, the boundary of Leslie Association soils may extend further than estimated (Figure 6.2), to include part of Helliers Water catchment area. It is concluded that P adsorption is efficient in soil from the Helliers Water catchment area because of P binding with Fe in soils of lower pH and Mg instead of Ca in soils of higher pH. Examining Mg and Ca concentrations in the remaining lochs reveals that Lochs of Cliff, Watlee, Snarravoe, Skutes Water and Papil Water also have high water Mg levels. Soil maps show that all of these lochs have areas of Leslie Association soil within their watersheds (Table 6.7). It is suggested that P in reseed within areas of Leslie Association soil types would be assimilated by the soil relatively efficiently *i.e.* in a comparable fashion to P uptake in soil from Helliers Water drainage basin.

Table 6.7 Soil types in the 31 catchments of the 1991 water survey (MISR, 1985)

Water body	Soil types
Arthurs Loch	peaty rankers, peaty podzols, brown rankers
Bu Water	peaty podzols, humus-iron podzols, peaty gleys, peaty rankers, peat
Loch of Brindister	blanket peat, deep: peaty gleys, non-calcareous gleys: some saline gleys
Loch of Brough (Bressay)	peaty gleys, peaty podzols, peaty rankers, some peat
Loch of Brough (Yell)	peaty gleys, peat: some peaty podzols and peaty rankers: some blanket peat
Loch of Brow	peaty gleys, non-calcareous gleys: some peat and saline gleys: basin and valley peats
Loch of Cliff	peaty gleys, peaty podzols, peaty rankers, non-calcareous gleys: some humic gleys and peat: magnesian gleys, some brown magnesian soils
Eela Water	peaty gleys, peat: some peaty podzols and peaty rankers: blanket peat, deep: some non-calcareous gleys, peaty gleys: some humic gleys
Loch of Gonfirth	blanket peat, deep: peaty gleys, peaty podzols and peaty rankers
Gossa Water	peaty podzols: some humus-iron podzols and gleys: blanket peat, deep
Gorda Water	peaty gleys, non-calcareous gleys: some peat, peaty podzols and rankers
Helliers Water	peaty gleys, peat: some peaty podzols and peaty rankers: some alpine soils, rankers, sub-alpine soils
Loch of Huesbreck	calcareous regosols, brown calcareous soils, calcareous gleys
Loch of Huxter	peaty gleys, peat: some peaty podzols and peaty rankers
Loch of Kettlester	peaty gleys, peat: some peaty podzols and peaty rankers: non-calcareous gleys: some humic gleys and peat
Lunga Water	blanket peat, deep: peaty gleys, peat, some peaty podzols and peaty rankers
Mill Pond	peaty podzols, humus-iron podzols: some peaty gleys and rankers
Papil Water	peat, peaty gleys, peaty podzols: magnesian gleys, some brown magnesian soils: regosols, some gleys
Punds Water	peaty gleys, peat: some peaty podzols and peaty rankers: blanket peat, deep
Roer Water	blanket peat, deep: peaty gleys, peat: some peaty podzols and peaty rankers
Sand Water	basin and valley peats: blanket peat, deep: peaty podzols and peaty rankers
Sandy Loch	peaty podzols, peaty gleys, peaty rankers: blanket peat, deep
Skutes Water	magnesian gleys: some brown magnesian soils

Table 6.7 (cont.)

Water body	Soil types
Loch of Snarravoe	peaty gleys, peat: some peaty podzols and peaty rankers: magnesian gleys: some brown magnesian soils and gley rankers: non-calcareous gleys: some humic gleys: some peaty alluvial soils
Loch of Spiggie	peaty podzols, humus-iron podzols: some brown forest soils and gleys: calcareous regosols, brown calcareous soils, calcareous gleys: basin and valley peats: some peaty alluvial soils
Strand Loch	basin and valley peats: peaty gleys, peat: some peaty podzols and peaty rankers
Loch of Tingwall	peaty gleys, peat, peaty podzols and peaty rankers: brown forest soils: some brown rankers and non-calcareous gleys
Turdale Water	blanket peat, deep: peaty gleys, peat: some peaty podzols and peaty rankers
Loch of Ustaness	peaty gleys, peat: some peaty podzols and peaty rankers
Loch of Watlee	basin and valley peats: magnesian gleys: some brown magnesian soils: peaty gleys, peaty podzols: peat, peaty gleys, peaty podzols
Whitelaw Loch	blanket peat, deep

The low organic content, low water content and relatively high pH of soils collected in the Loch of Cliff catchment area in 1991 indicate these soils are probably of the Leslie Association rather the Arkaig Association to which other areas of the watershed belong.

Unlike Loch of Tingwall which was high in Ca only and lochs which were high in Mg only, the following had high water concentrations of both: Lochs of Spiggie, Strand, Huesbreck and Brow. Strand Loch probably has elevated Mg levels due to sea water inflow, but is situated on calcareous bedrock. However soils of the catchment are mainly dystrophic peat (Table 6.7), the effect of which probably overrides that of Ca rich bedrock as it does in the catchment area of Turdale Water. Soils collected from drainage basins of the other three lochs all had relatively high pH and low organic content (except Loch of Spiggie Site 2, O horizon), and therefore would probably exhibit relatively efficient P assimilation. The entire catchment area of Loch of Huesbreck incorporates shelly sand, brown calcareous soils and calcareous gleys with regosols (Table 6.7), so probably has good P retention properties. Loch of Spiggie catchment area also incorporates this soil class, but Sites 1A and 1B were within an area of humus Fe podzols, brown forest soils and gleys (Table 6.7). Podzols are characterised by low pH and leaching of ions which would bind to P, noteably Fe, whereas in brown earths, P may be bound with Ca (Table 6.8).

In 1991, soil from catchment areas of Brough (Yell), Huxter and Lunga were sampled. These soils were peats, had low pH and high organic content (Table 6.2) and are therefore likely to have poor P sorption capacity. The same may be said of soil of Bu Water catchment, O horizons and Loch of Spiggie Site 2, O horizon. Catchments incorporating soils such as these would be most at risk of elevated P levels in drainage water if reseed operations were to be carried out.

In the Shetland Islands approximately 40% of all soils are classed as peat, most of this being more than 1 m in depth. A great proportion of the remaining 60% of soils have peaty surface horizons, occurrence of peaty gleys, peaty podzols and peaty rankers being common. More fertile brown forest and non-calcareous gley soils are limited in extent; cultivated land is relatively scarce (Dry and Robertson, 1982).

Table 6.8 Definitions of major soil types found in Shetland

Soil type	Characteristics of soil type (Etherington, 1982)
peat	organic, variety of different types formed from remains of vegetation, nutrient poor, low pH
brown earth	no eluviation of A horizon except in podzolic brown earths, mixing of soil (earth worm activity), nutrient (base) rich, not of low pH, little O horizon, formation typically on siliceous geology
podzol	high degree of horizon differentiation, free drainage, eluviation of surface horizons, movement of organic matter to lower levels, leaching of soluble inorganic matter (*e.g.* Mn, Ca, Mg, Al, Fe) from upper profile, desaturation of CEC, lowering of pH, accumulation of fibrous organic layer near surface, perhaps formation of Fe-pan causing some waterlogging in A horizon
gley	profile partly waterlogged, reducing conditions, slow decay of organic matter, increased organic content of A horizon or some peat formation, conditions depend on degree of wetness and acidity
peaty gley podzol	gley of lower pH, nutrient poor, Fe-pan in B horizon, aerated below Fe-pan, upper profile not free draining as in podzol
peaty gley	gley of lower pH, nutrient poor, formation of peat layer at surface, surface soil normally wet, thickening Fe-pan may exacerbate waterlogging
ranker	azonal (lithosol), little or no differentiation of profile, pedogenesis at early stage, found over nutrient deficient siliceous geology
regosol	azonal, little or no differentiation of profile, pedogenesis at early stage, formation from unconsolidated material (e.g. sand, loess, till)
arctic soil	formation through wind action, frost shattering and sorting, rocky, shallow

There are soils which have shelly sand incorporated in their structure, such as those in the catchments of Loch of Spiggie (NGR: HU 371 170) and Gorda Water (NGR: HU 167 607)(Dry and Robertson, 1982). Soils derived from limestone, such as those in the catchment of Loch of Tingwall (NGR: HU 417 430) are uncommon in this island group, although magnesian gleys have formed from the Leslie Association drift derived from the ultrabasic rocks of, principally, Unst and Fetlar (Dry and Robertson, 1982). As a result of the prevalence of peat in the Shetland Islands (Table 6.7), it is likely that a high proportion of Shetland soils have poor P retention characteristics.

6.5 CONCLUSIONS

Although there is a wide range of soil types in Shetland, prevalence of peat is important when considering potential effects of reseeding on standing freshwater resources. Compared to most mineral soils, peats tend to possess a high cation exchange capacity (CEC), but poor phosphate sorption properties *i.e.* they have inferior capacity for retention of P against leaching, as a result of the low aluminium and iron content of these soils (Cuttle, 1983). Under such conditions processes of P uptake by vegetation and rate at which fertiliser dissolves may be of greater importance than soil characteristics in determining P losses from a catchment.

Not only is there a potential problem with soil type, but underlying geology of Shetland is generally impermeable (Mykura, 1976). Impermeable bedrock suggests a low water storage capacity thereby causing 'flashy' stream flow *i.e.* rapid fluctuations in surface water discharge in response to a given precipitation event. An overlying layer of peat would obviously exacerbate this problem. Peat retains water, even during dry conditions, and this allows surface saturation to occur rapidly during a rainfall event, so resulting in a high runoff:rainfall ratio (Lyle and Britton, 1985). This in turn could have detrimental effects on soil nutrient retention. P loss immediately after peat fertilisation, is highest in surface runoff. With time, after P application, the quantity of P being lost in drainage outflows becomes higher than that in surface runoff (Burke, 1975).

When considering potential effects of P fertilisation on loch water quality, it would be useful to assess the organic content of the soil involved, as a relationship exists between %LOI and P adsorption capacity. Despite analysis showing this relationship

to be significant, P adsorption remains highly variable, so precluding accurate prediction of fertiliser effects on P removal in surface runoff and drainage water. However, if organic content of a soil is > 80%, it is highly likely that P sorption will be poor. Measurement of pH may also be helpful in characterisation of soil type for the purposes of predicting whether there may be problems of fertiliser P leaching into drainage systems. As with organic content, although the relationship between pH and soil P sorption capacity is significant, its usefulness as a predictive tool is limited by the inherent variability of the model. However, it is highly likely that soils with pH of around pH 4.0 or less will exhibit poor soil P sorption properties, especially if organic content is > 80%. Compulsory pH adjustment to the recommended level of pH 6.5 might assist in minimising potential pollution problems.

Because the capacity of peat to retain P and K is limited, emphasis must be on supplying immediate requirements rather than build up of fertility, since successive additions of fertiliser are likely to facilitate nutrient losses in a manner similar to that which occurs if a large single application is made (Burke, 1975). Increased hydraulic conductivity means that solutes spend less time in contact with soil. However, when peat has been drained and there is no precipitation, loss of nutrients from normal fertiliser applications is minimalised (Burke, 1975). Nutrient losses are more likely to occur in drain flow or surface runoff immediately after fertiliser application (Burke, 1975).

CHAPTER 7: CONSIDERATION OF THE OPTIONS FOR CATCHMENT MANAGEMENT IN SHETLAND

7.1 INTRODUCTION

From the results of Chapter 2, it is evident that a range of nutrient concentrations exists within the freshwater bodies of the Shetland Islands. Categorisation of the thirty one lochs studied according to trophic status (OECD, 1982) indicated that only six of these water bodies were oligotrophic. Monitoring of streams within the catchment areas of the five lochs studied in more detail indicated that loch inflow waters had higher nutrient concentrations in drainage basins incorporating septic tanks and supporting agricultural activities, such as improvement of grassland, than those in watersheds with little anthropogenic influence. Increases in water TP concentrations in lochs as a consequence of higher catchment loadings may cause augmentation of algal growth. In lochs with water column TP levels higher than 10 μg P L^{-1}, there is an increased risk of growth of dense algal populations within the water columns (OECD, 1982). Phytoplankton blooms have been observed in several water bodies studied (*e.g.* Turdale and Punds Water, Sandy Loch) in the present work, both before and during the current research (Chapter 4). Excessive phytoplankton growth is undesirable for a number of reasons (Chapter 4). Of particular concern are the potential effects on human health of the occurrence of toxic algae in potable water supply reservoirs. It is, therefore, good water management practice to prevent or eliminate dense phytoplankton populations within loch systems.

7.1.1 Methods of controlling blue-green algae

Many techniques have been put forward as being effective in control of the problem of excessive blue-green algal growth in freshwater lakes. There are two distinct approaches, the first being nutrient control, the second, alleviation of the effects of nutrient enrichment. Nutrient control measures may also be categorised as either preventative or reactive, the former being restriction of nutrient input to loch systems, the latter, manipulation of nutrient levels within the loch system. In cases where nutrient inputs have been high, and a management plan to reduce inputs is then undertaken, it may also be necessary to implement a nutrient manipulation strategy, the reduction of external nutrient loading alone being insufficient to improve water quality (Marsden, 1989). Measures to eradicate algal blooms are useful only in the short term. Prevention of nutrient enrichment is the most effective long-term measure

for restriction of phytoplankton growth. The different types of control strategies are considered below. In addition, several options for control of nutrient enrichment effects and the associated cost of each alternative are presented in Table 7.1 (Boers and Van der Molen, 1993).

7.1.2 Prevention of nutrient enrichment through control of inputs

In lakes of low nutrient status, development of water quality problems can be avoided by monitoring water quality and enforcing legislation. Estimates of the minimum TP loading necessary to cause exceedence of the EQS for a water body may be made, then limits to discharge set accordingly. Environmental modelling has been used for such lake management purposes (Jørgensen, 1983).

7.1.3 Modelling the effects of nutrient enrichment

Models of aquatic ecosystems have been developed to attempt to predict trophic status from existing TP loadings to lake catchments, in order to avoid problems of excessive phytoplankton growth. There are two types of model. Firstly there is the dynamic model which typically involves many detailed parameters within the catchment system incorporated into complex mathematical calculations. Secondly, empirical models have been developed from lake survey statistics (Beveridge, 1984).

7.1.3.1 Dynamic models

Dynamic models have good predictive ability for the particular loch studied, firstly, when the most influential subsystems of an ecosystem are studied, and secondly, when near optimum numbers of variables are used in calculations, which are calibrated and validated. However, the usefulness of dynamic models has also been found to be limited (OECD, 1982), as there are several difficulties with this model type, outlined by Jørgensen (1983):

(a) Many subsystems of the ecosystem must be accounted for, such as loch P, N, C, Si cycles; phytoplankton, zooplankton and fish growth, sediment-water interactions. It is therefore necessary to have an in depth knowledge of each system and the rates at which processes occur within the subsystems.

(b) It is difficult to estimate the optimum number of subsystems to consider. The more parts there are to the model, the more validation/calibration procedures are necessary and the more error may be incorporated in the model.

Table 7.1 Costs of various options for ameliorating eutrophication (from Boers and Van der Molen, 1993)

Measure	Costs (ECU/ha)
P removal at treatment plants to 1 mg P L^{-1} in effluent	130 yr^{-1}
P removal at treatment plants to 0.2 mg P L^{-1} in effluent	2,200 yr^{-1}
P removal from inlet waters	6,500-9,000 yr^{-1}
Sedimentation basins to treat inlet waters	6,500-13,500
P removal using aluminium salts in deep lake	400
P removal using iron salts in shallow lake	6,000
Dredging	14,000-40,000
Biomanipulation	900
Hypolimnetic aeration	400
Artificial circulation	250

(c) As every loch system is different, complex models based on individual lochs are not transferrable to other loch systems.

(d) The data requirement is high and the sampling strategy intensive (a monitoring programme of twice per month for a year is inadequate to fully describe loch dynamics). In addition, an equally large independent data set is required to validate the model. There has been a tendency to add to model complexity, but not to obtain sufficient data to calibrate the model.

7.1.3.2 Empirical models

Correspondingly, the disadvantages of the empirical models are that they take account of few variables in complex systems *i.e.* they are too simplistic. These are static input-output models, rather than dynamic representations of the ecosystem. In addition, transferrability of empirical models remains limited (Jørgensen, 1983).

The advantages of empirical models are that they are relatively simple and require less detailed information on the lake. They are therefore easily and rapidly utilised. In addition, the empirical models are more broadly applicable as they are less complex.

Empirical mass balance models which estimate water column TP concentration from TP loading, loch size, flushing rate and the proportion of TP in sedimentation include those of Dillon and Rigler (1974a), Vollenweider (1975) and OECD (1982). The Vollenweider model makes the following assumptions (Vollenweider, 1975):

(a) TP sedimentation rate is proportional to TP loading in the water column.

(b) The water body undergoes complete mixing, so that any variable entering the water body is equally distributed throughout the water column immediately upon arrival.

(c) Concentrations of TP in the lake outflow and in the water column are equal.

(d) TP loading rate does not vary seasonally.

Mass balance equations assume that the sum of all fluxes of TP in a lake system is zero, *i.e.* the system is in a steady state (Vollenweider, 1975). Although steady state conditions rarely exist in lakes, they may repeatedly exhibit similar characteristics over several years, so varying around constant mean nutrient concentrations. This has been referred to as repetitive steady state (OECD, 1982). The Dillon and Rigler

model is a modification of Vollenweider's original model (Dillon and Rigler, 1974a) and is based on dependence of water column TP concentration on TP loading to the water body, lake area and mean depth ($\bar{Z}$), water flushing rate and the proportion of TP lost through sedimentation processes (Beveridge, 1984). Both water residence time and $\bar{Z}$ are included as lakes with slow flushing rates are more sensitive to increasing eutrophication than is expected from $\bar{Z}$ alone (Vollenweider, 1975). The model was modified to incorporate a retention coefficient (R) owing to difficulties in measuring the original sedimentation rate involved in the Vollenweider model (Dillon and Rigler, 1974a).

Calculation of expected TP concentration within a lake allows its incorporation into a second model linking TP concentration and chlorophyll *a* concentration in the water column. A simple regression relates these two parameters (Dillon and Rigler, 1974b). A variety of relationships have been determined in different regions of the world, including the regression of Dillon and Rigler (1974b) for North American lakes and that of Sakamoto (1966) for Japanese lakes. The equation of Dillon and Rigler (1974b) for prediction of mean lake chlorophyll *a* concentration is outlined below (correlation coefficient 0.95):

$$\log_{10}[\text{Chl } a] = 1.449 \log_{10}[\text{TP}] - 1.136$$

where: [Chl *a*] chlorophyll *a* concentration

[TP] TP concentration

This form of equation then allows estimates of chl *a* concentrations to be expected for predicted (or observed) TP concentrations in the water columns of lakes, thereby assisting in catchment management plans. Dillon and Rigler models (1974a and b) are concerned with water column TP levels at spring overturn *i.e.* the maximum TP concentration in the water column prior to summer phytoplankton growth.

7.1.4 Control of nutrients within freshwater lake systems

7.1.4.1 Removal of nutrients

Sediment may act both as an internal source of nutrients, and a nutrient sink. This results from the specific conditions occurring between sediment and overlying water, or perhaps due to previous external inputs (Chapter 3). Success of sediment removal

in limiting nutrient availability to phytoplankton relies on complete removal of all settled material acting as a source. This may be logistically difficult and depth of sediment to be removed difficult to predict. The greater the depth of water concerned, the more troublesome this solution becomes. Adverse effects of such a solution include disturbance to the biological communities existing within the water body; in an area such as Shetland, where fishing and bird habitats are important, this may preclude the use of this technique. Secondly, disposal of dredged sediments is both environmentally contentious and expensive. Thirdly, transportation of heavy equipment and sediment to and from loch sites in Shetland would not be practical, requiring a road immediately adjacent to the site.

An alternative to removal is to isolate sediments from the water column, either by physical or chemical means. The former technique involves separating sediment from overlying water by, for example, covering the lake bottom in plastic sheeting. Degradation of this barrier and the consequences of anoxic conditions being promoted in the sediments beneath the impervious boundary, make this an unsuitable option in all but a few cases. Nutrient-poor sand has been laid down as a sediment cover with limited success. It is a porous substrate and therefore the correct depth of sand must be maintained over the affected area. In extreme cases, it may also reduce reservoir depth and volume (NRA, 1990).

Chemical additions may be more successful, as both ferric chloride ($FeCl_3$) and aluminium sulphate, (*i.e.* alum, $Al_2(SO_4)_3.14H_20$), have been used to reduce phosphorus release from sediments. Inactivation of sediment P through calcite ($CaCO_3$) additions has not yet received much interest, although it may prove to be relatively successful in eutrophic, hard water lakes (Klapper, 1992; Cooke *et al.*, 1993; Quaak *et al.*, 1993). Alum has been widely utilised in shallow lakes in the U.S.A. (Kennedy and Cooke, 1982; James *et al.*, 1991; Cooke *et al.*, 1993). Iron salts are reported to have only limited success as the development of low Eh may occur in the sediments, resulting in release of Fe-bound P (Cooke *et al.*, 1993).

Harmful effects to public health could occur if these procedures are not carried out with appropriate care, having taken all aspects of the nature of the water chemistry into consideration. For example, distribution of Al species is pH dependent; in the

range pH 6-8, dissolved Al concentrations are minimal. In addition, excessive inputs of alum cause low pH and alkalinity, and high dissolved Al levels (Kennedy and Cooke, 1982). A possibility that anaerobic conditions could occur in the sediments, as a result of the treatment also exists (NRA, 1990). These measures are best suited to a plan of bloom prevention, rather than a means to control excessive algal growth, once established (Reynolds, 1991). Inactivation of sediment P sources is ineffective in limiting algal productivity when the external P loading has not been reduced (James *et al.*, 1991).

7.1.4.2 Nutrient manipulation within the water column

Typically, in temperate lake systems during late summer, higher water temperatures and organic matter sedimentation rates at the sediment surface cause enhancement of the processes of degradation of organic matter. This results in a lowering of the redox potential and allows the potential for significant P release, as described by Mortimer (1941). In the majority of cases, oxidised N may prevent P release from sediments in lakes with anoxic hypolimnia, with nitrate acting as an electron acceptor, maintaining redox potential and sustaining the P binding capacity of the sediments (Tirén and Pettersson, 1985). Nitrate principally suppresses solution of Fe-bound P. Andersen (1982) found that in lakes with > 0.1 g N m^{-3} and no oxygen in the hypolimnion, P release from sediments was considerable, whereas at sites where there were N concentrations of ≥ 1 g N m^{-3}, no release of P was experienced. In shallow polymictic lakes, a less clear relationship was observed. Of twenty two such waters studied, fifteen exhibited an internal P source at N levels of < 0.5 g N m^{-3}, three had no sediment P supply and three of the remaining four waters showed no P increase, despite N being present at > 0.5 g N m^{-3} (Andersen, 1982).

During enrichment experiments in British Columbia (Stockner and Shortreed, 1988), additions of N and P to oligotrophic Kennedy Lake resulted in the development of late summer blooms of N-fixing cyanophytes. Subsequently, these were eradicated by increasing the molar ratio of added N:P from 15:1 to 35:1. In following years, hypolimnetic nitrate concentrations remained significantly higher than pre-experimental levels (Stockner and Shortreed, 1988).

The above examples of nutrient manipulation illustrate that there exists a possibility

of such principles being usefully employed in lakes prone to excessive cyanobacterial production. However, concentrations of N necessary to eradicate blue-green problems may conflict with the reqiurements of other water resouce users in many waters. High nitrate concentrations are particularly undesirable in waters supporting salmonid fish or potable water supply reservoirs. There is also the risk of stimulating growth of previously N-limited algae such as those cyanophytes which do not fix N, *e.g. Gomphosphaeria* (Chapter 4).

7.1.5 Alleviation of the symptoms of nutrient enrichment

As phytoplankton require light for photosynthesis, physical exclusion of light has been suggested a means of combating cyanobacterial populations, as have removal of surface scums and use of polystyrene floats on the water surface. However, the first may result in death of non-target species, the second is difficult in rocky lochs and may be regarded only as a temporary measure, whilst the third would be impractical in unsheltered waters. Alternative algal control strategies, which are based on physical, chemical and biological control methods and are intended to have more enduring results, are outlined below.

7.1.6 Manipulation of physical aspects of standing waters

Calm, stratified conditions in the upper water column favour over-production of cyanobacteria. In lakes which stratify, methods of artificial destratification allow for either continuous (Bailey-Watts *et al.*, 1987) or intermittent (Steinberg and Gruhl, 1992) mixing of the whole water column to take place. This should encourage the growth of diatom populations rather than many taxa of bloom-forming algae. When net photosynthetic depth is exceeded by mixing depth of a water body, growth of cyanobacteria may be discouraged. However, as some blue-green algae can survive these conditions, so selective advantage would pass to other genera such as *Oscillatoria*. Intermittent stratification favours diatoms and blue-greens alternately, whilst maintaining artificially low biomass (NRA, 1990). Another alternate method of algal control suggested is to use the pressures generated during pumping of water between supply reservoirs (Walsby, 1992). Changes in pressure can rupture the gas vacuoles of blue-green algae and prevent them from regulating buoyancy. The algal cells then fall out of the photic zone, which in turn halts photosynthesis in deep lakes and leads to scenecense of cells (Walsby, 1992).

However, in small shallow lochs, such as those in Shetland, wind action already ensures complete water column mixing for the great majority of the year (Chapter 2), whilst photosynthesis is possible in a large proportion of, if not the entire depth of many lochs. This means that artificial mixing and hypolimnetic withdrawal of water (another technique for amelioration of eutrophication effects in freshwater lakes) or encouragement of gas vacuole collapse would not be appropriate in Shetland.

As rapidly flushing water bodies, or those which have periodically high flows, do not generally support development of large phytoplankton populations, artificially increasing flushing rate would work against increasing biomass of slow-growing cyanophytes. However this solution is clearly unrealistic in many situations, and would be in direct conflict with the purpose of reservoirs (Reynolds, 1991).

7.1.7 Chemical destruction of phytoplankton

Several inorganic (copper sulphate) and organic (diquat) compounds have been employed in treating algal problems in standing water bodies. These do not have a uniform effect on all algae and are potentially harmful to non-target organisms. Profuse usage of such compounds is contrary to EC guidelines and employment of these poisons is heavily regulated (Reynolds, 1991). Aside from lethal toxicity effects, chronic toxic effects may go unnoticed. Exposure to elevated metals or organic compound concentrations activates detoxification mechanisms in fish and mammals which can result in production of more harmful, possibly carcinogenic compounds forming within the body (Haux and Förlin, 1988; Paine, 1981; Parke,1985).

Algicide usage results in death of dense populations of phytoplankton. However, these then sink to the sediments and decay, so causing a depletion in oxygen, a release of nutrients and clear water which could then stimulate another bloom. Copper sulphate kills blue-green algae, but green phytoplankton are more tolerant of this algicide and may replace the cyanobacteria as the bloom forming group (Moss, 1980).

7.1.8 Biological control of cyanophyte problems

Where it is impossible to limit nutrient input sufficiently to prevent bloom problems arising, the most favourable supplementary course of action is often to attempt some form of biological control (Moss, 1992). Whilst it is believed that this should cause

as little disruption to the existing ecosystem as possible, it is likely to be more difficult to achieve than control of eutrophication through nutrient source limitation, as it requires detailed understanding of the functioning of the ecosystem food web (Benndorf, 1992).

Although juveniles of most fish species are planktivorous, only one species of indigenous coregonid occurring in standing waters feeds on algae once mature. Powan (*Coregonus lavaretus*), however, are associated with deep waters of low nutrient status and feed mainly on zooplankton. Introductions of silver carp (*Hypophthalmichthys molitrix*) or grass carp (*Ctenopharyngodon idella*) have been used in Europe for algae control and if used in the UK would have the advantage of being unable to breed. An obvious drawback of this proposal is the probable lack of climatic suitability in northerly latitudes. These fish may also show preferences for particular kinds of algae, so giving selective advantage to other species. In Britain, introduction of non-indigenous fish would also require a licence and measures to prevent escapes occurring into non-target waters (NRA, 1990).

An alternative to the introduction of fish is complete removal of the existing fish population in order to encourage zooplankton growth and consequent phytoplankton consumption. This would be unacceptable in waters with a high angling value (*e.g.* Loch of Ustaness, Lunga, Gossa and Punds Water) or where the ecosystem is protected, such as in an SSSI (*e.g.* Tingwall and Asta, Spiggie and Brow and Sand Water). An obvious disadvantage of techniques which rely upon on consumption of problem algae is that blue-green algae are generally unpalatable to potential grazers. Avoidance of cyanophytes, in favour of other algal groups, would assist in the development of blue-green communities.

Other potential solutions to blue-green algal problems include the use of viruses, parasitic fungi and herbivorous ciliates. These microorganisms can significantly reduce scum-forming populations (Reynolds, 1991). Harvesting and maintenance of such organisms in culture has so far proved difficult (NRA, 1990). Certain bacteria have been found to produce a group of enzymes which break down microcystin LR (Anderson, 1995). More research is required on this topic, including environmental impact assessment of the effects of inoculating ecosystems with such organisms.

7.1.8.1 The use of barley straw in reduction of algal biomass

The simple technique of introducing rotting barley straw to waters prone to algal problems, appears to have been successful at locations in southern Britain (Barrett and Gibson, 1989; Jones *et al.*, 1989). Growth of *Cladophora glomerata* (Welch *et al.*, 1990; Gibson *et al.*, 1990; Ridge and Barrett, 1992), *Selenastrum capricornutum* (a standard laboratory bioassay test species) (Jones *et al.*, 1989; Gibson *et al.*, 1990), *Chlorella vulgaris*, *Klebsormidium rivulare*, *Oedogonium*, *Spirogyra*, *Stigeoclonium tenue*, *Ulothrix trentonense* (Gibson *et al.*, 1990) and *Microcystis aeruginosa* (Newman and Barrett, 1993) have been limited in laboratory experiments. The chemical in barley straw responsible for limitation of algal growth has not been identified. It has been suggested that the presence of microorganisms within the straw allows release of an organic algal growth retardant under aerobic conditions. There is also the possibility that a complexing agent is produced, making nutrients less available.

Results of utilisation of straw in the limitation of algal growth have shown the effect to be algistatic as opposed to algicidal, with algae from test conditions recovering after transfer to a control medium (Gibson *et al.*, 1990; Newman and Barret, 1993). Consequently, removal of straw from the test water results in recovery of algal production (Ridge and Barrett, 1992). Optimum effects are reported to occur when straw has been degrading for six months (Gibson *et al.*, 1990; Jones *et al.*, 1989) and barley straw, rather than hay, is recommended as having the more efficient algistatic effect (Gibson *et al.*, 1990). This potential method of phytoplankton control is of particular interest as straw is a cheap and plentiful material. Additionally, in reported tests, water quality has not been unduly affected and habitats have been provided for invertebrate fauna (Ridge and Barrett, 1992).

In aquatic systems where nutrient enrichment has occurred, the inherent variability of phytoplankton productivity becomes greater than in nutrient poor systems (Chapter 2). At least one biomass peak occurs annually, but also at least one period where processes such as low nutrient concentrations and zooplankton predation result in low algal biomass (Sommer *et al.*, 1986). Consequently, if growth inhibition effects occur through the use of straw, the change induced must be greater than that expected in the annual variation in order for this to be observed. Alternatively, biomass must be

suppressed for an extended period compared to that expected in a clear-water period. Unless the decrease in phytoplankton productivity is great and or prolonged, the following points are important:

(a) Differences in biomass and species present as a result of, for example, variation of internal or external nutrient supplies will probably be greater than those induced by introduction of straw.

(b) Frequent monitoring would be required in order to detect retardation of phytoplankton growth. It is possible that the sampling frequency of the present study was inadequate to detect an effect from the barley straw.

Newman and Barrett (1993) state that algal control was achieved in ponds, drainage ditches, lakes, canals and reservoirs. In a survey of unreplicated field trials of use of barley straw as an algal growth retardant (in Britain and Ireland), assessment of success was based on a scoring system from one (no effect) to nine (no algal growth). Assessments were made visually or on the basis of algal counts. However, visual assessments are probably unreliable and it is not stated whether in cases where algal counts were made if results were undoubtedly outwith variation caused by other factors.

Experimental procedures are necessary to investigate viability of this control method in a variety of water, algae and climatic types, as it is possible that it cannot be efficient with, for example, cyanophytes in cold, humic or hard waters. There also exists a lack of published information on controlled field trials. Identification of the active agent is also highly desirable for two reasons. Firstly, it would allow an investigation of the properties of that chemical. Ridge and Barrett (1992) stated that it is possible that residues might accumulate in sediments (perhaps resulting in future difficulties) presumably because sediments act as a sink for many substances including metals and hydrocarbons. Although there is no evidence that the compound produces an effect at the population level in organisms other than algae, there is a wealth of literature on chronic effects of xenobiotics on aquatic animals at a sub-population level (Sutcliffe, 1994). The stimulation of the mixed function oxidase reactions of detoxication/toxication mechanisms is such an effect (Parke, 1985). It is also possible that the substance produced is a phenolic compound. Secondly, should utilisation of straw prove harmless, it would allow manufacture of the chemical, thereby possibly enabling more efficient dosing.

7.1.9 Aims

The objectives of Chapter 7 are summarised below.

(1) As there is the possibility that unaffected water bodies may develop problems of excessive phytoplankton growth, should nutrient enrichment occur (Chapter 4), the implications of a models approach to catchment management were to be considered. The aim of this section of the study was to assess present loadings of TP to the five study lochs, through use of water column TP concentrations determined at the end of winter (March, 1992 and March, 1993) in the Dillon and Rigler (1974a) model.

(2) As establishment of TP - chlorophyll *a* relationships allows estimation of concentrations of chlorophyll *a* from calculated or observed water column TP levels, appraisal of the TP - chlorophyll *a* regression relationships in the Shetland lochs studied was to be undertaken.

7.2 MATERIALS AND METHODS

7.2.1 The use of the Dillon and Rigler (1974a) approach to loch catchment nutrient budgets

The Dillon and Rigler model used to estimate P loadings to the five study lochs was as follows:

$$[P] = \frac{Tw \times L \times (1 - R)}{Z}$$

where *[P]* = predicted loch phosphorus concentration

Tw = water residence time

L = areal loading rate

R = sedimentation coefficient

Z = mean loch depth

The model was modified by substituting actual March loch P concentration for predicted P concentration, in order to calculate estimated areal loading rate. Sedimentation was calculated using the equation of OECD (1982) as follows:

$$R = 0.426\, e^{(-0.271 \times qa)} + 0.574\, e^{(-0.00949 \times qa)}$$

where qa = hydraulic load = Z / Tw

Tw = net annual catchment water volume input / loch volume

Z = loch volume / loch area

Water residence time was calculated from the annual net volume of water entering the catchment as rainfall, adjusted for evaporation and evapotranspiration, compared to the loch volume, as calculated from bathymetric data. Evaporation from open water was estimated as 550 mm each year, evapotranspiration from the surrounding land as 450 mm on an annual basis. Rainfall figures were provided by the Meteorological Office, Lerwick Observatory, though November and December, 1993 figures were estimated as the mean of November and December, 1991 and 1992. No adjustment was made to account for abstraction volumes as these were always less than the net input of water to the catchment areas.

After estimation of the areal loading rate to each loch, *i.e.* the P loading rate per surface area of the water body, this was converted to absolute P loading rate. The absolute P loading rate was transformed to an estimate of the annual loading of P from the land area surrounding each loch, after subtraction of the approximate annual mass of P received directly by the loch through atmospheric deposition. It was not possible to correct land input values for atmospheric deposition as the fate of the latter was unknown. Rain water was collected simultaneously in three borosilicate glass duran bottles from 3rd-4th October, 1993. The pH values and TP concentrations in these samples were determined as described in Chapter 2. The mean TP concentration of 8.0 μg P L^{-1} (range: 6.7-10.0 μg P L^{-1}) (Table 7.2) was used to calculate TP input to the water bodies directly from rainfall. In order to calculate mass of P input in terms of land area surrounding Helliers Water, there was also a correction to subtract the annual loading of P attributable to the pumping scheme from Loch of Watlee. This was achieved using measured summer TP concentrations in the water from Loch of Watlee (10.4 and 7.2 μg P L^{-1} in 1992 and 1993 respectively) and the volume of this water which was pumped into Helliers Water each year (487 m^3 d^{-1} for 92 days).

Table 7.2 P and pH of rainfall samples collected 3-4/10/93

Sample	pH	TP (μg P L^{-1})
1	4.18	10.0
2	4.14	7.4
3	4.13	6.7

In the case of Sandy Loch, estimated areal loading rate in 1992 and 1993 was added to the conjectured additional areal loading expected from Loch of Brindister through pumping operations due to begin in 1994. (SIC expected 4300 m^3d^{-1} to be pumped from July to October *i.e.* approximately 92 days). This allowed estimation of total expected P loading rate to the Loch after employment of the pumping scheme. This was then used in the original model along with adjustments in water volume received by the Loch to surmise the resulting P concentration in the water column. P concentration in water from Loch of Brindister was estimated as the mean of summer 1991 values (8.5 μg P L^{-1}).

Further calculations were also made for Loch of Gonfirth. A value of 10 μg P L^{-1} was substituted into the original equation in order to estimate the maximum permissible P loading rate to retain the oligotrophic status of the Loch. By subtraction of the greater estimated present loading (inclusive of atmospheric deposition) from the greatest feasible, an estimate of the mass of P which could possibly be tolerated by the system in addition to that already received annually was made.

7.2.2 P-chlorophyll *a* relationships

Data from 1991 on summer P and chlorophyll *a* concentrations from three field visits to the thirty one lochs were examined through simple regression analysis and through use of a multiplicative model, using the Statgraphics computer package. All data from each of the five study lochs from 1991 to 1993 were analysed in the same way, as was the total data set from the five lochs combined.

7.3 RESULTS

7.3.1 The use of a modelling approach for management of loch catchment areas: estimation of loadings of P to the five water bodies studied

Estimated areal loading rates to Loch of Gonfirth in 1992 and 1993 were 0.59 and 0.56 kg P ha^{-1} yr^{-1}, corresponding to conjectured values of loading rates from the land surrounding the Loch of 0.15 kg P ha^{-1} yr^{-1} in 1992 and 0.13 kg P ha^{-1} yr^{-1} in 1993 (Table 7.3). The areal loading rates were the lowest calculated for any of the five lochs studied, though figures for land to loch loading rates were the second lowest values.

Table 7.3 Estimated P loadings to Loch of Gonfirth

Loch mean depth (m)	7.77		
Loch surface area (m^2)	145,625		
Area of catchment surrounding loch (m^2)	490,625		
Loch volume (m^3)	1,131,100		
Year	**1991**	**1992**	**1993**
Water residence time (*Tw*) (yr)	2.42	2.16	2.60
Hydraulic load (*qa*)	3.21	3.60	3.58
March P concentration (mg P m^{-3})	n.d.	4.7	4.4
Rainfall (m yr^{-1})	1.207	1.297	1.292
Retention coefficient (*R*)	0.735	0.715	0.716
Areal loading (*L*) (mg P m^{-2} yr^{-1})	n.d.	59.41	55.54
Total areal loading - rainfall areal loading (mg P m^{-2} yr^{-1})	n.d.	49.03	45.20
Loch loading from surrounding land (mg P m^{-2} yr^{-1})	n.d.	14.55	13.42

KEY:
n.d. No data

NOTE 1: mg P m^{-3} equals μg P L^{-1}
NOTE 2: Divide by 100 to convert mg P m^{-2} to kg P ha^{-1}

The areal loading of this water body could theoretically be doubled and the March P concentration in the water column remain below 10 μg P L^{-1}, assuming conditions described previously. An additional areal loading rate of < 0.618 kg P ha^{-1} yr^{-1} corresponds with a total mass addition of < 8.99 kg P yr^{-1}, or < 0.18 kg P ha^{-1} yr^{-1}, by catchment area (Table 7.4). Areal loading rates for Helliers Water were estimated at 0.97 kg P ha^{-1} yr^{-1} in 1992 and 0.99 kg P ha^{-1} yr^{-1} in 1993, a total mass loading of 0.47 kg P yr^{-1} and 0.32 kg P yr^{-1} respectively being attributable to water pumped into Helliers Water from Loch of Watlee (Table 7.5). The loading rate from the catchment area was estimated as 0.11 kg P ha^{-1} yr^{-1} in both 1992 and 1993. This was the lowest loading rate from land calculated for any of the five loch catchments.

Estimated areal loading rate was greater for Loch of Tingwall, in both 1992 and 1993 (totalling 2.52 and 1.94 kg P ha^{-1} yr^{-1} respectively), than for either Loch of Gonfirth or Helliers Water (Table 7.6). Catchment loadings in the Tingwall watershed were computed as 0.43 and 0.34 kg P ha^{-1} yr^{-1} in 1992 and 1993, respectively. Estimated areal loadings to Sandy Loch for 1992 and 1993 were similar (5.28 kg P ha^{-1} yr^{-1}) (Table 7.7). When converted to TP loading rate from the catchment of Sandy Loch, an export value of 0.87 kg P ha^{-1} yr^{-1} was derived. After estimation of an additional areal loading of 0.08 kg P ha^{-1} yr^{-1} to Sandy Loch through pumping of water from Loch of Brindister, the total potential areal loading, assuming 1992 and 1993 conditions of rainfall and TP input, increased slightly to 5.36 kg P ha^{-1} yr^{-1}. This increase in TP loading to Sandy Loch in addition to the higher water volume supplied to the Loch suggested a March TP concentration reduction in the water column of 2 μg P L^{-1} would be observed when the planned transfer of water from Brindister was undertaken (Table 7.8).

TP loadings to Turdale Water estimated by the Dillon and Rigler (1974a) model were in excess of those computed for any of the other four lochs studied (Table 7.9). Areal loading rate was considerably greater in 1993 (64.62 kg P ha^{-1} yr^{-1}) than in 1992 (41.19 kg P ha^{-1} yr^{-1}). A large difference remained when results were expressed as TP contributed to the water body from the surrounding catchment; in 1992 this was estimated as 3.03 kg P ha^{-1} yr^{-1}, whilst in 1993, an estimate of 4.77 kg P ha^{-1} yr^{-1} was calculated.

Table 7.4 Estimation of maximum permissible P loading to Loch of Gonfirth

Lowest areal loading predicted to give water column P concentration of 10 mg P m^{-3} (mg P m^{-2} yr^{-1})	121.16 (1991 data)
Greater estimate of areal loading with present water column P concentration (mg P m^{-2} yr^{-1})	59.41 (1992 data)
Increase in areal loading required to result in water column P concentration of 10 mg P m^{-3} (mg P m^{-2} yr^{-1})	61.75
Total increase in P mass to catchment area (mg P yr^{-1})	8,992,343.8
Total increase in P loading from catchment surrounding loch (mg P m^{-2} yr^{-1})	18.33

NOTE 1: Divide by 100 to convert mg P m^{-2} to kg P ha^{-1}

NOTE 2: The above calculations are based on a maximum permissible spring TP concentration in the water column of 10 μg P L^{-1}, therefore in order to maintain the TP concentration at less than 10 μg P L^{-1}, the total allowable increase in P loading would have to be less than those quoted in the table.

Table 7.5 Estimated P loadings to Helliers Water

Loch mean depth (m)	1.38		
Loch surface area (m^2)	44,375		
Area of catchment surrounding loch (m^2)	363,125		
Loch volume (m^3)	61,092		
Year	**1991**	**1992**	**1993**
Water residence time (*Tw*) (yr)		0.158	0.159
Hydraulic load (*qa*)		8.71	8.66
March P concentration (mg P m^{-3})	n.d.	4.8	4.9
Rainfall (m yr^{-1})	1.207	1.297	1.292
Retention coefficient (*R*)		0.569	0.569
Areal loading (*L*) (mg P m^{-2} yr^{-1})*	n.d.	96.98	98.57
Total areal loading - rainfall areal loading (mg P m^{-2} yr^{-1})	n.d.	86.61	88.24
Mass of P from Loch of Watlee (mg P yr^{-1})	n.d.	465,961.6	322,588.8
Loch loading from surrounding land (mg P m^{-2} yr^{-1})	n.d.	10.59	11.16

KEY:

n.d. No data
* Divide by 100 to convert to kg P ha^{-1} yr^{-1}

Table 7.6 Estimated P loadings to Loch of Tingwall

Loch mean depth (m)	4.26		
Loch surface area (m^2)	463,125		
Area of catchment surrounding loch (m^2)	2,633,125		
Loch volume (m^3)	1,971,770		
Year	**1991**	**1992**	**1993**
Water residence time (*Tw*) (yr)		0.765	0.77
Hydraulic load (*qa*)		5.57	5.53
March P concentration (mg P m^{-3})	n.d.	16.4	13.3
Rainfall (m yr^{-1})	1.207	1.297	1.292
Retention coefficient (*R*)		0.638	0.640
Areal loading (*L*) (mg P m^{-2} yr^{-1})*	n.d.	252.28	204.32
Total areal loading - rainfall areal loading (mg P m^{-2} yr^{-1})	n.d.	241.90	193.98
Loch loading from surrounding land (mg P m^{-2} yr^{-1})	n.d.	42.55	34.12

KEY:

n.d. No data
* Divide by 100 to convert to kg P ha^{-1} yr^{-1}

Table 7.7 Estimated P loadings to Sandy Loch

Loch mean depth (m)	3.63		
Loch surface area (m^2)	414,375		
Area of catchment surrounding loch (m^2)	2,458,125		
Loch volume (m^3)	1,503,058		
Year	**1991**	**1992**	**1993**
Water residence time (*Tw*) (yr)		0.63	0.63
Hydraulic load (*qa*)		5.78	5.74
March P concentration (mg P m^{-3})	n.d.	33.6	33.7
Rainfall (m yr^{-1})	1.207	1.297	1.292
Retention coefficient (*R*)		0.632	0.633
Areal loading (*L*) (mg P m^{-2} yr^{-1})*	n.d.	528.05	527.86
Total areal loading - rainfall areal loading (mg P m^{-2} yr^{-1})	n.d.	517.67	517.52
Loch loading from surrounding land (mg P m^{-2} yr^{-1})	n.d.	87.27	87.24

KEY:

n.d. No data
* Divide by 100 to convert to kg P ha^{-1} yr^{-1}

Table 7.8 Prediction of reduction of March water column TP concentration of Sandy Loch assuming similar conditions of rainfall and P areal loading as occurred in 1992 and 1993

Estimated P areal loading from Loch of Brindister (mg P m^{-2} yr^{-1})	8.11	
Rainfall and P areal loading data year	**1992**	**1993**
Areal loading (*L*) (mg P m^{-2} yr^{-1})	528.05	527.86
Total estimated areal loading (mg P m^{-2} yr^{-1})	536.16	535.97
Residence time (*Tw*) adjusted for increased volume of water input (yr)	0.539	0.542
Predicted hydraulic load (*qa*)	6.74	6.70
Predicted retention coefficient (*R*)	0.607	0.608
Predicted TP concentration (mg P m^{-3})	31.3	31.4
Predicted reduction of water column TP concentration (mg P m^{-3})	2.0	2.0

Table 7.9 Estimated P loadings to Turdale Water

Loch mean depth (m)	0.93		
Loch surface area (m^2)	63,750		
Area of catchment surrounding loch (m^2)	863,125		
Loch volume (m^3)	58,951		
Year	**1991**	**1992**	**1993**
Water residence time (*Tw*) (yr)		0.076	0.076
Hydraulic load (*qa*)		12.29	12.20
March P concentration (mg P m^{-3})	n.d.	159.0	250.5
Rainfall (m yr^{-1})	1.207	1.297	1.292
Retention coefficient (*R*)		0.526	0.527
Areal loading (*L*) (mg P m^{-2} yr^{-1})*	n.d.	4118.94	6462.28
Total areal loading - rainfall areal loading (mg P m^{-2} yr^{-1})	n.d.	4108.56	6451.94
Loch loading from surrounding land (mg P m^{-2} yr^{-1})	n.d.	303.46	476.54

KEY:

n.d. No data
* Divide by 100 to convert to kg P ha^{-1} yr^{-1}

7.3.2 TP-chlorophyll *a* relationships

The TP-chlorophyll *a* relationship of 1991 results for all thirty one lochs combined was not described efficiently by a simple linear model, R^2 value and correlation coefficient being low. However, the log model of 1991 data gave a significant slope estimate ($p < 0.001$) and a correlation coefficient of 0.695, although the R^2 value remained low (R^2 = 48.3%) (Table 7.10). Data from the five intensively studied lochs were pooled, and the log model produced a significant TP-chlorophyll *a* relationship ($p < 0.001$). This relationship was similar to that for the 1991 data from the synoptic survey of thirty one lochs, but had a greater R^2 value (61.8%) and correlation coefficient (0.79) (Table 7.10).

Separate investigations of the TP-chlorophyll *a* relationships for each of the five lochs studied from 1991 to 1993, revealed that none of the five sets of results exhibited a significant relationship between TP and chlorophyll *a*, using either the simple or multiplicative analyses.

7.4 DISCUSSION

7.4.1 The modelling approach in catchment areas of Shetland lochs

7.4.1.1 Estimation of water loss through evaporation

From review of literature on annual evaporation rates in Britain, the range of evapotranspiration figures from grassland was 370-438 mm and from heather covered land, 454-478 mm (Petts and Foster, 1985). Shaw (1983) stated an annual loss of 669 mm from open water in England from review of published work. Strahler and Strahler (1973) presented a contour map of the USA (after Mead) depicting rates of water loss from open water. At 50°N (including coastal areas) evaporation was approximately 510 mm. Bailey-Watts *et al.* (1987) estimated annual potential evaporation and annual water surface evaporation at Coldingham Loch (Scotland) as 493 mm and 592 mm respectively. Whilst water loss is likely to be positively influenced by the wind conditions in the Shetland Islands, it was also taken into account that evaporation rates decrease with increased latitude.

Table 7.10 Multiplicative models of P-chlorophyll *a* relationships in Shetland lochs

Model	*n*	*p*	Correlation coefficient	R^2 value (%)	F ratio (%)
$y = -0.66x^{0.772}$	93*	<0.001	0.70	48.3	84.9
$y = -0.61x^{0.74}$	60+	<0.001	0.79	61.8	93.9

$$\log y = 0.772 \log x - 0.66$$

$$\log y = 0.74 \log x - 0.61$$

KEY:

* corresponds with three data points of thirty one lochs (1991)
\+ corresponds with twelve data points of five lochs (1991-1993)

7.4.1.2 Limitations associated with use of the models

Although empirical models have proven useful in oligotrophic and mesotrophic systems, *e.g.* 4.1-15.3 μg P L^{-1} (Dillon and Rigler, 1974b), over a wide range of loadings and flushing rates, limitations in the usefulness of the models do exist. Confidence limits for chl *a* concentrations predicted from TP levels are broad (Dillon and Rigler, 1974b), and predicted water column TP levels are normally different from measured concentrations. Dillon and Rigler (1974a) found that for the majority of lakes examined, this difference was within the range $\pm$20%, *i.e.* if the actual TP concentration were 10.0 μg P L^{-1}, then the model would probably predict a value between 8.0 and 12.0 μg P L^{-1}. The Ontario Trophic Status Model is similar to the Dillon and Rigler (1974a) model (Hutchinson *et al.*, 1991). Differences in the predicted and actual total phosphorus levels during the ice-free period were found to be less than 20% in eleven of fifteen lakes examined in a validation study of this model (Hutchinson *et al.*, 1991).

If the initial conditions of the models are violated, estimated TP or chlorophyll *a* concentrations may be inaccurate. The following factors may all adversely influence the applicability of the models: low loch mean depth, sediment P release, incomplete water column mixing, differences in loch and outflow TP concentrations, seasonal TP loading differences, failure to account for all TP inputs, limitation of production by parameters other than P (such as N, light, water colour), biotic influences. These factors are all discussed in more detail below.

(a) Lake *Z* (mean depth) may be important in influencing applicability of a model. Dillon and Rigler (1974a) found predicted and actual lake water P concentrations to be similar. However, the correlation was improved when two lakes with $Z < 1$ m were removed from the data set. In the water residence time range 1.5-4.5 years, a comparison of eight models revealed that all gave similar results of estimated P loading. However, the Vollenweider (1976) model was found to overestimate P loading at lower water exchange rates and underestimate below the above range, whereas a model developed specifically from summer data of shallow lakes (FOSRES), rather than one calibrated from annual averages from deep and shallow lakes, could predict P loading more accurately under such conditions (Berge, 1990).

The FOSRES model was developed with the assumption that effects of P loading are depth dependent, with shallow lakes having a greater tolerance to P loading than those possessing a Z of approximately > 15 m. Although the limit for oligotrophic waters remained at 10μg P L^{-1}, it was suggested from the literature that 7 μg P L^{-1} would be more appropriate for deep lakes (Berge, 1990). However, though it is possible for shallow lochs to be more tolerant of increased P loading, these lakes are often associated with nutrient enrichment. Although the shallow nature of Shetland lochs may influence the accuracy of the estimates of the Dillon and Rigler calculation (1974a), models developed specifically for lakes of low mean depth (OECD, 1982; Berge, 1990) were not utilised in the present study; tolerance of higher TP loadings has not been established for the shallow Shetland lochs, compared with deeper water bodies. The response of a loch to nutrient enrichment is dependent upon rates of flushing, sediment adsorption and release of nutrients, rather than water depth alone.

(b) The models may underestimate TP or chlorophyll *a* levels in enriched systems due to sediment P release; they are not, therefore, applicable except when P loss to the sediment ≥ 0 (Vollenweider, 1975) *i.e.* there is not a net P input to the water column from the sediment. Vollenweider-type models differ from Dillon and Rigler-type models in that P sedimentation within the lake is dependent upon water column P mass and loading P mass respectively. The two associated processes are referred to as in-lake mass decay and loading decay (Prairie, 1988). An investigation into which approach is generally more relevant to lake modelling revealed that loading decay provided a more efficient predictive equation. However, incorporation of both sedimentation parameters into a model resulted in a further improvement in performance (Prairie, 1988). The latter approach was, however, beyond the scope of the present project.

(c) It is a condition of the model that P concentration in the outflow is equal to that of the water column. This may not be applicable if sediment resuspension occurs at the outflow, or P is trapped by macrophyte stands (Berge, 1990). However, in the present study of the five lochs, this condition was generally met, with the exception of Turdale Water. The outflow TP concentration was greater than that of the water column, during October 1993.

(d) It is a also a requirement of the model that the water body is completely mixed. When lakes stratify they are not continuously and uniformly mixed. Inflows may run to surface waters only (Prepas and Rigler, 1981). However, since no difference was detectable either horizontally or vertically within the water column of four of the Shetland lochs studied, this condition of the model was fulfilled. Turdale Water TP and chlorophyll *a* concentrations were however, found to differ over the surface area of the water body. TP and chlorophyll *a* levels varied within Turdale Water during May 1993 and June 1992 (Chapter 2).

(e) With regard to seasonal differences in lake inputs and outputs, it has been suggested that a seasonal model would be more appropriate for predictions under such circumstances (Prepas and Rigler, 1981). Using three equations dealing with the mixed layer only during the summer stratification period, Prepas and Rigler (1981) found predicted and actual mean summer lake water TP concentrations were comparable. This model may be generally applicable to medium-sized lakes, but it is necessary that seasonal changes in lake water P are known.

Inaccuracies in the calculations of the present study are likely to have occurred because P loading was not seasonally consistent. In all five catchment areas studied, there were ephemeral inflows in which there was no flow for a considerable part of the year (Chapter 2). In addition, sampling of loch inflows revealed that it was possible for there to be a high degree of variability in nutrient concentrations present within the same inflow at different times of sampling (Chapter 2). Both Helliers Water and Sandy Loch are now influenced by input of water from separate water bodies over the summer period only. Owing to episodic nature of agricultural P loading in the catchments of Loch of Tingwall, Sandy Loch and Turdale Water, rate of nutrient input is unlikely to have been consistent.

Annual variability of estimated P concentrations in inflow and outflow water may be determined only when data have been compiled for several annual cycles (Prepas and Rigler, 1981). The present study has data on spring P levels in the water column during two years only, so that the estimated P loading rates have been calculated using a limited data set.

(f) When using the Dillon and Rigler model to calculate expected P concentration in the water column, account must be taken of all P sources in the catchment. During studies of the applicability of the Dillon and Rigler (1974a) model in Scottish lochs supporting cage fish farming operations, actual and predicted P concentrations were similar when aquaculture was the only significant anthropogenic water user and there had been 'relatively small perturbations to the nutrient cycle' (Kelly, 1995). However, estimation of P loading from the drainage area and assumption of steady state become difficult in multi user watersheds, particularly where forestry or improved grassland provide irregular and diffuse P loadings (Kelly, 1995).

(g) If an environmental parameter other than P is limiting algal growth, predicted chlorophyll *a* concentration will exceed the actual concentration in the lake water. In the present study, for models relating TP and chlorophyll *a* concentrations, R^2 values were 48.3% and 61.8% for the 1991 (thirty one lochs) and 1991-1993 (five lochs) data respectively. These values corresponded to the percentage of variability in chlorophyll *a* concentrations accounted for by the TP concentrations. TP was the variable measured which was most strongly related to phytoplankton taxa present and to chlorophyll *a* concentrations (Chapter 4). However, other parameters influenced phytoplankton growth. TAN and TON were noted as important in phytoplankton growth patterns in the CCA analysis. It has been illustrated in the literature that spring N:P ratio affects the accuracy of model results (Dillon and Rigler, 1974b; OECD, 1982; Dillon *et al.*, 1988).

Considering the TP-chlorophyll relationship of Sakamoto (1966), lake waters with N:P ratio > 12:1 were found to deviate only slightly from the regression line, whereas those with low N:P ratios were more divergent from the relationship (Dillon and Rigler, 1974b). Lakes studied by Dillon and Rigler (1974b) had spring N:P ratios > 12:1. TP enrichment of the water column increases the rate of N metabolism within a water body, partly explaining the change from P to N limitation in eutrophic systems (Vollenweider, 1975). Sakamoto (1966) illustrated that in lakes with a N:P ratio of < 10:1, N and chlorophyll exhibited a better relationship than that found between P and chlorophyll (Dillon *et al.*, 1988). An important reason for variation in results from P and chlorophyll predictive studies is that lakes with water column N:P ratios < 10:1 have been incorporated in the work (Dillon *et al.*, 1988). In

studies of North American lakes, around 80% of the variability in chlorophyll *a* concentration could be explained by P concentration, but the residual variance was most highly correlated with N:P ratio (Dillon *et al.*, 1988). Unfortunately, measurement of TN was not possible in the present study, nor determination of TAN and TON after 1991. Investigation of possible adjustments of the models with N concentrations was therefore not feasible.

In enriched waters, light may become the dominant limiting factor for algal growth. This is also an important consideration, particularly in dystrophic lakes. According to Granberg and Harjula (1982) most of the developed nutrient-chlorophyll models in their original state cannot be used for brown water lakes, as their predictive capacity is based on data from clear water lakes. Consequently, models incorporating a light coefficient have been tested and primary production may be estimated from mean annual TP concentration and mean annual water colour (Granberg and Harjula, 1982). Granberg and Harjula (1982), however, obtained a relationship between observed and predicted phytoplankton production with $R^2 = 0.62$ only. This may have been associated with the poor $R^2 = 0.52$ of the relationship between mean seasonal primary productivity and maximum primary production. Tolstoy *et al.* (1988) compared models with and without a light parameter incorporated in the calculations and concluded that light was an important variable which the OECD (1982) study excluded. Of three Swedish lakes studied, only predictions for brown-water Lake Vänern fell outwith OECD model confidence limits. Using TP, water colour and transparency improved the primary production predictive capacity and uniformity of results compared to OECD models in Lake Vänern (Tolstoy *et al.*, 1988). In the present study, the CCA did not show light to be one of the most important factors accounting for differences in phytoplankton growth in different lochs at different times (Chapter 4). It appears unlikely, therefore, that in the TP-chlorophyll *a* models for Shetland lochs, inclusion of a light factor would have improved their explanatory power substantially.

(h) Biotic factors may influence the efficacy of the model. Chlorophyll concentrations vary between and within algal groups (Ahlgren *et al.*, 1988). Differences in cell chlorophyll content are known to occur between species and as a result of cell condition and environmental factors. For example, from literature review, Reynolds

(1984a) presented chl *a* contents per algal cell as follows: *Asterionella formosa* 1.38-2.21 pg; *Closterium aciculare* 89 pg; *Ankyra judayi* 0.45 pg; *Anabaena circinalis* 0.6-0.9 pg. Also, possible shifts in dominance of different phytoplankton are regarded as typical of P enrichment in water bodies. This is not accounted for in the TP-chl *a* model and consequently could explain differences found between predicted and actual effects of P on phytoplankton biomass, or between different predictive regressions (Dillon *et al.*, 1988). Mean seasonal chlorophyll *a* concentration and mean seasonal phytoplankton productivity are highly positively correlated. A comparison of chlorophyll *a* with phytoplankton biomass in estimation of trophic status revealed the latter to have a more significant regression equation, particularly when diatom biomass was discounted (Dillon *et al.*, 1988). However, chlorophyll *a* is a rapidly and easily measurable estimate of algal biomass. Zooplankton communities within the lake also influence chlorophyll *a* concentration (Ahlgren *et al.*, 1988), although in a study of North American lakes, total crustacean and herbivorous crustacean variables were included in the TP-chlorophyll *a* model and did not inprove the efficacy of the model (Dillon *et al.*, 1988).

7.4.2 Implications of the results for catchment management of the five sites

Neither Loch of Gonfirth nor Helliers Water had any anthropogenic inputs of P from the land within the drainage basin. Consequently the estimated TP loadings from these catchment areas were the lowest calculated (Tables 7.3 and 7.5). That Helliers Water catchment TP loadings were lower and more consistent from 1992 to 1993 is possibly explained by the soil types present in each catchment. Soils present in the Helliers Water catchment were found to be more efficient in adsorption and binding of P than those in the Loch of Gonfirth watershed (Chapter 6). Consequently, in the Helliers Water catchment area, P released from soil or vegetation would be rapidly readsorbed. In addition, release of water soluble P from this soil is far less likely than from soil of the Loch of Gonfirth drainage basin. In terms of rates of soil erosion, it is also more likely for the loading of particulate P to the water body to be greater in the Loch of Gonfirth watershed, as loss of P increases with slope (Goldman and Horne, 1983). The Helliers Water catchment area has lower slopes than those at Loch of Gonfirth (OS 1:25000 Sheets HP 40/50/60 and HU 26/36 respectively).

However, despite the oligotrophic status of Helliers Water indicated by the March TP concentrations in the water column and the capacity of the soil for P uptake, in summer, the TP levels in this water body have been observed to be as high as 9.8 μg P L^{-1} (May, 1992). During summer, this reservoir is "topped up" with Loch of Watlee water, which has a greater TP concentration than that of Helliers Water. As the Helliers Water has a water residence time of approximately 0.16 yr *i.e.* it flushes 6.3 times per year, this action probably does not have a lasting effect. However, increased loading in summer can increase phytoplankton productivity and result in sediment P binding sites being occupied. Addition of P to a freshwater system is likely to have the greatest impact in the summer, when conditions of light and temperature are most favourable for algal growth. It is therefore not considered advisable to have any additional P loading to this catchment area.

In contrast, Loch of Gonfirth drainage basin has been estimated as being able to tolerate a further P loading rate from the surrounding land of < 0.18 kg P ha^{-1} yr^{-1} (total mass addition of < 8.99 kg TP yr^{-1}). Soil in this catchment area is, however, unlikely to retain a large proportion of any applied fertiliser P, should reseeding be undertaken. Of the three catchments studied which had experienced soil fertilisation, none had a loading rate as low as 0.33 kg P ha^{-1} yr^{-1} *i.e.* the maximum estimated permissible loading rate from the land to Loch of Gonfirth.

Loch of Tingwall ranked third in terms of trophic status and in catchment TP loading rates. The elevated P loading rates are accounted for by the nature of the land use in the catchment, a greater proportion of the loading being attributable to the west side of the watershed. Possible sources of P in this part of the drainage basin include:- ten septic tanks, two slurry stores, one dairy, one beef unit, one golf course, substantial areas of reseed and some arable land (Okill, J.D., SIC, *pers. comm.*, 1994). Mean TP concentration in the water column of Loch of Tingwall during summer was found to range from 8.5-10.7 μg P L^{-1}. However, during March and May, 1992 and March, 1993, mean water column TP levels of 16.4, 14.7 and 13.3 μg P L^{-1} were recorded respectively. In addition, mean chlorophyll *a* concentrations in Loch of Tingwall exceeded OECD (1982) limits for oligotrophic waters on all sampling dates except May, 1992, when mean water column concentration was at the OECD (1982) limit of 2.5 μg chl*a* L^{-1}. Of the five lochs studied, this water body had the greatest water

retention time (0.77 yr), corresponding to a flushing rate of 1.3 times annually. It is therefore recommended that, despite relatively high soil P uptake potential, no further land improvement is undertaken in this catchment area, nor are loading rates of P to this water body increased through any other nutrient source.

Monitoring of the inflow waters of Loch of Tingwall revealed that existing point sources of discharge may not be continually maintained to standards required for protection of freshwaters. Inflow 6, though ephemeral, was found to exhibit excessive nutrient levels and growth of "sewage fungus", which is typical of heavily enriched systems. It is suggested from a knowledge of land use that this was attributable to either a dairy unit or silage storage, in which case it would probably also exhibit an unacceptable biochemical oxygen demand. There exists the potential for improvement of present discharges. As there is now a sewage scheme in the Tingwall area for removal of waste from human habitation, and it is desirable that future developments be incorporated into this scheme, with sewage being pumped to the sea, rather than septic tanks discharging within the catchment area. Under EC legislation, emission of sewage to the sea will be unlawful from 1998. However, inclusion of all waste outputs in the existing scheme would provide the framework for sewage collection and disposal in the future.

TP loading rates to Sandy Loch were greater than those to Loch of Tingwall (Tables 7.6 and 7.7). Whereas soil in Loch of Tingwall watershed has relatively high P binding capacity, that in Sandy Loch drainage basin is highly organic and retains little P against leaching. Therefore, the combination of a peaty catchment area and additional nutrient loadings have resulted in relatively high TP loading rates. The TP concentrations measured in inflow 1 and a drain from the north east of the catchment, suggest that the cultivated land in this area of the drainage basin contributes a TP loading to the Loch in excess of that which would be expected naturally. Two other potential TP sources in the watershed are the disused tip to the north of the water body, and the old area of reseed in the south west of the catchment area. It is likely that much P is imported to the Loch in particulate or humic-bound form. Little difference was apparent in Sandy Loch TP concentrations or loadings in 1992 and 1993, thereby suggesting that small additions in forms readily available to plants are extremely important.

Table 7.11 P loss coefficients from various land use types

Land use	Rate (kg P ha^{-1} yr^{-1})	Source
Improved grassland, Scotland	0.25	Holden (1975)
Conifer forest, Scotland	2.0	Malcolm and Cuttle (1983)
Pastoral, N. Zealand	0.75	Smith (1987)
Various, Finland	0.00-0.01	Ahl (1988)
Various, S. England	0.28-1.55*	Johnes and O'Sullivan (1989)
Agriculture, Finland	0.90-1.80	Rekkolainen (1989)
Pastoral/forests Australia	0.57	Cosser (1989)
Peatlands, Finland	0.08-0.14	Heikkinen (1990)
Drained/undrained peat bogs, Finland	0.1/0.21	Lundin and Bergquist (1990)
Agriculture, Scotland	0.18-0.22	Bailey-Watts and Kirika (1991)
Various, Finland	0.05-0.26*	Bilaletdin *et al.* (1991)
Polders, Netherlands	0.63-1.48	van Huet (1991)
Arable, Denmark	1.69-1.87	Kronvang (1992)
Various, Sweden	0.02-0.08*	Ahl (1994)
Farmland, Central Scotland	0.82-1.59	Grieve and Gilvear (1994)
Alpine pastoral, France	0.6	Dorioz and Ferhi (1994)

KEY:

* indicates calculated load estimate

Estimated P loading rates to the different catchments were generally within the range of values presented in the literature for P losses from various types of land use found in these drainage basins (Table 7.11). The exception was Turdale Water, which had estimated P loss values in excess of those in the literature. A high proportion of the Turdale catchment area was reseeded. This in combination with the small volume of the Loch, the low P retention characteristics of the highly organic soil (Chapter 6) and the failure in adjusting soil pH to the less acid conditions required for soil improvement (Chapter 6) account for the high TP loss rates from the land in the Turdale Water catchment area and its subsequent upon Loch water quality.

7.4.3 Comparison of water management in the present study with other reported examples

TP loadings can be estimated by continuous monitoring of TP concentrations and discharge in all loch inflows, but this is an expensive an labour intensive approach. Consequently, estimation of the TP loading to a loch through the use of loss coefficients for different land uses observed in catchment studies elsewhere are favoured (Table 7.12). Estimates of TP loadings are calculated from the proportions of different land uses within the watershed. In the technique of hindcasting, loss coefficients are also used to estimate the "original" TP concentration in the loch water column.

Typically, there is no account taken of slope, soil P adsorption capacity, or extent of vegetation cover in these types of calculation. However, slope of the land is incorporated in PLUS (Marsden, 1995). Inclusion of this factor might improve TP loss estimates in a relatively steep-sided drainage basin, such as that of Loch of Tingwall. However, many of the Shetland watersheds are of relatively flat topography, so slope may not be such an important influence on TP losses. The results of the P retention in soil experiments in the present study suggest that TP loadings calculations involving loss coefficients should be interpreted with extreme care. Assuming the same loss coefficients for the same land use is inappropriate when different soil types are present. Highly organic soils, especially those of low pH, retain little of the P added to them, compared with more mineral soils of high pH (Chapter 6). Not only is there P lost in the particulate form, as suggested in the literature (Sinclair *et al.*, 1992; Reynolds, 1994), but also in the dissolved fraction

(Chapters 2 and 6).

A different approach to estimation of TP loadings to five study lochs was undertaken in the present study. The Dillon and Rigler (1974a) model was rearranged to calculate TP loading from loch water column TP concentrations. From these calculations it is apparent that small changes in loading may have a significant effect on phytoplankton productivity. Similarly, only small differences in loch water P concentrations (μg P L^{-1}) are necessary to increase or decrease the probability of excessive phytoplankton growth. Therefore, only a small error in the loadings estimated from loss coefficients observed elsewhere could be significant.

It is doubtful whether a return to the original state of a water body can be achieved following development in the catchment of more intensive agricultural or forestry land use. Similarly, the majority of Scotland was originally forested naturally. The hydrology and nutrient dynamics of a naturally forested catchment cannot be the same as those of the cleared watershed. These objections raise serious doubts as to the suitability of hindcasting as an effective management tool. It is suggested that attempting to manage systems as they are is more practical than the hindcasting approach.

Errors also exist in the use of a model such as that of Dillon and Rigler (1974a) (Chapter 7). In addition, catchment TP loadings calculated with the rearranged version of this model do not give loss coefficients for individual land uses, unless there is one land use only within the drainage basin. However, use of the Dillon and Rigler (1974a) model in estimation of export of TP from catchment to loch systems requires only information on lake morphometry and the TP concentration in the water column at the end of winter. Validation of this model has been undertaken in its original form for calculation of water column TP concentrations from TP loadings to the loch. In addition, the model in its original form may be utilised in assessing the theoretical maximum tolerable additional TP loading to a loch system.

7.4.4 Reduction of P losses to loch systems

7.4.4.1 Good agricultural practice

Reductions in losses of nutrients to the catchment drainage system are possible through appropriate farm management regimes which effectively limit surface runoff quantity and quality. Measures for minimisation of enrichment of waters are outlined by NRA (1992), the Control of Pollution (Silage Slurry and Agricultural Fuel Oils)(Scotland) Regulations 1991 and the Code of Good Agricultural Practice (SOAFD, 1991). Several major reduction strategies are suggested, including:

(a) soil analysis for determination of fertilisation requirements
(b) restoration of improved grassland to semi-improved or rough grazing
(c) use of unfertilised strips of land adjacent to drainage channels and standing waters
(d) operation of a set aside policy
(e) replacement of silage with hay for winter livestock feed
(f) ploughing late in winter
(g) limitation of slurry spreading between October and March
(h) careful storage/containment of silage/slurry.

7.4.4.2 Soil assessment

With respect to point (a), Soil Survey maps indicate that few soils are present in the thirty one catchment areas studied which would be efficient at P sorption (Table 6.7). The majority of soil designations signify soils of peaty, wet and cation leached natures (Table 6.7). Soil Survey information confirms that there are areas in certain drainage basins which incorporate soils more likely to have a relatively good P sorption capacity: Arthur's, Cliff, Huesbreck, Papil, Skutes, Snarravoe, Spiggie, Tingwall and Watlee. Also indicated in the maps and illustrated by %LOI and pH measurements was the fact that poor soils were also present in the catchments with relatively efficient P sorping soils, such as Tingwall and Spiggie. Consultation of soil maps is therefore recommended as good practice for initial assessment of likely effects of reseeding procedures. Measurements of soil pH and organic content are simple to undertake and may assist in the estimation of the likely magnitude of TP loss following fertilisation. As efficiency of P sorption is dependent upon soil type, and previous additions of fertiliser affect the P sorption capacity of a soil (Chapter 6), it

is important to determine actual, rather than estimated fertiliser requirements.

7.4.4.3 Future options for land and runoff management procedures

With reference to points (e)-(h), ploughing late in winter minimises nutrient loss through increased surface run-off resulting from waterlogging or freezing of the soil. Minimal spreading of slurry between October and March is recommended for the same reasons. Incidences of organic enrichment of water bodies from farm sources have often been associated with inadequate containment of slurry/silage. Difficulties have arisen as a consequence of storage receptacles having insufficient volume, structural defects and cracks in the drainage system, in addition to poor management practices (NRA, 1992).

Considering points (c) and (d), in drainage basins where land improvement has been undertaken such as Loch of Tingwall, Sandy Loch and Turdale Water, the use of buffer zones as recommended by NRA (1992) is suggested. Buffer zones have a beneficial effect on water quality as the area of land receiving fertiliser is distanced from the water body. Suspended soil particles and nutrients in drainage water from the affected area are then trapped, broken down or assimilated into biological material of the catchment soils and not discharged to the water course. NRA (1992) advocated examination of the possibility of "set aside" being used for such a purpose.

The width of a vegetated buffer zone is recommended as 10-20 m, depending upon slope, size of water body, soil nutrient retention capacity and vegetation type (Ahola, 1990). This will have implications for field size in small land holdings in Shetland.

Finally, a strategy which has not been considered in the present study is the implementation of macrophyte based water treatment methods. The utilisation of vegetated ditches and wetland systems to control run-off quality is not dissimilar to the use of buffer zones. In vegetated ditches and wetland systems, the plants do not account for a high percentage of the nutrient removal efficiency. Bacterial transformations such as nitrification/denitrification and physicochemical processes, such as sedimentation, adsorption and precipitation. However, the use of more than one plant species is recommended for increased efficacy of nutrient removal (Hammer, 1989). Species of *Typha*, *Scirpus*, *Juncus* and *Phragmites* have all been

used in constructed wetlands. Deep penetration of the substrate by *Phragmites* root systems results in increased soil stabilisation, hydraulic conductivity and aerobic microbial activity (Lawson, 1987). The main problem with wetland systems is the area of land required for efficient nutrient removal. In sewage treatment, 1.34-4.44 ha ML^{-1} d^{-1} (or 1.78-2.22 ha ML^{-1} d^{-1} after primary treatment) is required (Hammer, 1989).

Vegetated drainage systems have been utilised in nature conservation areas in the Netherlands (Meuleman and Beltman, 1993). Polluted river water has been routed through drainage ditches or reed marshes and a zonation from eutrophic to mesotrophic plant types has been observed along the vegetated ditch. Low N removal efficiency has been observed, in contrast to high efficacy of P removal (90-95%), the latter being associated particularly with an area of *Fontinalis antipyretica* (Meuleman and Beltman, 1993). It is concluded that use of such treatment systems as vegetated ditches and wetland systems in Shetland may be worth investigating in the future.

7.5 CONCLUSIONS

(1) Many algal and nutrient control methods have been considered (Section 7.1), but there are few techniques which would be appropriate to the requirements of Shetland.

(2) The predictive ability of the Dillon and Rigler (1974a) model has been observed to be better than that of the other empirical models available (Beveridge, 1984). However, there are limitations to the use of the Dillon and Rigler (1974a) model for prediction of loch trophic state and therefore for estimation of TP loadings from loch TP concentrations.

(3) Calculated loadings of TP to the five study lochs were within the range of values observed elsewhere, with the exception of TP loadings in the Turdale Water watershed. TP loadings in this drainage basin were higher than those in the published literature.

(4) The implications of the investigations into the TP budgets of the study catchment areas are that further TP inputs to the lochs should be discouraged and where possible, existing discharges should be improved.

CHAPTER 8: CONCLUSIONS

8.1 Thesis aims

As stated in the introductory chapter, section 1.18, the aims of the thesis were to determine the following:

(a) present status of water quality in Shetland Island lochs

(b) susceptibility of Shetland standing waters to excessive primary production problems associated with nutrient enrichment

(c) the potential for fertiliser applications on land to cause nutrient enrichment of standing freshwaters

(d) possible preventative or remedial measures to preserve water quality should problems of elevated plant productivity occur.

Aim (a) was acheived by undertaking three successive annual water sampling programmes, with the initial survey in 1991 encompassing thirty one sites throughout the Shetland Islands (Chapter 2). Samples taken were analysed for a wide range of physico-chemical parameters, including P and N concentrations.

Aim (b) was completed by using the nutrient status information obtained in the 1991 survey and comparing this data to the OECD (1982) trophic status classification scheme for freshwaters (Chapter 2). The potential for sediment to act as a source or sink of nutrients was evaluated (Chapter 3). In addition, an examination of the resident phytoplankton (Chapter 4) and macrophytes (Chapter 5) in freshwaters both affected and unaffected by fertilisation was undertaken.

Aim (c) was acheived by three methods. Firstly, the analysis of inflow water nutrient chemistry in fertilised catchment areas (Chapter 2). Secondly, calculation of P loss coefficients from such areas (Chapter 7), and thirdly, through laboratory examination of P adsorption and desorption from soils collected from five representative catchments (Chapter 6).

Aim (d) was completed by consideration of available technologies for water quality preservation in nutrient enriched areas, and their applicability in the Shetland Islands freshwater environment (Chapter 7).

8.2 Thesis conclusions

(1) A variety of loch types, incorporating a range of physical and chemical characteristics was observed within the thirty one water bodies surveyed.

Parameter	Range
pH	5.09-9.80
Conductivity (μS cm^{-1})	151-695
Water colour (at 400nm)	0.027-0.887
LAC	0.06-5.33
TP (μg P L^{-1})	4.1-154.3
TDP (μg P L^{-1})	2.8-59.2
DRP (μg P L^{-1})	<1.0-90.8
TAN (μg N L^{-1})	10-145
TON (μg N L^{-1})	<5-58
Ca (mg L^{-1})	1.3-80.0
Mg (mg L^{-1})	2.8-20.9
Na (mg L^{-1})	24.3-52.8
K (mg L^{-1})	0.8-3.3
Chlorophyll *a* (μg L^{-1})	1.0-32.8

(data excluding saline Strand Loch)

(2) Values for pH, alkalinity, conductivity and water cation concentrations were slightly elevated in comparison with lochs elsewhere in Britain, but water chemistry was as would be expected in shallow, lowland waters, with influences from fertile geology and maritime salts.

(3) A range of trophic states was observed, from oligotrophic to eutrophic. Only six water bodies were classified as oligotrophic and therefore unlikely to exhibit excessive phytoplankton production. These were Arthur's, Helliers, Lunga and Roer Water and Lochs of Gonfirth and Ustaness.

(4) A degree of variation in TP concentrations is to be expected in loch and inflow waters and in chlorophyll *a* levels of standing freshwaters, even in situations where there is no anthropogenic nutrient input, other than in the

form of airborne substances.

(5) Data collected suggested that inflow waters were likely to be a source of loch nutrient enrichment in catchment areas incorporating improved grassland, cattle and septic tanks.

(6) Working in favour of good water quality in the standing waters of Shetland are the prevailing meteorological conditions which ensure that stratification of the water column is rare. This effect is augmented by the shallowness of the loch basins. Stable water column conditions were noted only infrequently, even in the deeper basins examined. Stratification when present was weak, constituting a temperature change of approximately 2°C from surface to deep water.

(7) %C, %N and %P contents of the sediments examined were all within the ranges of values observed elsewhere:

Parameter	**Range**
%C	**0.94-36.7%**
%P	**0.03-0.34%**
%N	**not detectable-1.49%**

(8) Eh conditions in the sediments of the four basins were generally in agreement with water column nutrient status information. Sediment Eh decreased in the following order: Loch of Gonfirth, Helliers Water, Tingwall North, Turdale Water, Tingwall South.

(9) In Shetland lochs, the same sediment may act as both a sink and a source of P. There was a tendency for P stored in sediment to be present in highest quantities at approximately 3-5 cm sediment depth.

(10) A proportion of the P present in the upper 5 cm of sediment was in a readily releasable form, possibly loosely bound to humic substances, in sediment from Lochs of Gonfirth, Tingwall and Turdale Water.

Range of sediment P release: 0.00-0.52 μg P g^{-1}

(11) External P loading was an important influence on sediment P dynamics. Turdale Water had the highest water column TP concentration, in addition to having the most organic sediment and the highest P release. Loch of Tingwall sediment had the lowest organic content, but the second highest water column TP concentration and sediment P release.

(12) The P adsorption capacity of sediments studied decreased in the following order: Helliers Water, Loch of Tingwall, Loch of Gonfirth. Sediment in Helliers Water assists in maintaining water column P concentration at levels lower than would be expected from P loading on the water body. Lochs in catchment areas incorporating more mineral soils are likely to have sediments which have relatively good P sorption properties. Conversely, lochs in drainage basins of peaty soil types are likely to have sediments of poor P sorption capacity.

Range of sediment P uptake: 0.03-0.54 μg P g^{-1}

(13) It is concluded that, if the external P loadings were removed from Loch of Tingwall, Sandy Loch and Turdale Water, an internal P loading would remain. However, in Helliers Water, it is likely that the P immobilised in the sediment would be retained. Although Loch of Gonfirth sediment was found to release P, there has been no artificial loading on this water body, so that the internal loading is not considerable.

(14) Presence of green algae and cyanobacteria in lakes was not in itself an indicator of nutrient enrichment. Blue-green algae, such as *Gomphosphaeria* and *Merismopedia*, were observed in water bodies of low trophic status. Similarly, green algae, such as desmids, *Monoraphidium/Ankistrodesmus* and *Oocystis* were present in low nutrient waters.

(15) Chrysoflagellates were widespread in Shetland lochs. These algae often dominate in Scottish lochs (Brook, 1964; Bailey-Watts and Duncan, 1981a).

(16) A range of phytoplankton assemblages was observed in the lochs surveyed. CCA analysis indicated that distribution and abundance of phytoplankton

genera in the thirty one sites varied with the levels of TON and TAN found in the water column. However, TP concentration remained the most important parameter measured in this respect in the Shetland lochs.

(17) Changes in phytoplankton community structure with time demonstrated similarities with those expected in temperate lake systems, such as the occurrence of the spring diatom increase. Deviations from the model may be partly attributable to the individual nutrient status of each loch.

(18) *Anabaena* was the only blue-green genus of phytoplankton ranked highly on the TP gradient and in addition associated with increased TAN and low TON concentrations. Other cyanobacteria exhibited a range of nutrient preferences.

(19) In 1991, on at least one water sampling date, lochs in which cyanobacterial blooms had been observed were associated with increased TP, TAN, and chl *a* levels, together with low TON concentrations. The sites were Turdale, Bu and Punds Water, Sandy Loch and Loch of Brough (Yell).

(20) Other water bodies which experienced similar water column conditions on at least one occasion were Gossa Water and Lochs of Brow, Snarravoe and Cliff. It is postulated that *Anabaena* blooms did not develop in these water bodies because P in the water column was bound to Ca or Mg, rather than being present in more bioavailable forms.

(21) Macrophyte species present in Shetland Island lochs were typical of those observed elsewhere in Scotland, in lowland areas under maritime influence, in water bodies situated on fertile and non-fertile geology.

(22) In terms of water quality, macrophyte species present in the Shetland lochs 3surveyed were found to be influenced most by pH, Ca and Mg concentrations. The classification system of Shetland lochs by TWINSPAN division was therefore likely to be indicative of different water pH values, CO_2/HCO_3^- levels, hardness and alkalinity.

(23) Macrophytes may not be competing for the same nutrient sources as phytoplankton. Typically, aquatic macrophytes obtain their P requirement from sediment sources, rather than the water column, therefore macrophytes cannot be used as direct indicators of the susceptibility of waters to development of high phytoplanton biomass.

(24) A wide range of soil properties were observed in Shetland:

Parameter	**Range**
pH	**3.69-6.90**
Water content (%)	**0.1-189.4**
Loss on ignition (%)	**0.9-97.7**

(25) The prevalence of peat in Shetland is important when considering potential effects of reseeding on standing freshwater resources. Compared to most mineral soils, peats have poor phosphate sorption properties.

(26) If organic content of a soil is > 80%, it is highly likely that P sorption will be poor. Similarly, if soil pH <4.00, sorption will also be depressed.

(27) When considering potential effects of P fertilisation on loch water quality, it would be useful to assess the organic content and pH of the soil involved, as a relationship exists between both %LOI and pH and P adsorption capacity. Despite analysis showing this relationship to be significant, P adsorption remains highly variable, so precluding accurate prediction of fertiliser effects on P removal in surface runoff and drainage water.

Range of P uptake: 0.05-2.06 mg P g^{-1}
Range of P release: 0.00-0.07 mg P g^{-1}

(28) The less acidic and organic soils in the drainage basins of Arthur's Loch, Lochs of Cliff, Huesbreck, Spiggie and Tingwall are likely to have superior P sorption ability compared to soils of the watersheds of Sandy Loch, Lochs of Gonfirth, Huxter, Brough (Yell) and Lunga, Turdale and Bu Water. With few exceptions, soils within watersheds of the latter group of lochs were found

to be of high organic content (83.0-97.6%) and low pH (pH 3.69-4.91) and therefore unlikely to sorp P effectively.

(29) Many algal and nutrient control methods have been considered but few techniques which would be appropriate to the requirements of Shetland.

(30) There are limitations to the use of the Dillon and Rigler (1974a) model for prediction of loch trophic state and therefore for estimation of TP loadings from loch TP concentrations.

(31) Calculated loadings of TP to the five study lochs were within the range of values observed elsewhere, with the exception of TP loadings in the Turdale Water watershed. TP loadings in this drainage basin were higher than those in the published literature.

(32) The implications of the investigations into the TP budgets of the study catchment areas are that further TP inputs to the lochs should be discouraged and where possible, existing discharges should be improved.

(33) Lochs which are likely to be most susceptible to development of phytoplankton blooms when fertiliser is applied to the surrounding land are those highly coloured waters within catchments incorporating peaty soils and sediments, located on geology of low Fe, Mn, Al, Ca and Mg content.

(34) As reseeding within catchment areas has effects upon the receiving loch systems, to prevent problems of deterioration of water quality, as a consequence of augmentation of phytoplankton growth, watershed management, rather than within loch restoration measures are necessary.

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