THE DEVELOPMENT AND APPLICATION OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF TECHNETIUM-99 IN THE AQUATIC ENVIRONMENT

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DECLARATION

The work described in this thesis was performed in the Environmental Radioactivity division of the Scottish Universities Research & Reactor Centre, East Kilbride, during the period from August 1992 to December 1996, under the supervision of Dr Martin McCartney.

This thesis contains the results of some original research by the author and no part of the material offered has previously been submitted by the candidate for a degree in this or any other university. Where use has been made of the results and conclusions of the other authors in the relevant studies, care has been taken to ensure that the source of information is always clearly indicated, unless it is of such general nature that indication is impracticable.

Place: East Kilbride

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ABSTRACT

^{99}Tc is a high yield fission product with a long half-life (t½ = 2.1×10^5 years) and relatively high solubility in natural waters. Consequently, it is of potential radiological concern if released to the environment either in the long term from a high-level nuclear waste repository or as an immediate result of nuclear fuel reprocessing. The environmental chemistry of ^{99}Tc is not, however, well characterised since there are no stable isotopes of Tc and the analyses of ^{99}Tc is difficult due to a combination of its low concentration in the environment, its long half-life and the relatively low energy of the beta-particle emitted in the decay. Recent advances in analytical techniques coupled with increased ^{99}Tc levels in Irish Sea, however, should now provide an ideal opportunity to study the behaviour of ^{99}Tc in the marine environment. The aims of this study were: 1) to develop an analytical method for the determination of ^{99}Tc in the marine environment, and 2) to study the initial response of the Irish Sea environment to the increased discharges of ^{99}Tc from Sellafield.

An analytical method, based on Inductively Coupled Plasma Mass Spectrometry, has been developed. Pretreatment of samples was necessary to concentrate ^{99}Tc and reduce the level of potential interferences (in particular ruthenium - ^{99}Ru natural abundance, 12.7%). This was achieved by a combination of ion-exchange, ashing, leaching, precipitation and selective extraction chromatography, using a short-lived technetium isotope (e.g. ^{95m}Tc or ^{99m}Tc) as a yield monitor. Decontamination factors of 10^5 - 10^6 were obtained for Ru and a detection limit of 13 Bq kg^{-1} was achieved for routine analysis. The chemical procedure could also be used to provide samples suitable for analysis by liquid scintillation counting.

Technetium-99 levels in the Irish Sea were found to vary between species (seaweeds >> mussels > winkles > sediments) and within seaweed species (brown algae >> green algae > red algae). ^{99}Tc accumulation in seaweeds, mussels and winkles has also varied temporally. For example, ^{99}Tc levels increased from 2.33±0.3 to 75.6±8.7 kBq kg^{-1} (dry wt.) in seaweeds (Whitehaven harbour) between. 1989 and 1995. Saltmarsh plants collected from Newbiggin, have also shown a similar increase in ^{99}Tc levels. During this time period discharges from Sellafield increased from 6 to 190 TBq y^{-1}. Increases in ^{99}Tc levels in seaweeds have also been observed outwith the Irish Sea. A general increase in

^{137}Cs/^{99}Tc activity ratios with distance from Sellafield in 1995, however, indicates that these sites are yet to be exposed to the highest ^{99}Tc discharge levels. Data obtained from a sediment core suggest that historical levels of ^{99}Tc in the Irish Sea environment may have been far higher than would have been expected from discharge estimates. Contributions of ^{99}Tc to the Irish Sea from other nuclear establishments (Capenhurst and Springfields) were found to be insignificant, although, at a local level, could result in relatively high environmental levels (e.g. 30 kBq kg^{-1} (dry wt.) in green algae from Rivacre Brook, Capenhurst area).

CHAPTER 1: INTRODUCTION

1.1 INTRODUCTION.

The name Technetium comes from the Greek word *'technetos'* meaning 'artificial'. Its existence was first demonstrated by Perrier and Segré (1937) when the isotopes ^{95m}Tc and ^{97m}Tc were found on a molybdenum plate that had been bombarded with deuterons. Since then, 21 isotopes along with their various isomers have been produced, ranging in mass from 90-110 (Rioseco, 1987). All isotopes of technetium are radioactive, and are presented in Table 1.1 (Long & Sparkes, 1988). All primordial technetium isotopes will have decayed as the longest lived isotope, ^{98}Tc, has a half-life of 4.2×10^6 years and the age of the earth is approximately 4.5×10^9 years.

Of the three technetium isotopes with half-lives greater than a year only ^{99}Tc is of environmental concern. ^{99}Tc is a high yield fission product and although it is a weak beta emitter (Emax = 292 keV), it is of radiological significance due to its long half-life and relative ease of mobility in the aquatic environment.

Discharges of ^{99}Tc to the environment are quite low at present. This together with its low specific activity and problems associated with its radiometric determination means that environmental data are relatively scarce. As ^{99}Tc emits no gamma radiation it has been historically neglected by the nuclear industries, and hence, in many radiological assessments. It is also known, from the two international symposia conducted on technetium (Cadarache, France (1984) and Seattle, USA (1986)), that the behaviour of technetium in the environment is very complex. Certain aspects like, the ultimate 'sink' for Tc in the environment and its bioavailability are not yet sufficiently well documented. Most ^{99}Tc will end up in high level waste and it is thought that it will make a very significant contribution to the long-term dose from this source. Indeed, it is recognised as one radionuclide that will not be adequately contained by the forthcoming UK NIREX repository. Considering these points, much more work is required into understanding the complex behaviour of Tc in the environment.

Isotope	Half Life	Type of decay
^{90}Tc	50 s	β^+
^{90}Tc	7.9 s	β^+
^{91}Tc	3.14 m	β^++EC, γ
^{91}Tc	3.3 m	β^++EC, γ
^{92}Tc	4.4 m	β^++EC, γ
^{93}Tc	2.7 h	EC + β^+, γ
^{93m}Tc	43.5 m	IT, EC, γ
^{94m}Tc	53 m	β^+ + EC, γ
^{94}Tc	4.9 h	EC + β^+, γ
^{95}Tc	20 h	EC, γ
^{95m}Tc	61 d	EC + β^+, IT, γ, e^-
^{96}Tc	4.3 d	EC, γ, e^-
^{96m}Tc	52 m	IT, EC, β^+, γ, e^-
^{97m}Tc	91 d	IT, γ, e^-
^{97}Tc	2.6×10^6 a	EC
^{98}Tc	4.2×10^6 a	β^-, γ
^{99}Tc	2.1×10^5 a	β^-
^{99m}Tc	6.0 h	IT, γ, e^-
^{100}Tc	15.8 s	β^-, γ
^{101}Tc	14 m	β^-, γ
^{102}Tc	6.3 m	β^-, γ
^{102m}Tc	4.3 m	β^-, IT?, γ
^{103}Tc	50 s	β^-, γ
^{104}Tc	18 m	β^-, γ
^{105}Tc	7.6 m	β^-, γ
^{106}Tc	36 s	β^-, γ
^{107}Tc	21 s	β^-, γ
^{108}Tc	5 s	β^-, γ
^{109}Tc	1 s	β^-
^{110}Tc	0.8 s	β^-, γ

Table 1. 1 Technetium Isotopes.

1.2 GENERAL PROPERTIES OF TECHNETIUM.

Technetium is a silver-grey metal which tarnishes in moist air. It is similar to its closest analogue rhenium in crystalization. Technetium is useful in superconductive applications at low temperatures. The critical temperature T_{cr} is approximately 8K (Picklessimer & Sedula, 1962), which is one of the highest for metals. A summary of the main physical properties of technetium is given in Table 1.2.

Atomic Number	43
Melting point	2200°C
Boiling point	4700°C
Atomic radius	1.358 A
Density	11.50 g m^{-3}
Critical temperature	8 K

Table 1. 2 Main physical properties of technetium.

Technetium is a group VII element, residing between molybdenum and ruthenium in the second transition series of the periodic table. It is closer to rhenium, as a result of lanthanide contraction, than its other analogue manganese. Technetium metal may be prepared in two ways, a) by reducing pure technetium sulphide or ammonium pertechnetate electrolytically (Flagg and Bleidner, 1945) and, b) by electrodeposition of technetium in the presence of small quantities of fluoride (Boyd et al., 1960). The metal can be dissolved in concentrated sulfuric acid, nitric acid and aqua regia, but does not dissolve in hydrochloric or perchloric acid. Technetium heptoxide (Tc_2O_7), produced from the burning of technetium metal in oxygen, is very soluble in water, forming pertechnetic acid. The dioxide, TcO_2 which may be produced by reduction of pertechnetate, is more volatile than the heptoxide and can be oxidised to the heptoxide by oxidising agents, such as nitric acid or hydrogen peroxide. Technetium reacts with chlorine at 400°C to form technetium hexachloride or tetrachloride and with fluorine to form technetium hexafluoride. At higher temperatures, (about 1000°C) technetium will also react with carbon to give TcC (CRC Handbook, 1983).

Technetium can exist in oxidation states ranging from -1 to +7, in common with manganese and rhenium. The most important oxidation state is +7, being more stable than any of the others and tending to be associated with technetium complexes. It forms the pertechnetate ion producing many compounds ($K(TcO_4)$ $Cs(TcO_4)$, $Rb(TcO_4)$, $Li(TcO_4)$, $Ag(TcO_4)$, $Tl(TcO_4)$, $(C_6H_5)_4As(TcO_4)$ and $NH_4(TcO_4)$) of which ammonium pertechnetate (NH_4 TcO_4) is the most water soluble.

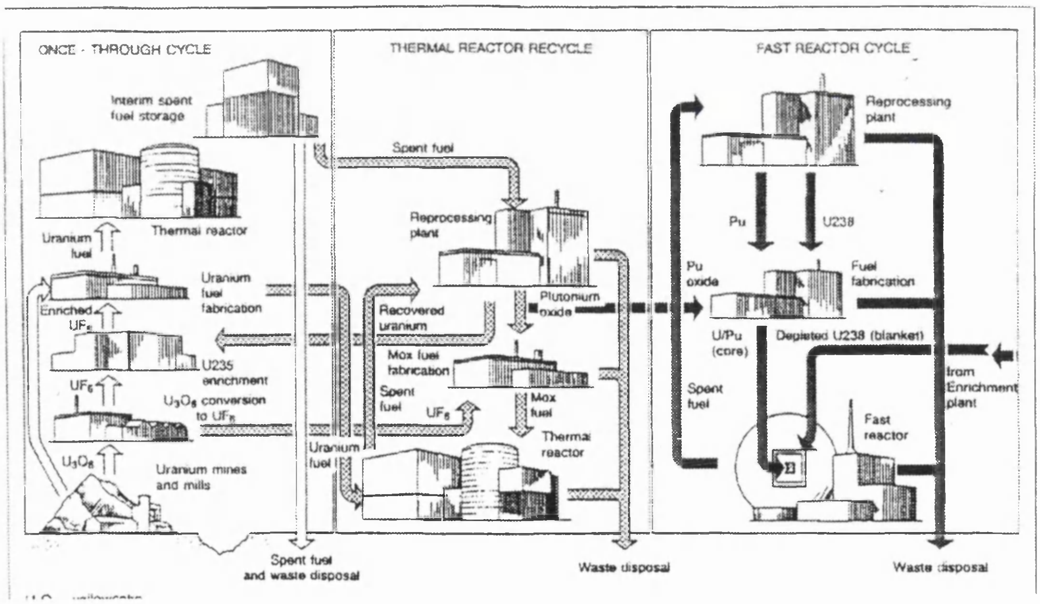
Detection of technetium often involves evaporation processes, however, Tc in the +7 state is volatile and can be lost. Reduction to the +4 state can minimize the loss of Tc by volatilization but complete reduction of TcO_4^- is rather slow.

1.3 SOURCES OF ^{99}Tc IN THE ENVIRONMENT - OVERVIEW.

The major source of technetium in the environment is the nuclear fuel cycle. Additionally, atmospheric nuclear weapons tests (1945-1980) and nuclear medicine have contributed smaller amounts than that of the nuclear fuel cycle. It is also reported that in nature very low levels of ^{99}Tc can be produced by the spontaneous fission of ^{238}U.

1.3.1 Technetium in the nuclear fuel cycle.

The nuclear fuel cycle involves mining, fuel fabrication, fuel irradiation and reprocessing of 'spent'(irradiated) fuel. In terms of the nuclear fuel cycle there are several distinct approaches shown in Figure 1.1.

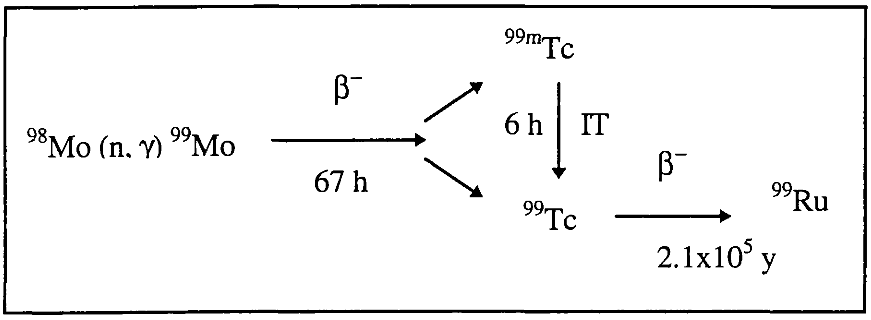


U_3O_8 = yellocake
UF_6 = uranium hexafluoride
MOX = mixed oxide fuel (uranium/plutonium)

Figure 1. 1 Different types of nuclear fuel cycles - Schematic diagram showing different stages (Source: IAEA, 1993).

In the 'once through' fuel cycle, spent fuel is not reprocessed but is stored on site until disposal in a repository is possible. Alternatively, this fuel can be reprocessed into new fuel elements as in the 'thermal reactor cycle' and the 'fast breeder cycle'.

Technetium is produced in large quantities during thermal fission of ^{235}U (Table 1.3). The major isotope produced is technetium-99, with a yield of approximately 6%, though other isotopes of Tc are also produced with smaller yields. Technetium-99 is also produced in significant amounts from fission of other isotopes presents in nuclear fuel (Table 1.4) (Cartledge, 1955). Several mechanisms exist for production of ^{99}Tc aside from direct fission, including (n, γ) reaction with ^{98}Mo as shown below:



Isotopes	Yield, %
^{99}Tc	6.06%
^{101}Tc	5.6
^{102}Tc	4.3
^{103}Tc	3.0
^{104}Tc	1.8
^{105}Tc	0.9
^{107}Tc	0.19

Table 1. 3 Yield of Technetium from Fission of ^{235}U.

Isotopes	Yields, %	Neutron Energy
^{233}U	4.8	Thermal
^{235}U	6.1	Thermal
^{238}Pu	6.3	Fast
^{239}Pu	5.9	Thermal
^{232}Th	2.7	Fast

Table 1. 4 Technetium-99 yields from fission of various nuclei.

Tc releases from the nuclear fuel cycle result from reactor operations, nuclear fuel reprocessing, UF_6 conversion, uranium enrichment, U fuel fabrication, high-level waste solidification, high-level waste disposal and low-level waste disposal.

Globally, Sellafield (UK), Cap de la Hague (France) and Trombay (India) are the major reprocessing facilities that release radioactive wastes into coastal waters.

In reprocessing, spent fuel is dissociated in nitric acid and Jenkins & Brown (1984) have reported that some metallic particles containing Mo, Tc, Ru, Rh and Pd may remain after dissociation. These particles can enter the environment as highly active wastes. Kubota (1993) has discussed the likely constituents of HLLW (High Level Liquid Waste) and has estimated that 771 g or 0.49 TBq of Tc is produced per ton of spent fuel (Table 1.5).

Nuclide	**Half-life**	**Quantities (cooling time, 5 years), g (TBq)**
Pu-239	$2.4x10^4$ y	25.1 (0.06)
*Pu		44.0 (18.46)
Np-237	$2.1x10^6$ y	444 (0.01)
*Np		444 (0.01)
Am-241	432 y	289 (36.74)
*Am		370 (37)
Cm-242	162.8 d	0.007 (0.89)
Cm-244	18.1 y	17.9 (55.5)
*Cm		19.1 (55.5)
Sr-90	28.8 y	477 (2408)
*Sr		830 (2538)
Cs-137	30.2 y	1.06 k (3411)
*Cs		2.56 k (4440)
Tc-99	$2.1x10^5$ y	771 (0.49)
Ru-106	367 d	4.8 (599)
*Ru		2.17 k (599)
Rh		461 (0.01)
Pd-107	$6.5x10^6$ y	212 (0.004)
*Pd		1.34 k (0.004)

Table 1. 5 Main constituents of High Level Liquid Waste per ton of spent fuel (3.3% enriched U) burned up to 33, 000 MWd/MTU at 30 MW/MTU in PWR (*Total).

Reprocessing involves the separation of uranium, plutonium and other highly radioactive products by a series of solvent extraction stages. An established method of reprocessing is the PUREX process in which the fuel elements are dissolved in nitric acid. In the PUREX process TcO_4^- is extracted with U due to the equilibrium;

$$UO_2(NO_3)_2(TBP)_2 + TcO_4^- \rightleftarrows UO_2(NO_3)(TcO_4)(TBP)_2 + NO_3^-.$$

In agreement with this equilibrium, the distribution coefficient of Tc between the organic and the aqueous phase depends on the concentration of NO_3^- (Figure 1.2).

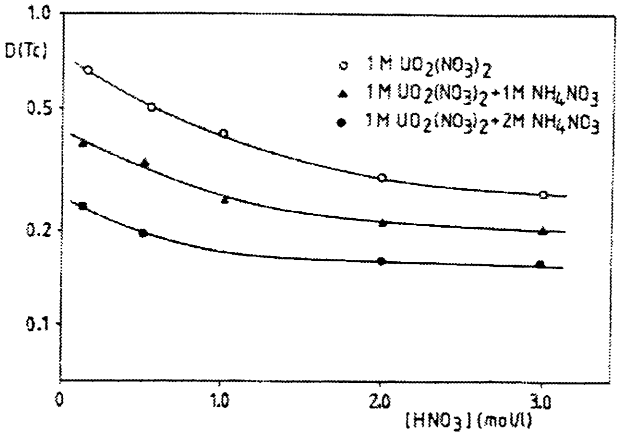


Figure 1. 2 Distribution co-efficient D of TcO_4^- between the organic phase (30% v/v in n-dodecane) and the aqueous phase as function of the HNO_3 concentration in the aqueous phase at various concentrations in the aqueous phase (Lieser, 1993).

As TcO_4^- present in the complex is bound more strongly than NO_3^-, appreciable amounts of Tc will accompany U on removal, even at rather high concentrations of NO_3^- (Lieser et al., 1981). Tc which is not extracted with U remains with other fission products and actinides forming highly active waste. If no special precautions are taken, Tc may be found in all products and waste streams including the U product, the Pu product and in the wastes from the purification of U and of Pu. It is estimated that 3.7 TBq or 6 kg of technetium is returned with separated uranium for fuel fabrication in one year for a 1000 MW(e) nuclear power plant. Prior to enrichment, uranium is converted to volatile hexafluoride and at this time Tc present can react to form TcF_6. Also, in this process, a small amount of technetium can be released to the atmosphere. In the fuel fabrication process some ^{99}Tc may also be released to the environment.

During reprocessing, many radionuclides (including ^{99}Tc) are separated from the uranium stream and are stored for an extended period on-site as high level wastes (HLW). Medium level waste (MLW) arising from separation of plutonium from uranium, and delay storage prior to discharge. Low level wastes (LLW) containing Tc also arise, from these processes and released into the environment subject to authorizations.

1.3.1.1 Technetium-99 production and release rates.

Luykx and Fraser (1982) and Luykx (1986) have estimated that 1000 TBq of ^{99}Tc had been released to the environment up to 1980. These calculations assumed that up to 1980 10% of nuclear fuel was reprocessed with 100% Tc release. After 1980 the same amount of fuel is reprocessed, however, with only 10% of Tc being released during reprocessing. Based on the same approach it can be estimated that 5374 TBq of Tc will be produced in fuels of which a total 1477 TBq will be released up to 1995. Based on these assumptions and future electricity production estimates (IAEA, 1995), it can be estimated that 7480 TBq will be produced of which 2743 TBq will be released up to 2015 (Figure 1.3).

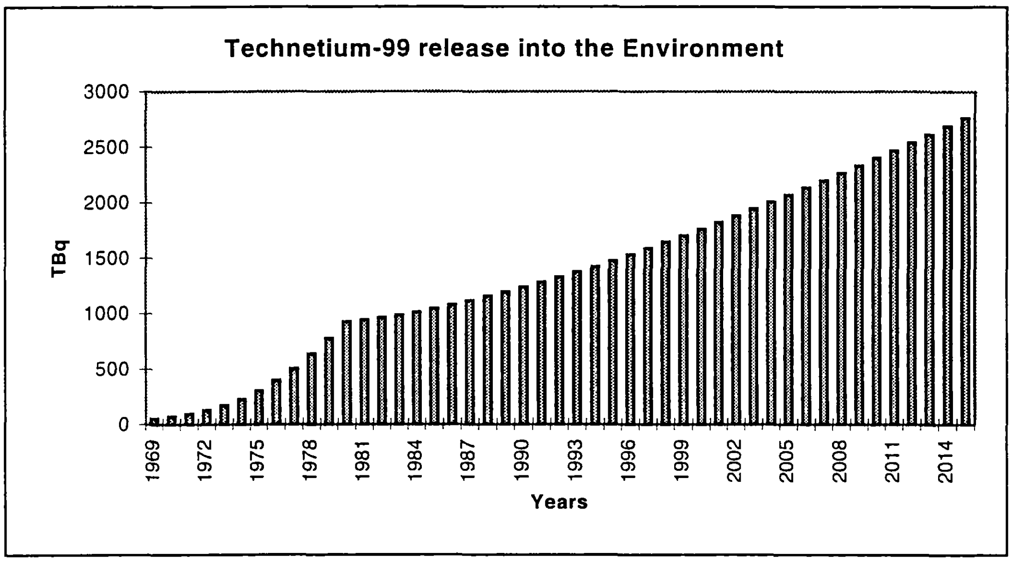


Figure 1. 3 Cumulative ^{99}Tc releases calculated from global nuclear electricity production.

1.3.1.2 Long-term Radioactive waste disposal and ^{99}Tc.

Radioactive waste may be disposed directly or after reprocessing to recover the unburned fissile material in the spent fuel rod (ca.30%). Currently Japan, France, United Kingdom, Belgium, Germany and Italy reprocess spent fuel on a large scale. For every ton of uranium reprocessed, 5 m^3 HLW is created with a specific activity of 10^7 GBq/m^3 (Choppin et al., 1995).

The HLW containing many long lived nuclides including ^{99}Tc would require several millennia isolation for its decay. The toxicity index for HLW presented in Figure 1.4, highlights the long-term importance of ^{99}Tc.

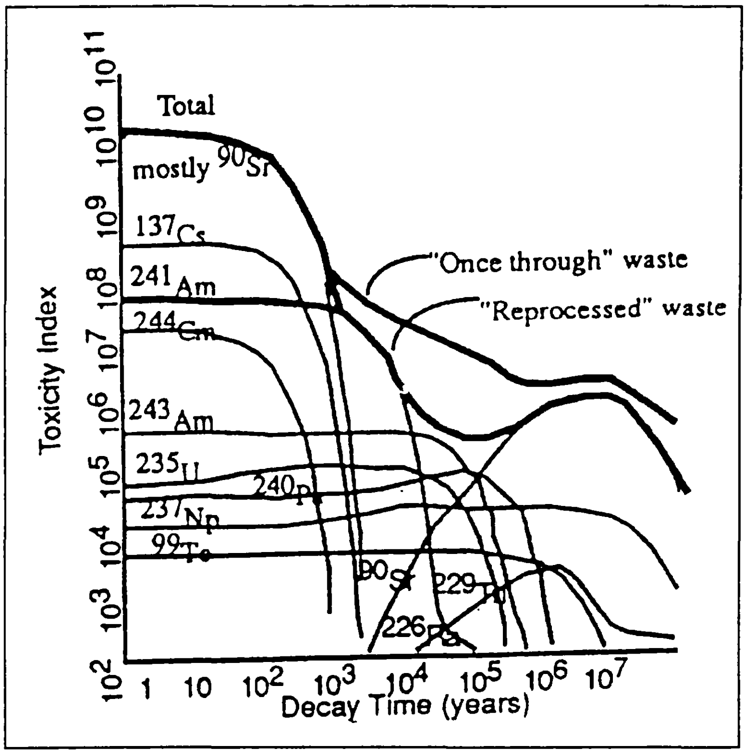


Figure 1. 4 Concentration changes in waste species (Choppin & Wong, 1996).

1.3.2 Nuclear detonations.

The detonation of nuclear explosives can produce ^{99}Tc by the fission of ^{235}U and ^{239}Pu (6% yield) and by the activation of ^{99}Mo in the atmosphere, which is formed during the explosion. The high temperatures experienced during explosions oxidizes elemental ^{99}Tc rapidly combining with atmospheric oxygen to form Tc_2O_7. On cooling with air this may react with water vapour to form pertechnetic acid, $HTcO_4$. Pertechnetic acid, pertechnetate and technetium heptoxide can absorbed on particulate matter present in the atmosphere and precipitate as 'fallout'.

It was assumed by Holm (1993) that 1 Mt fission energy corresponds to 1.45×10^{26} fissions and that ^{137}Cs was produced with a representative fission yield of 5.57%. If the global stratospheric injection of nuclear debris was about 168.5 Mt and ^{99}Tc and ^{137}Cs are produced with the same fission yield, the global activity of ^{99}Tc released into the stratosphere is 140 TBq.

1.3.3 Chernobyl accident.

On the 26th of March, 1986, an explosion in one of the reactors housed in the Chernobyl nuclear power station caused a massive release of radioactive debris into the atmosphere. This accident resulted in the release of approximately 7×10^{16} Bq ^{137}Cs (Cambray et al., 1987). The fallout from Chernobyl was deposited in most areas as a single pulse according to the rainfall patterns in the following week (de Vries & Van der Kooy, 1986; Fowler et al., 1987). The activity ratio ^{99}Tc/^{137}Cs was identified as 1.5×10^{-5} in fallout from the Chernobyl accident (Aarkrog et al., 1988). This is lower than the theoretical ratio from fission (1.5×10^{-4}). From these values and reported total releases of ^{137}Cs, it was estimated that about 0.75 TBq of ^{99}Tc was released into the environment from the Chernobyl accident.

1.3.4 Nuclear medicine.

The short-lived isomer ^{99m}Tc is one of the most widely used radionuclides in nuclear medicine because of its favourable properties. It has a short half-life (6.02 hours), a low radiation dose (99.996% IT; $E\gamma = 142$ keV) and the γ radiation is easily measurable. ^{99m}Tc is obtained from its mother nuclide by radioactive decay.

$$^{99}\mathrm{Mo} \xrightarrow[\text{67 hours}]{\beta^-} {}^{99m}\mathrm{Tc}$$

In radionuclide generators, ^{99}Mo is fixed on a column (usually Al_2O_3) and the daughter nuclide is eluted with a solution of NaCl. The selective separation of ^{99m}Tc from ^{99}Mo occurs because MoO_4^{2-} is more strongly sorbed on Al_2O_3 than TcO_4^- (Lieser, 1986).

The mother nuclide ^{99}Mo can be produced in two ways:

1) by irradiation of Mo:

$^{98}Mo(n,\gamma)^{99}Mo$ (abundance of ^{98}Mo in natural Mo:24%; $\sigma n,\gamma = 0.13$ b)

2) by nuclear fission of U (preferably U highly enriched in ^{235}U)

$^{235}U(n,f)^{99}Mo$ (η=6.13%).

Irradiation of Mo leads to ^{99}Mo of relatively low specific activity that means low loading of the generator with ^{99}Mo and limitation of the activity of ^{99m}Tc. By nuclear fission of ^{235}U, ^{99}Mo of high specific activity is obtained and high activities of ^{99m}Tc are available. Radionuclide purity is a major problem in the production of ^{99}Mo of high specific activity by nuclear fission of ^{235}U (Hoffmann et al., 1980).

In nuclear medicine, the eluent of the $^{99}Mo/^{99m}Tc$ generators containing $^{99m}TcO_4^-$ may be used in the form of a dilute NaCl solution as obtained from the generator, but preferably Tc is brought into a chemical form in which it is easily carried within the body to the place of application. ^{99m}Tc has also been used in large quantities at research laboratories for radiochemical method development and subsequent sample preparations.

The presence of ^{99}Tc in ^{99m}Tc-pertechnetate from ^{99}Mo generators will also contribute to the presence of technetium in the environment. The activity ratio $^{99}Tc/^{99m}Tc$ in a ^{99}Mo generator used at a nuclear medicine department is $(0.1\text{-}2)\times10^{-7}$ depending on the elution pattern. All the ^{99}Tc generated from the ^{99}Mo (~108 GBq) will be released to the environment, i.e., about 200 kBq per year from a nuclear medicine department (Holm, 1993).

1.3.5 Natural Production.

In 1952, Merrill discovered the presence of technetium in certain stars by a spectroscopic method. Following Merrill's work, Burbidge et al. (1957) reported that unstable elements such as technetium were being synthesized by s-process nucleosynthesis in certain stars.

^{99}Tc occurs naturally in the earth's crust primarily from spontaneous fission of ^{238}U and from the slow neutron-induced fission of ^{235}U (Curtis et al., 1987; Kenna & Kuroda, 1964). Kenna and Kuroda (1964) compared ^{99}Tc activities separated from Belgian Congo pitchblende (42% U) with ^{99}Tc activities in rain water given by Attrep (1962) and concluded that the ^{99}Tc in pitchblende was being produced by the spontaneous fission of ^{238}U. The activity of ^{99}Tc expected to be present in uranium ores is:

$$N_{99}\,\lambda_{99} = N_{238} * \lambda_{238f} * y \qquad (1)$$

Where N_{99} and N_{238} are the number of atoms of ^{99}Tc and ^{238}U, respectively; λ_{99} is the decay constant of ^{99}Tc; λ_{238f} is the spontaneous fission decay constant of ^{238}U and y is the fission yield for the mass 99 chain. If we assume that y is about 6 percent, introducing the spontaneous fission half-life of $(8.04 \pm 0.3) \times 10^{15}$ years into Equation (1), we obtain, taking into account the atomic weight of the substances, $^{99}Tc/^{238}U = 6.6 \times 10^{-13}$ (gram/gram).

1.3.6 Environmental levels of ^{99}Tc.

Fallout from atmospheric weapons testing, Chernobyl fallout and discharges from reprocessing works are the most important sources of technetium to the environment on a global scale. The environmental levels which can be expected from such sources are now discussed.

Fallout.

Fallout from atmospheric weapons testing has been primarily detected in rain waters (Attrep, 1962; Attrep et al., 1971). The average value of 66.7 mBq l^{-1} ^{99}Tc observed for 1961 was found to decrease to 1.3 mBq l^{-1} ^{99}Tc during 1962. Very recent studies, remote from reprocessing facilities, showed detectable levels of technetium-99 attributable to fallout from earlier atmospheric weapons tests. Dahlgaard et al. (1995) measured ^{99}Tc (5 μBq l^{-1}) in North Atlantic water in 1992. This was claimed as the first published value (characteristic of 1960's global fallout) for fallout "background" ^{99}Tc in oceanic Atlantic water. Momoshima et al. (1995) measured levels of technetium-99 (1.0-7.4 μBq l^{-1}) from coastal waters of Fukuoka (Japan) and attributed them to the global fallout of technetium-99. Tagami and Uchida (1995) measured ^{99}Tc levels of 0.23 - 0.36 mBq m^{-2} from rain and dry fallout in 1993 from Nakaminato city, Japan.

Hirano and Matsuba (1993) measured ^{99}Tc from a brown seaweed (*Sargassum thunbergii*) collected from Kita-Ibaraki city (Japan) coast. The concentrations of ^{99}Tc in seaweed (6-18 Bq kg^{-1} fresh wt.) are attributable to fallout from nuclear weapons tests.

Chernobyl.

Chernobyl fallout has also been detected in European coastal waters. Holm et al. (1984) found a ^{99}Tc concentration of 3.0±0.3 Bq kg^{-1} (dry wt.) in seaweed from the East coast of Sweden with a ^{99}Tc/^{137}Cs activity ratio of 0.27±0.02 which he attributed to Chernobyl fallout. ^{99}Tc deposition of 540±50 mBq m^{-2} at 62°N was identified from the analyses of carpets of mosses, lichens and underlying soils after the Chernobyl accident (Holm & Rioseco, 1987). Monaco experienced a relatively high concentration of technetium-99 (20,000±2500 mBq l^{-1}) in rainwater during 1986 (Holm et al., 1988) reflecting the debris from the Chernobyl accident.

Reprocessing works.

Worldwide reprocessing of nuclear wastes has resulted in ^{99}Tc discharges into the environment. European nuclear fuel reprocessing plants, Cap de la Hague (France) and Sellafield (UK) are known as major contributors to anthropogenic radioactivity including ^{99}Tc. Both sources have increased the background level of ^{99}Tc and have caused its concentration within different marine compartments (e.g., seawater, sediments, seaweeds and other biota). Technetium-99 concentrations found in seawater from various areas are shown in Table 1.6. With the exception of the Irish Sea and the English Channel, levels of ^{99}Tc are close to fallout levels. Significantly enhanced levels, however, can be observed near reprocessing facilities.

Sample/Date	Place	Concentration ($mBq\ l^{-1}$)	Reference
Seawater (1981)	Irish Sea	15-74	Riley & Siddiqui, 1982
Seawater (1989)	Irish Sea	21-53	Nicholson et al., 1992
Seawater (1981)	North Sea	3.5	Holm et al., 1988
Seawater (1983)	Channel water (French coast)	20	Patti et al., 1984
Seawater (1983)	Baltic Sea	0.07	Holm et al., 1984
Seawater (1984-1986)	Mediterranean Sea	0.05	Barci-Funel et al., 1991
Seawater (1987-1988)	Japan coast	<0.225	Hirano & Matsuba, 1993

Table 1. 6 Concentration of ^{99}Tc in seawater from different coastal waters.

1.4 BEHAVIOUR OF ^{99}Tc IN THE MARINE ENVIRONMENT.

1.4.1 Introduction.

The behaviour and effects of Tc in the environment are largely controlled by its source, its chemistry in soil, sediment and water and its biological interactions. Several reviews have been written about the chemistry of technetium (Anders, 1960; Wildung et al., 1979; Till et al., 1979; Pentreath et al., 1980; Coughtrey & Thorne, 1983), however its behaviour in the environment is still poorly understood, mainly due to the lack of any stable isotopes.

Technetium may exist in the valence states Tc(VII), Tc(IV) and Tc(0) (Schulte & Scoppa, 1987), with the Tc(VII) pertechnetate anion (TcO_4^-) being the dominant species in aqueous solutions and consequently in the environment (Figure 1.5).

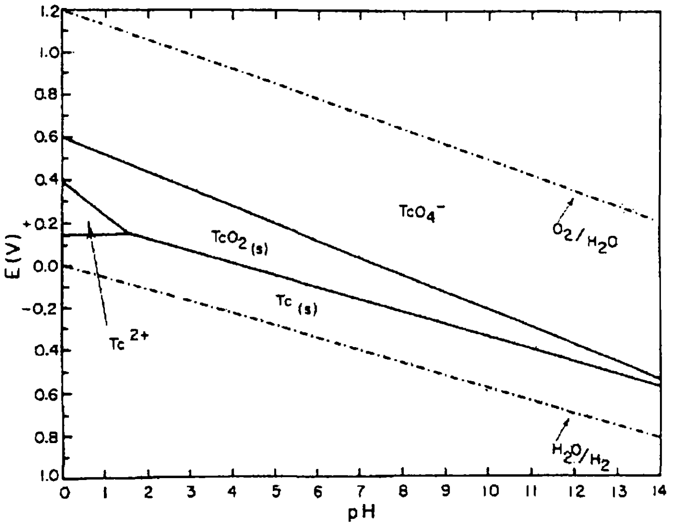


Figure 1. 5 pH and Eh diagram for Tc distribution in the environment (Beasley & Lorz, 1986).

The principal form of ^{99}Tc discharged into the environment from nuclear fuel facilities is probably the heptavalent (+VII) pertechnetate ion (TcO_4^-) (Pentreath et al., 1980). Technetium (+VII) may be reduced to its tetravalent (+IV) state by Zn, HCl, hydrazine, hydroxylamine, ascorbic acid, tin (II) chloride and dilute H_2SO_4 (Anders, 1960). However, in oxic seawater, reduced technetium is readily oxidised to the heptavalent (VII) pertechnetate anion (TcO_4^-) form which shows a very low affinity with particulate matter (Schulte & Scoppa, 1987). These attributes would appear to make this nuclide an ideal candidate for use in water movement tracer studies.

1.4.2 Accumulation of technetium by marine organisms.

The ability of marine organisms to bioaccumulate seawater pollutants is well known. Marine organism can remove chemical species from solution, convert them into various compounds, excrete them and after death decompose thus adding decomposition products and skeletal remains (organic detritus in the case of plankton) to seawater. The capacity of marine organisms to concentrate pollutants is characterized by an accumulation coefficient, K_{ac} (sometimes called an enrichment or concentration factor).

After Dutton & Ibbett (1973) observed the ability of *Fucus vesiculosus* to concentrate technetium from the Irish Sea (16 kBq kg^{-1} fresh wt.), laboratory studies on technetium uptake by phytoplankton (Gromov, 1976) and other organisms (Fowler et al., 1981) took place. Phytoplankton were observed to have concentration factors of $7\pm3\times10^4$. These high affinities along with those found in *Fucus vesiculosus* in the Irish Sea (Dutton & Ibbett, 1973) implied that uptake of Tc by marine biota might possibly be of such a magnitude as to substantially influence the transport of Tc within the ocean and perhaps constitute an important transport pathway back to man. Further experiments (Fisher, 1982) to verify Gromov's (1976) findings failed when phytoplankton were not found to show any marked affinity for Tc either as TcO_4^- or in reduced forms. In support of Fisher's work, Fowler et al. (1981) and Beasley et al. (1982) also observed virtually no TcO_4^- uptake by a population of mixed flagellates (mixed plankton) or by *Pseudoisochrysis paradoxa* (phytoflagellate). From this evidence, it was suggested that uptake of Tc by oceanic phytoplankton is not a significant process (Beasley & Lorz, 1986).

In contrast to phytoplankton, certain marine macroalgae do concentrate Tc to a significant degree (Beasley et al., 1982; Topcuoglu & Fowler, 1984). Experimental studies on seaweeds (marine macroalgae) showed that technetium was readily accumulated by brown seaweeds (e.g., *Fucus* species), however, concentration factors were very low (20) when compared to concentration factors calculated based on field data (Masson et al., 1989). All species of red and green algae investigated were found to show little affinity for Tc either in the +7 or +4 valence state (Beasley et al., 1982).

Routine monitoring of radionuclides in surface and coastal waters has indicated high concentrations of ^{99}Tc, in *Fucus vesiculosus* (2,300 - 11,000 Bq kg^{-1} fresh wt.) from the Irish Sea (Mitchell, 1975; Hunt, 1979-1989). Distribution of technetium-99 in seaweeds appears to vary between species. The seaweeds, *Fucus vesiculosus* (0.71 kBq kg^{-1} fresh wt.), *Ascophyllum nodosum* (1.7 kBq kg^{-1} fresh wt.) and *Porphyra sp.* (0.0015 kBq kg^{-1} fresh wt.) collected in 1985 have accumulated substantially different levels of ^{99}Tc at St. Bees Head near Sellafield (Hunt, 1979-1989). This present study intends to further investigate inter-species variations in technetium-99 accumulation in seaweed species in the Irish Sea (Chapter 3).

Detailed seasonal variations in ^{99}Tc concentrations were carried out using the seaweed *Fucus serratus* taken from around the French nuclear reprocessing plant, Cap de la Hague

(Patti et al., 1990). At 200 km away from the release point, seasonal variations were observed, with maximum values in summer and minimum values in winter. This is explained by the fact that technetium-99 accumulation in seaweed is metabolically controlled being dependent on temperature and light which influences the primary production. Summer maximums can be attributed to higher metabolic activities at higher temperatures and more light than in winter. However, a similar seasonal variation study from the eastern Swedish coast made between 1977 and 1983 (Holm et al., 1986b) found maximum ^{99}Tc activities during winter in *Fucus* species. This winter maximum was claimed to be due to higher inflows of contaminated water from the North Sea to the Baltic Sea, and a higher outflow during the spring-summer.

Technetium fixation by brown algae appears to be an active process rather than one of simple passive adsorption (Topcuoglu & Fowler, 1984). Uptake is both temperature and light dependent with rapidly growing parts of the plant showing highest activities per unit weight.

Next to primary producers (phytoplankton and seaweeds), secondary producers (zooplankton) are also found responsible for transfer of pollutants from one tropic level to another. There are few reported data on the biokinetic behaviour of Tc in zooplankton. Scoppa et al. (1983) showed that uptake of $^{95m}TcO_4^-$ by the brine shrimp *Artemia salina* reached an equilibrium concentration factor of 2.7 while Fowler et al. (1983) found concentration factors near 1 for the euphausiid *Meganyctiphanes norvegica*. In contrast to live euphausiid, dead euphausiid were found to show pronounced increases (CF=50) over a 7-day period. This was explained by bacterial mediation (reduction or accumulation of Tc by bacteria living on the surface of dead euphausiid). Further experiments on this are warranted in particular to calculate the transfer of technetium from surface water to deep water through this pathway. In marine animals, the uptake of Tc by species of marine amphipod and crustacea is dependent upon the speciation of the Tc, with reduced Tc(IV) being accumulated by the animals to a significantly greater extent than the pertechnetate (Sparkes and Long, 1988).

Molluscs (mussel and winkles) have been observed to have a very low uptake of pertechnetate. The concentration factor when three different species of mussel (*Mytilus edulis*, *Mytilus galloprovincialis* and *Mytilus californianus*) were studied never exceeded a value of 2 (Fowler et al., 1981; Beasley et al., 1982). Shells of dead mussel have also been found to accumulate $^{95m}TcO_4^-$ in levels comparable to that of live animals (Beasley et al., 1982). This indicates that the low uptake of pertechnetate by bivalve molluscs appears to be unrelated to any ability of these invertebrates to regulate their Tc content (Beasley, 1981). Dead shells of winkles have also been found to show $^{95m}TcO_4^-$ accumulation in comparable levels to live winkles. Winkles fed with seaweed fronds (*Fucus serratus*) have been observed to have lower technetium retention when compared to animals that have been starved (Swift, 1985). The uptake of technetium by limpets was found to be greater than that for mussels with a metallothionein-like protein being proposed as the Tc binding site in the soft tissue (Spies, 1975; Beasley et al., 1982). Pentreath (1981) confirmed that the fish, plaice, (*Pleuronectes platessa*) also accumulate technetium at very low levels (CF=9), however, lobster (*Homarus gammarus*) had a relatively high concentration factor (CF=1160). Irrespective of the animals, most technetium tends to accumulate in the digestive glands (including kidneys) and less so in muscle tissue. This preferential behaviour of technetium in the animal body reduces bio-magnification from one trophic level to another trophic level.

1.4.3 Technetium in sediment.

The principal form of technetium in the water column, TcO_4^-, is not removed by anionic colloids and suspended sediments and is, therefore, highly mobile in aerobic sediments and soils (Wildung et al., 1979; Scoppa et al., 1983). Under oxic conditions, anionic technetium sorbs poorly onto particulate matter - ion exchange sites in geological materials being almost exclusively cationic (Higgo, 1990). The fate of Tc in sediments and soils, however, may be strongly influenced by physical, chemical and biological processes.

Changes in redox conditions can effect the uptake of Tc in marine sediments. Reducing sediments rich in organic matter retain Tc strongly and may immobilise it as insoluble $TcO_2 . 2H_2O$ or Tc(IV) sulphides or co-precipitate Tc(IV) with iron sulphides (Wildung et al., 1979). Bacterial activity and organic matter probably promote the reduction of Tc(+7) and the fixation of Tc by consumption of oxygen and maintenance of reducing conditions in the sediments. Wildung et al. (1986), however, commented that changes in redox conditions were considered to be more important to Tc mobility than uptake and sorption by microbes. A minor change in pH, about 1 unit, may cause a substantial shift in Tc from one geochemical sink to another (Stalman et al., 1986).

Under anoxic conditions, in soil and sediments, organic matter is likely to be responsible for stabilizing reduced Tc in complexes with amine, carboxyl, sulfhydryl and hydroxyl groups (Van Loon et al., 1986). Hence the organic matter fraction in soils constitutes an important geochemical sink for Tc. While studying soil to plant transfer, Hoffman et al. (1982a & 1982b) reported that Tc mobility in soils decreases over time. Sediments with a high organic content can retain the technetium especially under reducing conditions. It has been postulated that technetium in sediments beneath the depth at which reduction occurs will remain relatively immobile (Beasley & Lorz, 1986).

The interactions of Tc with various organic compounds in the environment are more complicated than Tc in pure inorganic systems. Tc(IV) forms complexes with organic compounds of groundwater or surface waters (e.g. humic acids), similar to those found with other tetravalent elements and result in the immobilisation of technetium in the environment. The presence of humic acid causes technetium to deposit under anaerobic condition (Sekine et al., 1993), and thus technetium in soils and sediments may be immobilised and made less biologically available by precipitation or association with humic acid. The remobilization of Tc probably requires the oxidation of the lower valence state to the heptavalent (VII) state.

The interactions of different chemical forms of Tc with sediments are described by a distribution co-efficient (Kd).

$$\text{Kd} = \frac{\text{Activity per unit mass of sediment (Bq kg}^{-1}\text{)}}{\text{Activity per unit mass of water (Bq kg}^{-1}\text{)}}$$

The Kd values are determined by the nature of the sediment and are higher for fine particles in muddy sediments than for coarse particles in sandy sediments. Distribution co-efficients for pertechnetate partitioning between aerobic sediments low in organic matter and seawater are generally very low (Masson et al., 1981). For example, the Kd values for sediments from the North Atlantic abyssal planes never exceed 3.5 (Fowler et al., 1983). Further, the Kd for both Tc (+4) and Tc (+7) were not significantly different in experimental conditions, probably due to oxidation of +4 to +7 during these experiments in aerobic seawater (Aston et al., 1984).

Sediments show very low affinities for technetium-99 present in seawater (Harvey & Kershaw, 1984). Therefore, pertechnetate is highly mobile under the oxic conditions that are prevalent in pelagic environments and in the upper layers of many sediments. Support for the nature of the dominant technetium species (TcO_4^-) in oxic seawater comes from the fact that it is strongly absorbed by a strongly basic anion exchange resin from neutral and alkaline solutions. Furthermore, $Fe(OH)_3$ precipitation experiments for seawater samples confirmed that very little ^{99}Tc present in oxic seawater is in the reduced form (Lavrukhina & Pozdnyakov, 1970; Harvey et al., 1991b).

Typically in the Irish Sea, Kds of <100 were reported indicating the high mobility of technetium in the upper column of seawater (Harvey et al., 1991b). The IAEA (1985) have also recommended a Kd for ^{99}Tc of 10^2 for both pelagic and coastal sediments. However, Nicholson et al. (1992) observed a Kd of 10^3 based on the ^{99}Tc activity in two Irish Sea sediment cores.

1.4.4 Technetium-99 as a marine tracer.

^{134}Cs (t½ = 2.06 years) and ^{137}Cs (t½ = 30 years), mainly discharged from fuel reprocessing plants in Western Europe, have been successfully used as oceanographic tracers for many years (Jefferies et al., 1982; Livingston et al., 1982; Aarkrog et al., 1987). However Cs levels in northern Europe were seriously perturbed by the release of radiocaesium from the Chernobyl accident (Aarkrog et al., 1988). ^{99}Tc, on the other hand, has a large ratio of reprocessing derived emissions compared to weapons and Chernobyl fallout (Dahlgaard, 1995). Furthermore, its conservative behaviour in seawater would seem to make it an ideal candidate for an alternative tracer. Several studies (Aarkrog et al., 1986 & 1987; Dahlgaard, 1994) have analysed Sellafield derived ^{99}Tc at remote sites (e.g. Arctic and east Greenland waters). Seaweeds have been mainly used to trace technetium-99 dispersion in the aquatic environment. Holm et al. (1986a) estimated a transit time of 4-6 years for the transport of technetium released from Sellafield to the Baltic Sea. From a similar study on technetium-99 distribution in *Fucus vesiculosus* and *Fucus disticus*, the transport time from Sellafield to the East Greenland Current has been estimated to be 7 years (Aarkrog et al., 1987). Despite the apparently successful use of ^{99}Tc as a marine tracer, more work on its environmental behaviour is required to assess its suitability for continued use. For example, a recent study of anthropogenic radionuclides in an anoxic fjord, Framvaren, Norway indicated a higher degree of ^{99}Tc transport downwards (based on its vertical profiles) than shown by ^{137}Cs (Roos et al., 1993).

1.5 ^{99}Tc AND THE UK NUCLEAR POWER PROGRAMME.

1.5.1 Introduction.

In UK, no mining or uranium ore processing takes place as imported uranium is used. There is, however, a facility for uranium refining and fuel fabrication operated by British Nuclear Fuels Limited (BNFL) at Springfields in England. A facility for fuel enrichment also exists at Capenhurst and is also operated by BNFL. The first power station in Britain was Calder Hall and was commissioned in 1956. These Magnox reactors are CO_2 gas cooled, graphite moderated and use natural uranium fuel. The second generation reactor in the UK is the Advanced Gas-cooled Reactor (AGR). The main difference with this reactor is that it uses slightly enriched oxide fuel. The latest addition is the Pressurised Water Reactor (PWR) which uses ordinary water as moderator and coolant. Figure 1.6 highlights other UK sites which are also responsible for LLW discharges into the aquatic environment.

In UK, there are 37 nuclear power reactors with a total net generating capacity 142 GW(e)y. Reprocessing of spent fuel from the UK nuclear power programme takes place at Sellafield, where the vast majority of ^{99}Tc discharges to the aquatic environment occur.

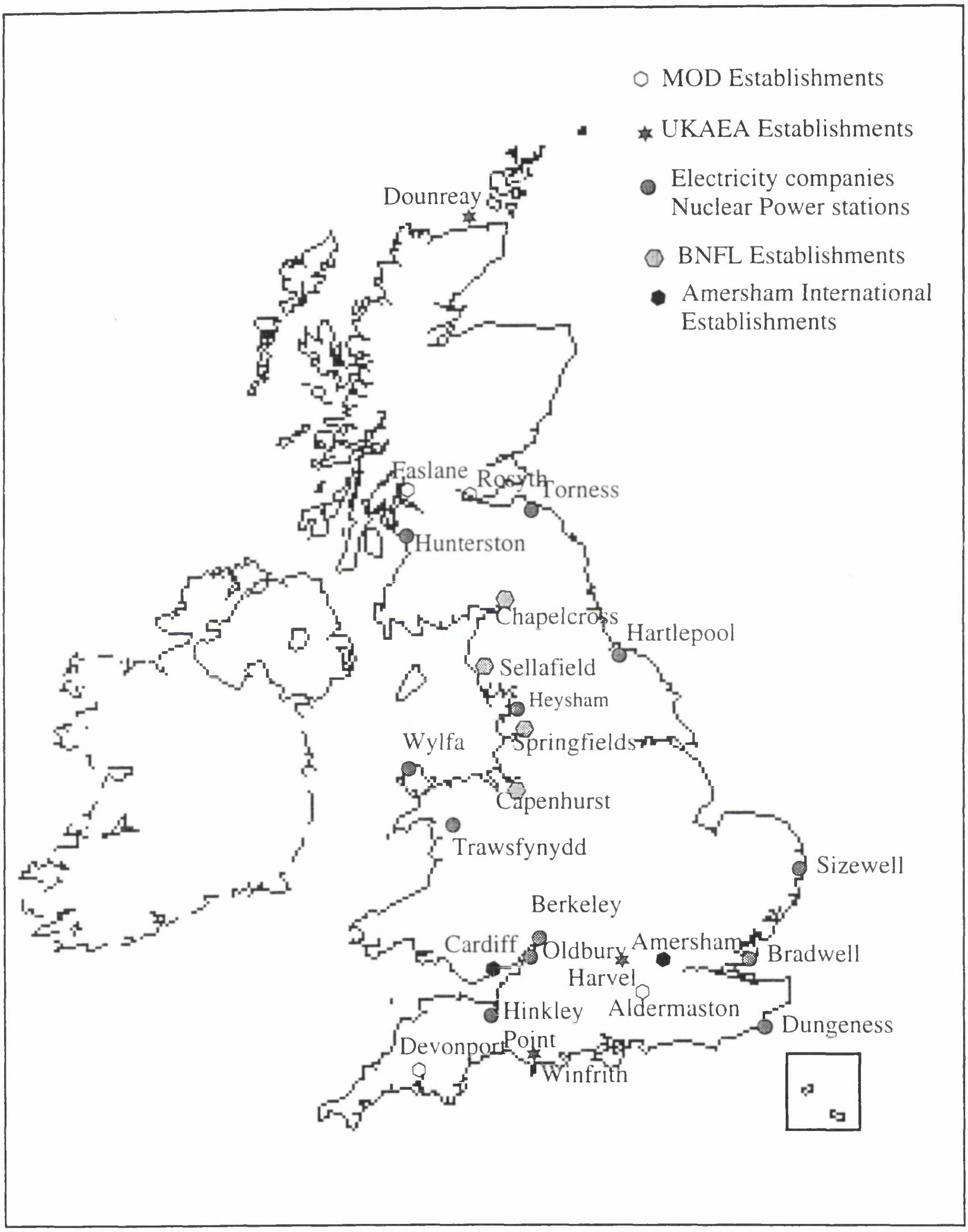


Figure 1. 6 Various nuclear sites in UK.

1.5.2 Sellafield - Discharge History.

The Sellafield site is located in Cumbria and has had a variety of operations since the 1950's. Originally, the site had been used in the production of plutonium using two air cooled reactors which began operations in 1950 and 1951. These reactors ceased operation in 1957 after one of the reactors caught fire releasing a host of radionuclides, most importantly iodine-131. Around the same time the first nuclear power station Calder Hall started operation. However, the vast majority of radioactive discharges to the Irish Sea from this site are a result of the reprocessing.

To explain the magnitude of radioactive discharges from Sellafield, annual discharge rates for ^{137}Cs and ^{239,240}Pu are presented in Figure 1.7. It is clear from the shapes of these profiles that in general discharges were at their highest in the 1970s due to a higher throughput in the reprocessing of fuel and the discharging of medium level wastes without treatment. By late 1980s, introduction of new clean-up procedures (for example, SIXEP (site ion exchange plant), salt evaporator plants and the storage, on site, of medium level wastes), had resulted in major reductions in the discharge levels.

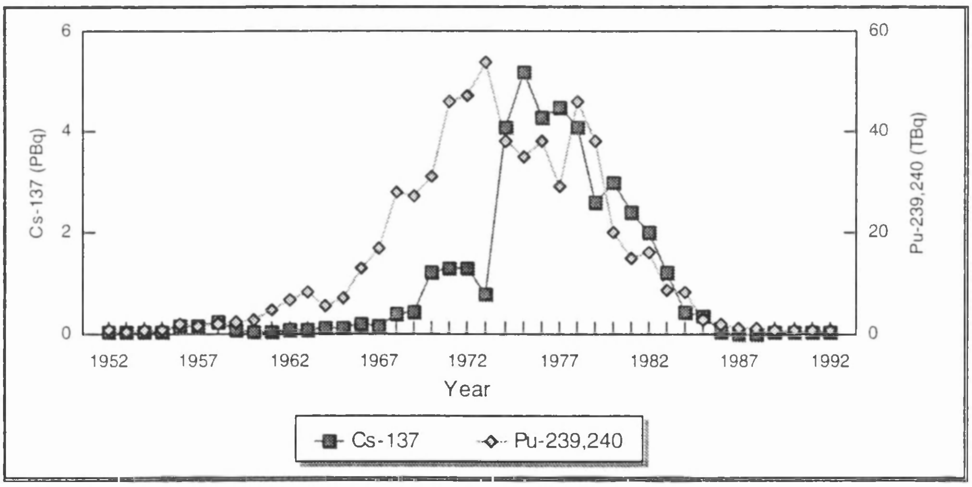


Figure 1. 7 Annual discharge rates for ^{137}Cs and ^{239,240}Pu from Sellafield (1952-1992) (Gray et al., 1995).

In the case of ^{99}Tc, discharge data are available only from 1978 onwards and are presented in Figure 1.8. Over this period, discharges have generally decreased. For example in 1978 ^{99}Tc discharges were 180 TBq but by 1993 had decreased to 6 TBq.

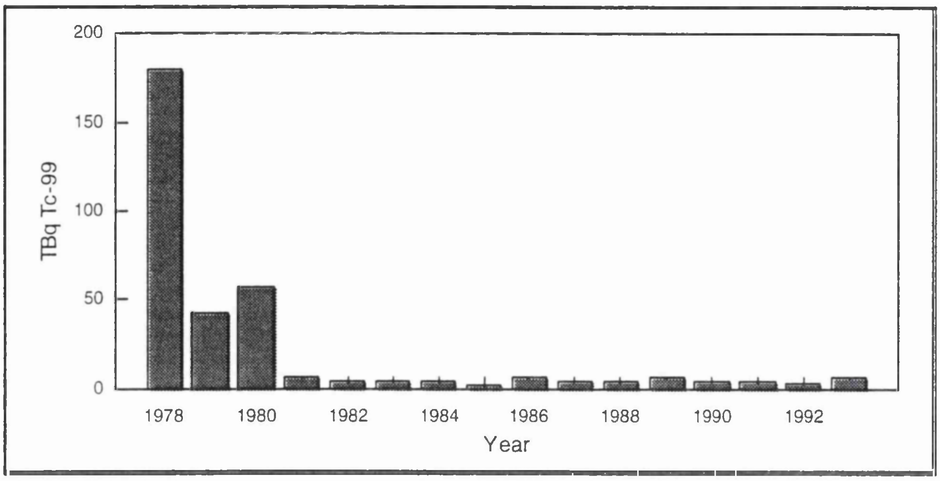


Figure 1. 8 Annual discharges of ^{99}Tc from Sellafield reprocessing plant (1978-1993).

Using seaweed (*Fucus* sp.) from Greenland waters as a biological indicator for ^{99}Tc, Aarkrog et al. (1987) estimated the discharges of ^{99}Tc from Sellafield prior to 1978. The predicted annual discharge rates were 8 TBq (1952-1969), 52 TBq (1970-1973), 32 TBq (1974-1976) and 65 TBq (1977), and are subsequently used in Chapter 3. Levels of ^{99}Tc, measured in *Fucus vesiculosus* from around Sellafield during the 70s, 80s and 90s (Figure 1.9), however, indicate that discharges in the early 70s may have been in excess of the maximum reported level of 180 TBq in 1978.

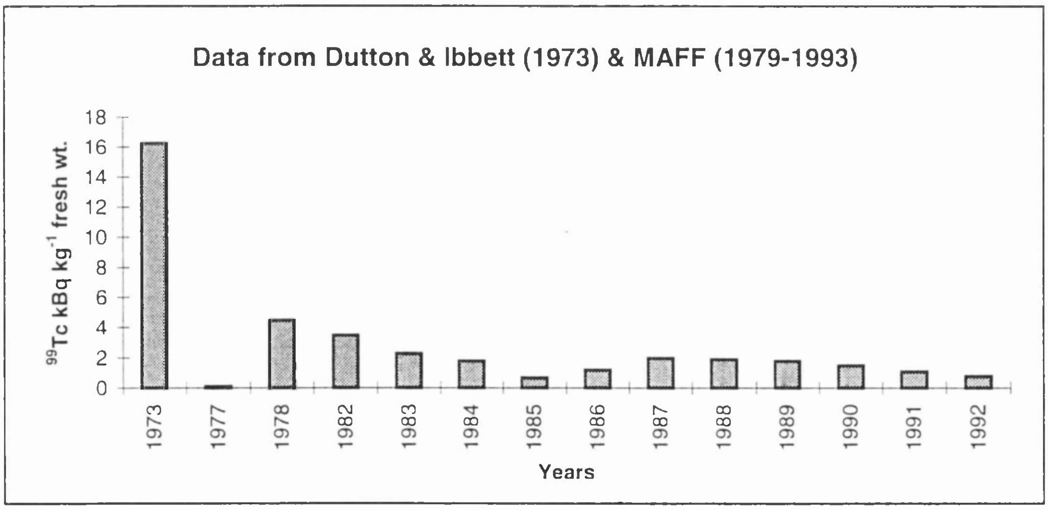


Figure 1. 9 Distribution of ^{99}Tc in *Fucus vesiculosus* from Sellafield area.

Major increases in the ^{99}Tc discharge rate have recently resulted from the commissioning of EARP (Enhanced Actinide Removal Plant). EARP started operations along with the Thermal Oxide Reprocessing Plant (THORP) during early 1994 and is being used to treat MLW stored on site since the early 80s along with continuous arisings of current reprocessing effluents. Although, the operation of EARP has resulted in significant reductions (~30%) in the releases of alpha emitters (e.g., americium and plutonium etc.), discharges of technetium-99 and a few other beta emitters have increased as EARP does not remove these efficiently.

By processing current arisings along with old MLW stored on site, a 30% rise in the discharges of total beta activity was expected. In the first year of EARP operation (1994), 72 TBq of technetium-99 (only 36% of the authorised limit) were released. However, in the second year (1995), 192 TBq of technetium-99, which is 95% of the authorised limit, were released due to the continuous operation of EARP. Technetium-99 discharge rates estimated (Aarkrog et al., 1987) for pre-1978 and reported for 1978 onwards are shown in Figure 1.10.

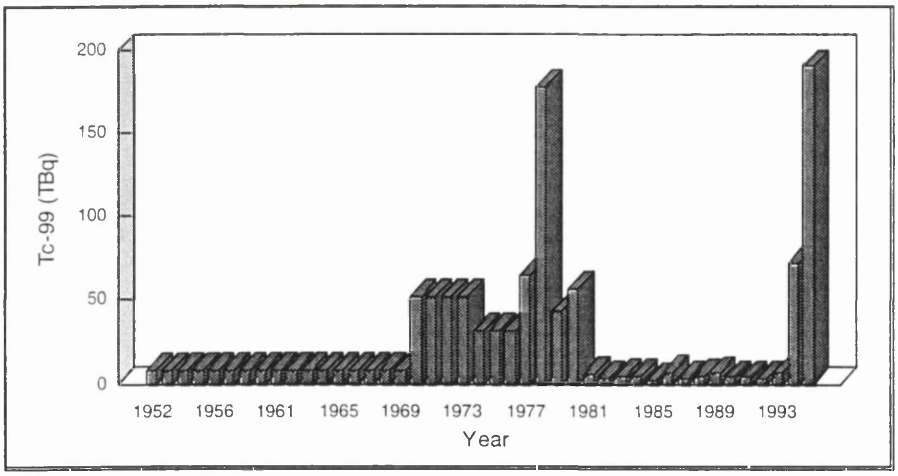


Figure 1. 10 Discharge rates of ^{99}Tc estimated (1952-1977) and reported (1978-1995) from Sellafield.

Discharges of technetium-99 in 1994/1995 are comparable to levels reported for 1978 - 1980. This enhanced discharge of ^{99}Tc from EARP is likely to increase technetium-99 levels in the Irish Sea at least for a decade (assumed) and thus it provides an ideal opportunity to study technetium-99 behaviour in the aquatic environment. Further, ^{99}Tc had been identified as the single largest contributor (47%) to the committed effective dose of 0.06 mSv yr^{-1} to the Sellafield critical group of high seafood consumers due to discharges in 1994 (MAFF, 1995) and it would seem desirable to obtain more accurate information on the environmental behaviour of this nuclide.

1.5.2.1 Transfer of Technetium-99 to Man.

Man is exposed through a number of routes to radionuclides discharged to the sea from nuclear installations. The pathways which have received most attention since the early days of the nuclear industry are the consumption of seafood (including seaweed) and external exposure on shorelines from radioactive silt and mud. In the case of technetium-99, there are three important pathways. These are the ingestion of *Nephrops* (Norwegian lobster), the ingestion of meat from live-stock grazing on saltmarshes and the ingestion of crops grown using seaweed fertilizer (Nicholson et al., 1992).

1.5.3 Other Sources of Technetium-99 in the Irish Sea.

Springfields and Capenhurst.

BNFL fuel division's manufacturing site at Springfields (near Preston in Lancashire, England) produces fuel and intermediate fuel products for the nuclear industry in the UK and abroad. Uranium ore concentrates are processed to either uranium metal for use in Magnox reactors or to uranium hexafluoride (UF_6), on-site. This UF_6 is sent for enrichment at Capenhurst or alternatively abroad. Enriched UF_6 received on-site is converted by the Integrated Dry Route to provide oxide fuel or intermediates for use in Advanced Gas cooled Reactors or Light Water Reactors. Depleted uranium trioxide (a product of reprocessing irradiated Magnox fuel at Sellafield) is also processed to UF_6 prior to re-enrichment and processing into oxide fuel. The liquid wastes arising from Springfields operations are discharged via pipelines into the tidal waters of the River Ribble. Recently BNFL (1996) reported ^{99}Tc discharge levels from Springfields works into the Ribble against an authorised limit of 0.6 TBq (Table 1.7).

Year	Activity (TBq ^{99}Tc)
1991	0.05
1992	0.10
1993	0.10
1994	0.016
1995	0.030

Table 1. 7 Annual ^{99}Tc discharge rate from Springfields works (1991-1995).

At the Capenhurst site, BNFL operates a uranium enrichment plant. Liquid discharges are regularly released from Capenhurst works into Rivacre Brook by means of a culvert and ditch. Discharge data for ^{99}Tc from Capenhurst to Rivacre Brook are given in Table 1.8.

Years	^{99}Tc (TBq)
1989	0.00087
1990	0.00660
1991	0.00767
1992	0.00389
1993	0.00490
1994	0.00335
1995	0.00530

Table 1. 8 Annual ^{99}Tc discharge rate from Capenhurst works (1989-1995).

^{99}Tc releases from Springfields to the Ribble estuary have been reported only recently, however, it has been released from Capenhurst since 1978. Discharges of ^{99}Tc from both these sites are small relative to Sellafield discharges.

1.6 AIM OF STUDY.

Technetium-99 is a high yield fission product with a long half-life and relatively high solubility in natural waters. Consequently it is of potential radiological concern if released to the environment either in the long-term from a high level nuclear waste repository or as an immediate result of nuclear fuel reprocessing and, thus, it is desirable to have a sound knowledge of its environmental behaviour.

As stated earlier in this section, it is believed that technetium is present in seawater mainly in the form of pertechnetate (TcO_4^-), which is extremely mobile and can be transported very long distances in aqueous media. Very little is known, however, about the possible existence of other chemical forms, their stability and their bioavailability. Along with radiological considerations already discussed, therefore, the great potential of Tc as a tracer of water movement provides another valid reason for studying its behaviour in the aquatic environment.

Environmental data, to date, are scarce due to difficulty associated with its beta detection and the low levels present in the environment. The systematic error associated with beta counting after separation of ^{99}Tc from large volumes of seawater (Holm, 1993) has resulted in overestimates of the ^{99}Tc levels in most cases by an order magnitude according to Momoshima et al. (1995). However, recent analytical advances (e.g. mass based determinations) and the large increase in ^{99}Tc discharges (from EARP, Sellafield) into the Irish Sea make this an ideal location to obtain necessary environmental data. The present study had a number of objectives.

Firstly:

- to develop an analytical method based on Inductively Coupled Plasma Mass Spectrometry (ICP-MS); and,
- check the applicability of the analytical method developed to an alternative mode of measurement, Liquid Scintillation Counting (LSC).

Having developed a suitable analytical method, the secondary objectives were to determine:

- technetium-99 accumulation patterns in different environmental species;
- temporal variations in ^{99}Tc levels in the environment pre- and post- EARP;

- spatial variations in ^{99}Tc levels in the environment pre- and post- EARP;
- the extent of ^{99}Tc transfer from the marine to a saltmarsh environment;
- temporal and spatial variations in Cs/Tc levels in the environment;
- historic levels of ^{99}Tc in the Irish Sea environment.
- the magnitude of other sources (in addition to Sellafield) of ^{99}Tc to the Irish Sea (Springfields and Capenhurst).

From the results of the environmental studies a better understanding of the behaviour of ^{99}Tc in the Irish Sea should be derived.

CHAPTER 2: THE DETERMINATION OF ^{99}TC IN ENVIRONMENTAL SAMPLES - METHOD DEVELOPMENT

2.1 INTRODUCTION.

^{99}Tc is a pure soft beta emitter (E_{max}=292 keV) with a long half-life (2.1×10^5 years) and thus, its analyses requires elaborate chemical procedures to pre-concentrate and purify the low levels present in the environment. Various physical and chemical properties of technetium, such as its beta radioactivity; complex formation; absorption bands of X-rays, UV and IR light; mass to charge ratio, etc., can be used for its qualitative, as well as its quantitative analysis. Several reviews are available on various methods for the detection of technetium (Kotego et al., 1968; Lavrukhina & Pozdnyakov, 1970; Robb, 1983; Long & Sparkes, 1988), the most important points from which are now discussed.

2.1.1 Classical Technique.

This method involves the precipitation (gravimetric) of a stable, insoluble or very slightly soluble form of the element of interest. The gravimetric methods available mainly involve the formation of insoluble Tc compounds such as Tc_2S_7 and TcO_2 or the formation of an insoluble compound from the reaction between TcO_4^- and a large organic molecule (e.g., formation of tetraphenylarsonium pertechnetate $(C_6H_5)_4$ $AsTcO_4$, or nitron (4,5 dihydro-1, 4-diphenyl-3, 5-phenylamino-1,2,4, triazole) pertechnetate. The precipitation of Tc_2S_7 is carried out in hot HCl or H_2SO_4 by bubbling H_2S. However, reducing agents, which convert Tc(VII) to lower oxidation states, must be absent. Other species that form insoluble sulphides will also interfere and must be absent (Boyd et al., 1960; Robb, 1983; Long & Sparkes, 1988; Handoll, 1989). These interferences limit the use of gravimetric methods for the routine detection of ^{99}Tc from environmental samples.

2.1.2 Radiometric techniques.

A variety of radiometric techniques (counting of beta particles emitted from ^{99}Tc) have been successfully used for the determination of ^{99}Tc at environmental levels. Many studies on environmental levels of ^{99}Tc in water, sediment, and other biota samples have used low background GM counters (Dutton & Ibbett, 1973; Patti et al., 1981; Riley & Siddiqui, 1982; Malcolme-Lawes et al., 1982; Kaye et al., 1982; Robb et al., 1985; Holm & Rioseco, 1987). Recent studies have used low background gas-flow proportional counters (Holm et al., 1986a; Aarkrog et al., 1986; Ballestra et al., 1987; Rioseco, 1987;

Hurtgen et al., 1988; Chen et al., 1990; Harvey et al., 1991a). A few other studies (Holm et al., 1981; Takizawa et al., 1995) have used surface-barrier detectors for measuring beta particles from ^{99}Tc.

Very low detection limits can be achieved by radiometric methods. However, the low efficiency experienced during beta counting necessitates long counting times. In addition, complex and time-consuming chemistry is required for the separation of other beta emitters (e.g., ruthenium) from technetium and the preparation of thin sources for counting; and thus only a small number of samples can be analysed in a unit time.

To overcome difficulties associated with low background beta counting, such as time reduction and simplification of sample preparation, liquid scintillation counting (LSC) techniques have been developed (Walker et al. 1980; Luxenburger & Schuettelkopf, 1984; Cattarin et al., 1985; Koide & Goldberg, 1985; Lawson et al., 1985). Colour quenching caused by the solvent matrix and interference due to other low energy beta emitters (e.g.. ^{125}Sb, ^{110m}Ag, ^{32}S) are potential problems (Rucker & Mullin, 1980) in LSC but these can be avoided by employing various chemical clean-up methods (Scarpitta, 1994; Nevissi et al., 1994; Jordon et al., 1995).

2.1.3 Neutron Activation Analysis.

Neutron activation analysis (NAA) is a very sensitive technique for the determination of ^{99}Tc. Irradiation of ^{99}Tc with thermal neutrons produces ^{100}Tc by the (n, γ) reaction that has a relatively high neutron capture cross section (20 barns). Foti et al. (1972) have applied neutron activation with a thermal neutron flux of 5×10^{13} n cm^{-2} sec^{-1} to produce ^{100}Tc (15.8 s, half-life) for the determination of technetium from filter paper and vegetation samples. Samples were counted on a low background beta counter and detection limits of 3.18 mBq ^{99}Tc in filter paper samples and 5.7 mBq in vegetation samples were obtained using a 25 g sample. Houdek et al. (1979) used a similar method except that samples were counted using gamma spectrometry, but this was not sensitive enough to achieve these detection limits due to the small emission probabilities of γ rays from ^{100}Tc (540 keV=7%, 591 keV=5.7%). NAA for ^{99}Tc detection was also described by Bate (1980) from Oak Ridge National laboratory, USA. In this method, the sample was irradiated after loading onto an anion-exchange resin. The above method gave detection limits of 3.18 Bq of ^{99}Tc and it was used for nuclear reactor fuel solution and for off gas trap samples.

The major disadvantage of this method is the short half-life of ^{100}Tc. Interference from chloride, iodide, and sodium ions are also encountered during gamma spectrum analysis for ^{100}Tc. Ikeda et al., and Sekine et al. (1989) described two different nuclear excitation techniques for the detection of ^{99}Tc, from low level radioactive wastes. Sekine et al., quoted 0.63 Bq ^{99}Tc as the detection limit for the gamma (γ, γ') nuclear excitation technique. Ikeda et al., however, used the neutron excitation reaction (n, n$'$) and gave 10 Bq ^{99}Tc as the detection limit. These techniques are still limited in use, however, due to the high levels of radiation involved with irradiation and subsequent counting of environmental samples.

2.1.4 Mass Spectrometry.

More recent analytical research into ^{99}Tc analysis has centred around the use of mass spectrometry. Very low activities of ^{99}Tc can be detected by mass spectrometry, since it is based on the number of atoms present in the samples. Isotope Dilution Mass Spectrometry (Anderson and Walker, 1980) was used to measure ^{99}Tc with a detection limit of 0.67 mBq. Laser Resonance Mass Spectrometry has been found capable of detecting as little as 0.63 mBq of ^{99}Tc (Sattelberger et al., 1989). Negative Thermal Ionisation Mass Spectrometry (Rokop et al., 1990) was found to have better detection limits (~0.06 mBq of ^{99}Tc) based on measurement of pertechnetate anion (molecular mass of 163 amu). Interference in mass spectrometry is caused mainly by isobars (elements having similar mass); molybdenum-97 and ruthenium-99 presents an isobaric interference in technetium-97 and technetium-99 determinations respectively. Although, very low detection limits have been achieved by these mass spectrometry methods, lengthy sample preparation procedures and the requirement of access to very expensive instruments limits their routine use.

Inductively Coupled Plasma sources, however, offer several advantages over a thermal source, including increased sample throughput, the ability to ionise samples with a high work function and the elimination of time dependent fractionation effects.

Morita et al. (1991) determined ^{99}Tc levels from environmental samples (soil and sediments) using ICP-Mass Spectrometry. The limit of detection was given as 1.1 mBq ml^{-1} (1.73 pg ml^{-1}). Ishanullah & East (1990), using a similar technique reported a limit of detection of 2.5 mBq ^{99}Tc. Table 2.1, shows some of the recent works on ^{99}Tc detection using ICP-MS, from environmental samples.

MATRIX	REFERENCE
Soil and Sediment samples	Morita et al., 1991
Seawater, seaweed samples	Ishanullah, 1991
Sediment samples	Sumiya et al., 1994
River water samples	Beals, 1995

Table 2. 1 Recent references on ^{99}Tc determinations using ICP-MS.

The principal advantages of ICP-MS over radiation counting include speed of measurement, greater sensitivity, and, for some applications reduced sample preparation (Ross et al., 1993).

2.1.5 Summary of Available Techniques.

For the determination of technetium, radiometric methods are widely used. Measurements based on β-ray counting of ^{99}Tc with low background Geiger Mueller counter, gas-flow proportional counters or surface-barrier detectors, however, require a careful chemical separation from any other β-ray emitter and the preparation of thin samples to prevent self-absorption and back scattering effects. Technetium-99 can also be determined by liquid scintillation counting which is more specific due to pulse-height analysis and is less time-consuming because the preparation of thin counting samples can be omitted (Luxenburger and Schuettelkopf, 1984). Trace amounts of technetium have been detected by activation analysis, however, highly purified samples with fast procedures for separating and measuring the formed ^{100}Tc, half-life of 15.8 seconds (Foti et al., 1972) are necessary.

Extremely sensitive mass spectrometry techniques for the determination of ^{99}Tc have been recently developed. Indeed, many recent studies have used ICP-MS for the low level determinations of ^{99}Tc from the environment. The range of detection limits achievable by various techniques for ^{99}Tc have been summarised in Table 2.2.

ANALYTICAL METHOD	LOD (mBq)	REFERENCE
Gravimetric	3.18×10^6	Nelson et al., 1954
Low background Geiger Mueller tube	44	Kaye et al., 1982
End-window proportional counter	14	Harvey et al., 1991a
Anti-coincidence shield gas flow counting	3	Chen et al., 1994
Neutron activation (γ', γ')	630	Sekine et al., 1989
Neutron activation (n, γ')	3.18	Foti et al., 1972
Liquid scintillation counting	5	Jordon et al., 1995
Mass spectrometry	0.63	Sattelberger et al., 1989
ICP-MS	1.1	Morita et al., 1991

Table 2. 2 Limits of detection for the determination of ^{99}Tc.

Based on features like sample throughput, versatile application of the instrument, acceptable sensitivity and availability of the instrument for the present study, the ICP-MS method has been selected for the determination of ^{99}Tc. The analytical method to pre-concentrate and purify technetium from a range of environmental matrices has been developed and optimised for ICP-MS method. The method has also been used with LSC and the details of its development are now discussed.

2.2 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY - METHOD DEVELOPMENT.

2.2.1 Development of ICP-MS.

Before the commercial development of ICP, Spark Source Mass Spectrometry (SSMS), using a radio frequency (RF) spark in vacuum, was extensively used in trace metals analysis. It is, however, adversely affected by polyatomic ion peaks such as M^{2+}, MO^+, MOH^+ etc., due to inadequacy of RF spark source in the dissociation of the sample and the production of single charged ions. Attention therefore turned to the possibilities of higher ion source pressures (e.g., atmospheric pressure direct current (DC) and RF plasma) at which the problems of energy transfer to the analyte molecules necessary for adequate dissociation might be expected to be less intractable. Initial work carried out with the ARL Laboratory on DC plasmas, using solution samples, introduced by both pneumatic and ultrasonic nebulisers, showed that very low detection limits should be possible, partly because of the very low background levels obtained. However, it was clear that at the temperatures (3000 to 5000K) achieved in the DC plasma, the sensitivity for elements with ionisation energies above 8.5eV was much lower. Thus not only was a poorer degree of ionisation achieved than expected but dissociation of the sample molecules was poor and matrix effects severe (Gray, 1974, 1975). It showed, however, that an atmospheric pressure ion source could be used to give high sensitivity for those elements which were adequately ionised. It also showed that a hotter, more suitable, plasma such as the ICP was necessary (Gray, 1978).

Nowadays, Inductively coupled plasma (ICP) is a very important ion source in the field of multi-element analysis at trace levels (Greenfield et al., 1964; Wendt and Fassel, 1965). The characteristics of the ICP which make it so suitable as an ion source have been extensively described in the literature (Fassel, 1977, 1978; Montaser and Golightly, 1987; Boumans, 1987; Moore, 1989).

Mass spectrometry, of all the alternative spectrometric methods available for multi-element analysis, was found to offer the best combination of simple spectra, adequate resolution and low detection limits (Gray, 1989) for trace determination in complex matrices.

The first commercial ICP-MS instruments were released in 1983. Since then the technique has become increasingly accepted by analytical chemists worldwide.

2.2.2 ICP-MS system.

A schematic diagram of the ICP-MS is shown in Figure 2.1.

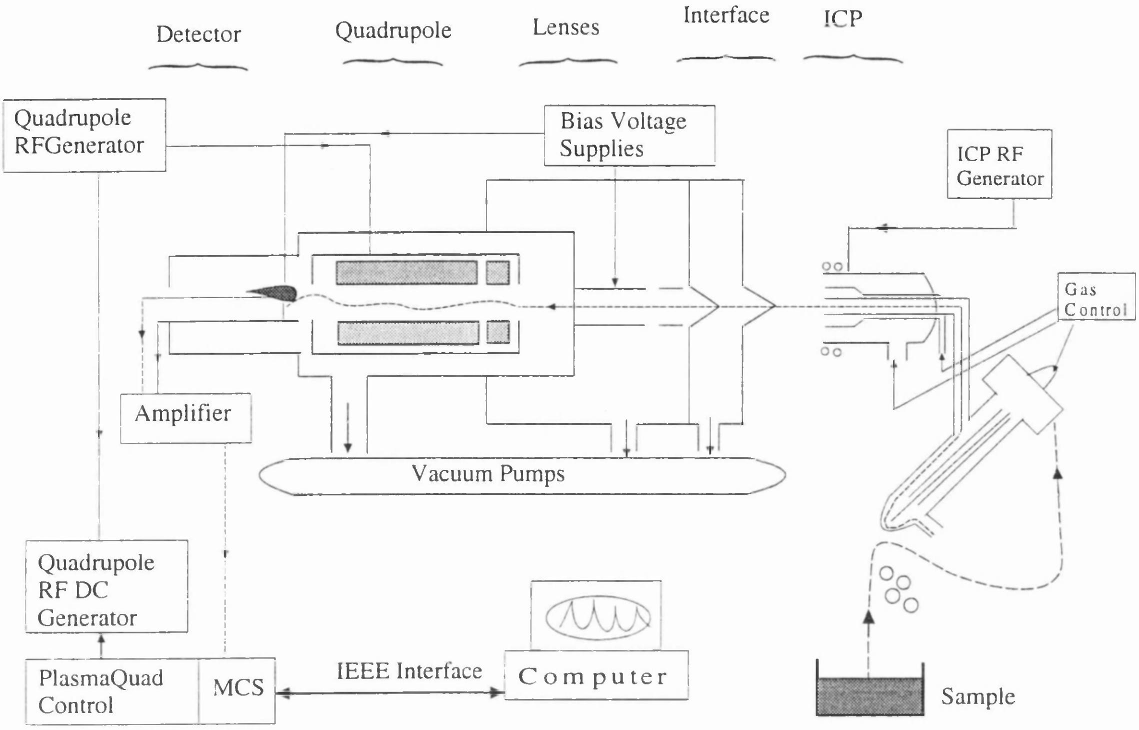


Figure 2. 1 Schematic diagram of typical ICP-MS system.

The ICP-MS consists of a nebuliser (sample introduction system), ICP as an ion source (torch and plasma system), sampling interface (ion extraction stage), quadrupole mass filter (quadrupole system), and detector (data acquisition system). These systems are detailed individually below.

2.2.2.1 Sample introduction.

The ICP requires any sample to be introduced into the central channel gas flow as a gas, vapour or aerosol of fine droplets or solid particles. A wide variety of methods may be used to produce these such as pneumatic or ultrasonic nebulization of a solution, electrothermal volatilisation of micro samples from a hot surface, laser or spark ablation from a solid, and generation of volatile hydrides or oxides from a reaction vessel.

The ICP-MS installed at SURRC is equipped with a pneumatic nebuliser as standard, in which a high velocity gas stream produces a fine droplet dispersion of the analyte solution. The larger droplets are removed by a spray chamber (Figure 2.2) which allows only those below about 8 μm diameter to pass on to the plasma. These small droplets carry only about 1% of the solution which is usually metered to the nebuliser by a peristaltic pump.

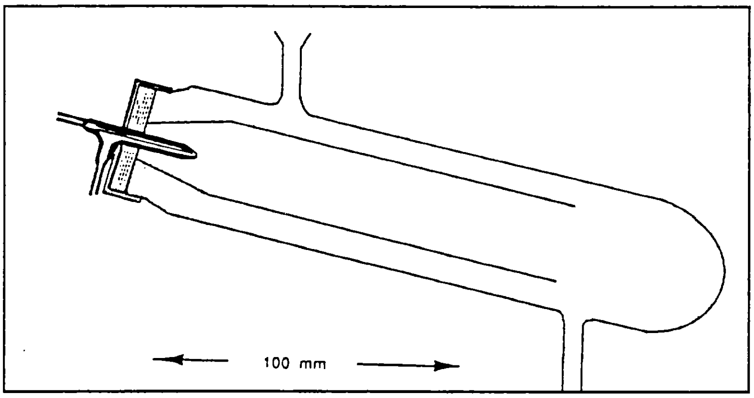


Figure 2. 2 Spray chamber (Scott et al., 1974).

Although universally recognised as a very inefficient system, the pneumatic nebuliser, of which there are many forms, retains its popularity because of its convenience, reasonable stability, if correctly operated, and ease of use with multiple sample changers.

2.2.2.2 Torch and plasma.

An assembly of quartz tubes known as the torch (Figure 2.3) is used to generate a plasma at its open end. Thus the ICP is an electrode less discharge in a gas at atmospheric pressure which is maintained by energy from a RF generator. This is done by a suitable coupling coil. The gas commonly used is argon which attains a temperature of about 7500°K.. The sample in solution is passed via the spray chamber into the plasma where the sample is atomised and ionised. The degree of ionisation, however, is dependent on the ionisation conditions in the plasma, as well as the ionisation constant and partition functions for the atom concerned.

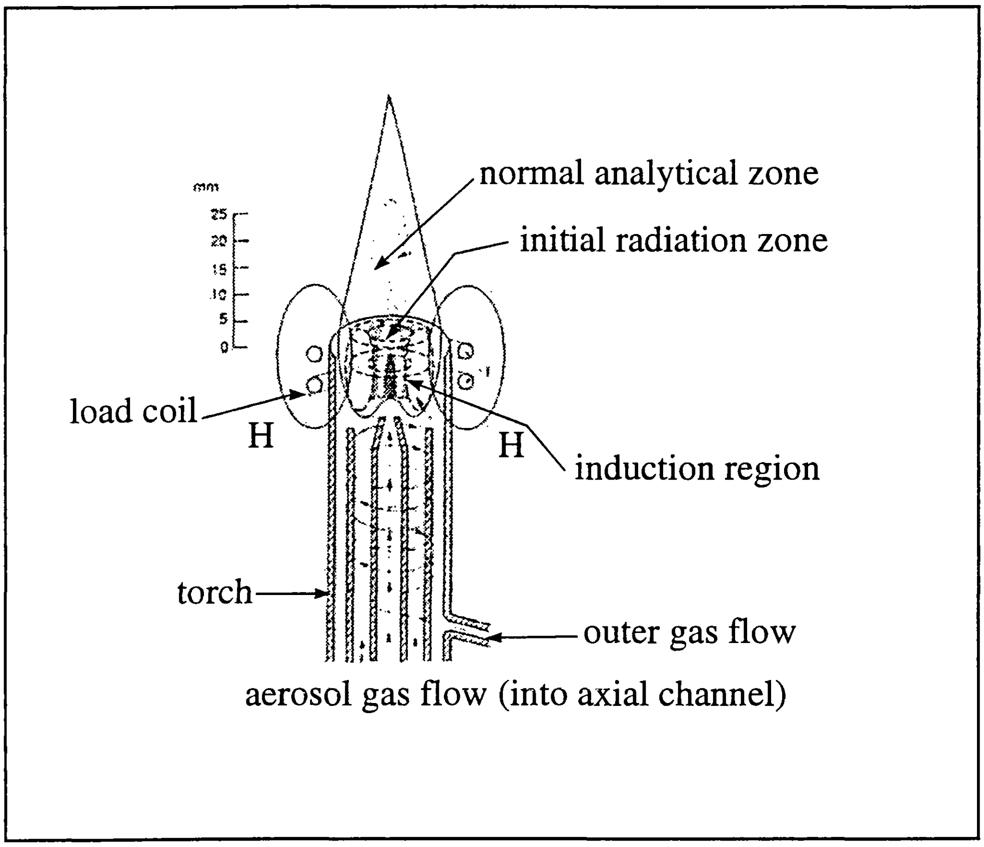


Figure 2. 3 Schematic of ICP torch, gas flows and the induced magnetic field (Houk, 1990).

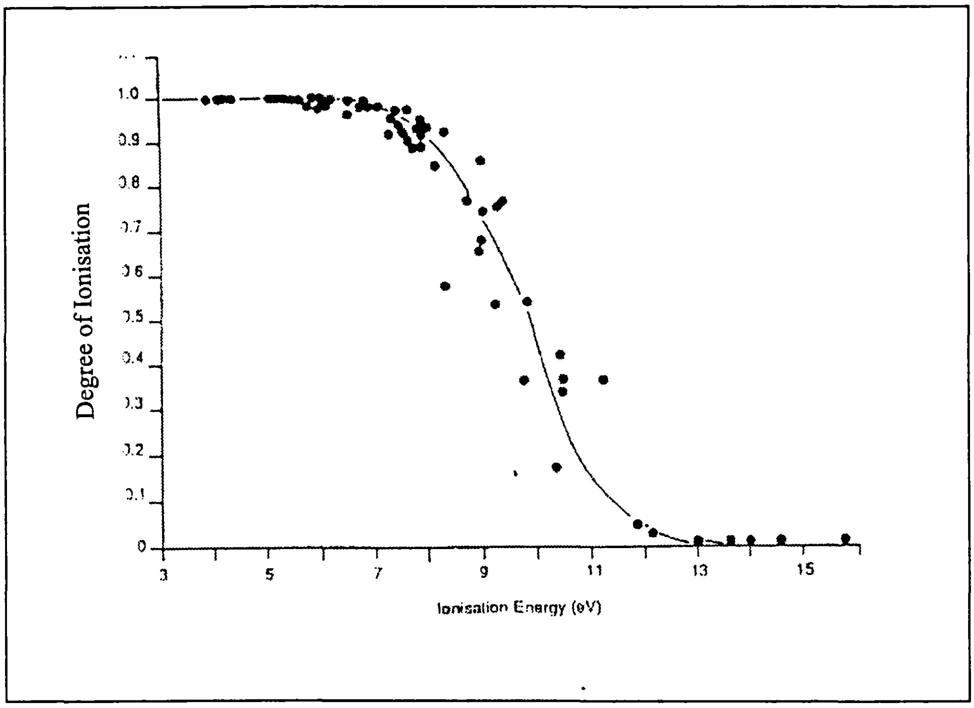


Figure 2. 4 Degree of ionisation versus ionisation energy for singly charged ions in the ICP (Gray, 1989).

Figure 2.4 shows the dependence of degree of ionisation on ionisation energy for the production of singly charged ions in an ICP, from which it may be seen that the response falls away rapidly above 9 eV. Most elements, including technetium (7.2 eV (1^{st}) & 14.9 eV(2^{nd})), have first ionisation potentials below 9eV, and second ionisation potentials above 9eV (Gray, 1989).

Thus the ICP forms a very convenient ion source with a high yield of singly charged analyte ions and relatively few doubly charged and oxide or other molecular and adduct ions.

2.2.2.3 Ion extraction.

A schematic diagram of a typical extraction interface is shown in Figure 2.5. Ions first flow through a sampling orifice (approx. 1 mm diameter) into a mechanically pumped vacuum system, where a supersonic jet forms.

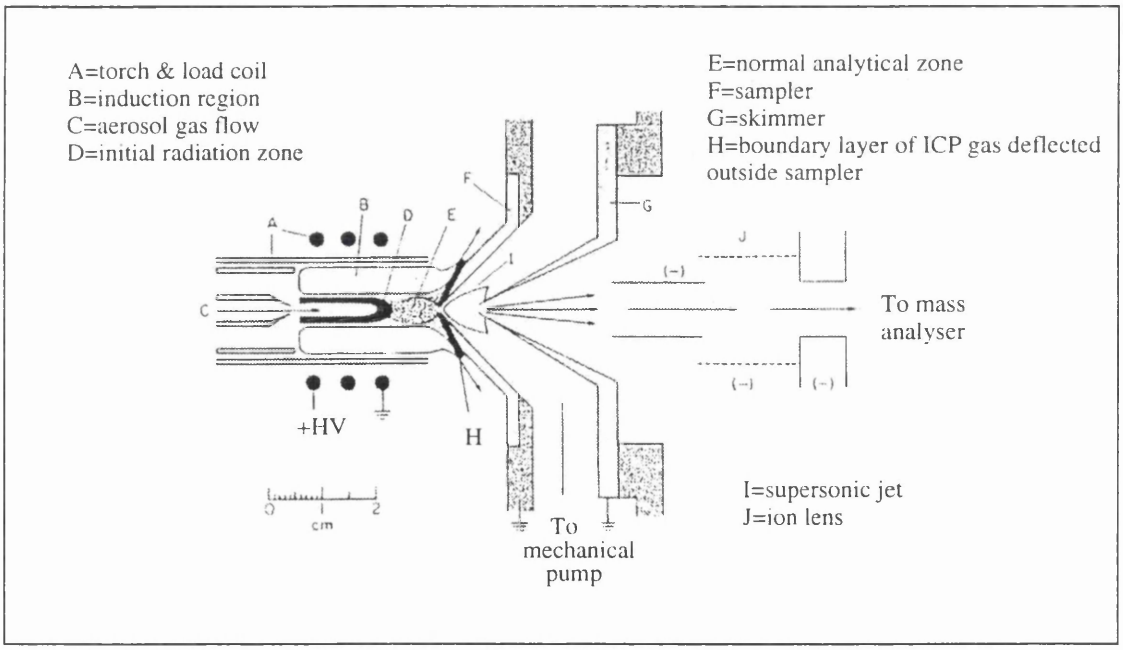


Figure 2. 5 ICP and sampling interface for ICP-MS (Houk, 1986).

The central section of the jet flows through the skimmer orifice, which is also approximately 1 mm diameter. After the ions leave the skimmer, they must be conveyed to the mass analyser. Ion lenses are used for this function. Ion lenses in the PlasmaQuad instrument are shown in Figure 2.6.

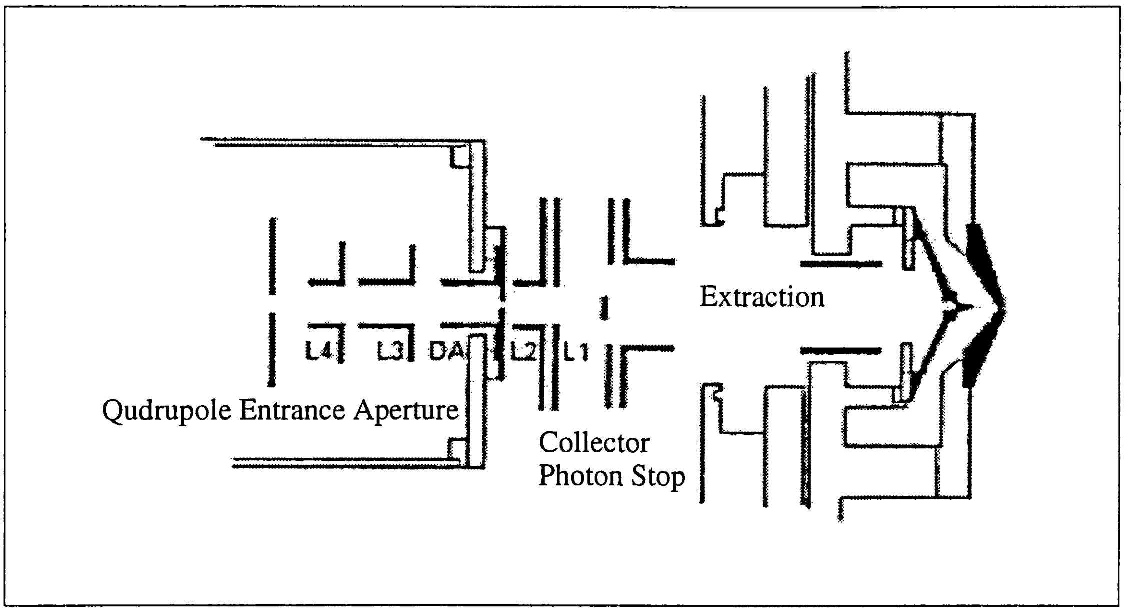


Figure 2. 6 Ion lenses from PlasmaQuad.

In each lens, several electrodes are strung together to confine the ions on their way to the mass analyser. The first lens incorporates a central disc to prevent photons from the plasma from reaching the detector. Offsetting the entrance to the quadrupole from the line of sight through the lens and sampler is another effective way to minimise the background from photons.

Space charge effects (the mutual repulsion of ions of like charge limits the total number of ions that can be compressed into a beam of a given size) should become substantial in ICP-MS at total beam currents of the order of 1 μA (Olivares and Houk, 1985; Gillson et al., 1988), roughly three orders of magnitude below the actual beam current. The space charge effects are a major cause of matrix interference in ICP-MS. Many workers have reported that matrix effects are more severe in ICP-MS than in ICP emission spectrometry (Houk et al., 1980; Olivares and Houk, 1986; Vickers et al., 1989). Also, the mass of both interferon and analyte are important. Heavy matrix ions suppress analyte signals more extensively than light matrices, and heavy analyte ions are suppressed less severely than light ones (Tan and Horlick, 1987; Crain et al., 1988; Gillson et al., 1988).

2.2.2.4 *Quadrupole mass spectrometers.*

A diagram of a typical quadrupole mass filter is shown in Figure 2.7. Four straight metal rods or metallised surfaces are suspended parallel to and equidistant from the axis. The rods are manufactured and mounted to very high dimensional tolerances (10 μm or less).

Opposite pairs are connected together. DC and RF voltages of amplitude U and V, respectively, are applied to each pair. The ions are introduced along the axis into one end of the quadrupole structure at velocities determined by their energy and mass. If the RF and DC voltages are selected properly, only ions of a given *m/z* ratio will have stable paths through the rods and will emerge form the other end.

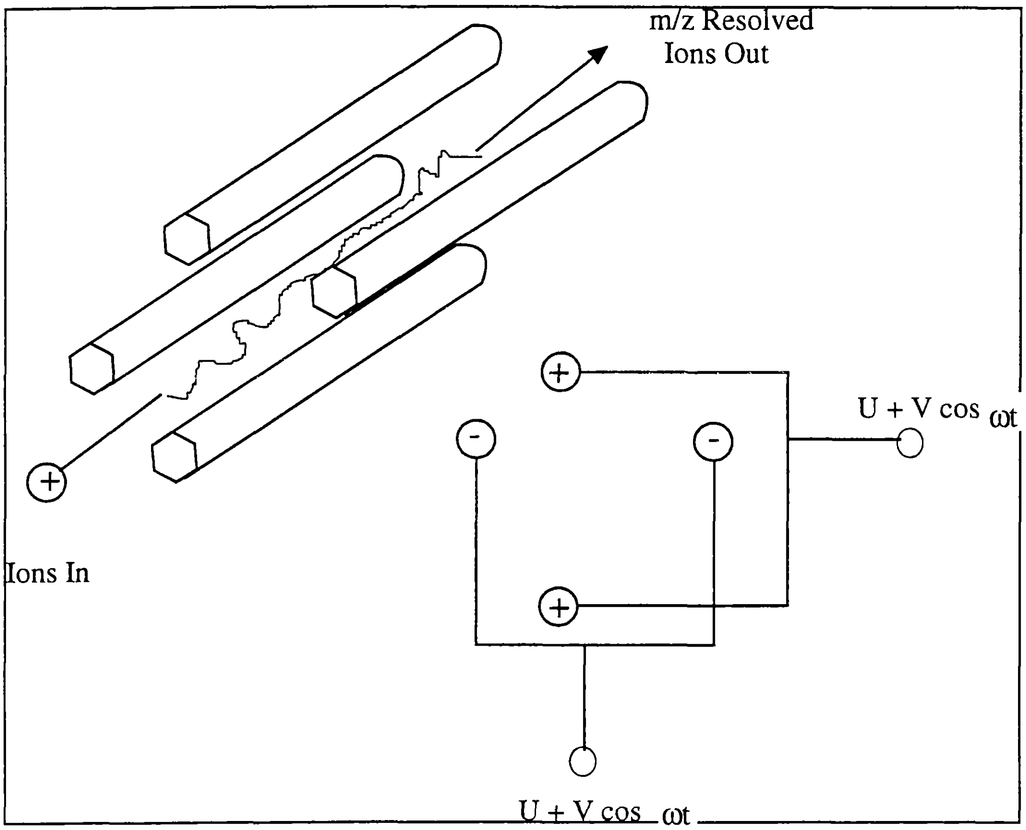


Figure 2. 7 Schematic diagram of quadrupole rods showing ion trajectory and applied voltages.

2.2.2.5 Scanning and data acquisition.

As described above, the *m/z* transmitted by a quadrupole mass analyser is determined by constant factors such as the dimensions of the rods, the frequency of the RF voltage and by the variables U and V. If U and V are not changed, the mass filter transmits only one *m/z* value continuously. This mode is called selected ion monitoring or single ion monitoring. Alternatively, U and V can be changed under computer control rapidly between selected discrete values (peak hopping), or the quadrupole can be scanned repetitively through the *m/z* region of interest (multi-channel scanning). A Personal Computer equipped with special software (VG Elemental PlasmaQuad) is used to control the data acquisition and manipulation procedures.

2.2.3 Analytical Method Development.

2.2.3.1 Introduction.

Detection of technetium-99 in the environment is difficult due to its low specific activity (6.2×10^{11} Bq kg^{-1}) combined with the very low levels present in the environment. As such, the levels of Tc are not enough to measure directly, preconcentration from as large a sample size as possible is necessary. Interference in the mass based determination of ^{99}Tc is mainly from the isobaric nuclide, ^{99}Ru. Ruthenium has a natural abundance of 12.7% at mass 99 and exists at a concentration of about 1 ng l^{-1} in seawater (Bowen, 1979; Letokhov, 1987). Thus ruthenium-99 can interfere with the detection of technetium during ICP-MS analysis and has to be removed by chemical separation from technetium-99. When preparing solutions for analysis by ICP-MS, an important consideration is the concentration of total dissolved solids (TDS) present in the solution when analysed. As a general rule, this concentration should not exceed 0.1% (1000 μg ml^{-1}) as, above this level, sample cone blockage may occur, which can lead to severe analyte signal drift (Date & Jarvis, 1989).

For the quantitative analysis of technetium at low concentrations in environmental samples it is normally necessary to separate technetium from the bulk matrix components. However, the accurate level of technetium in the original sample can only be obtained when the relationship between the amount recovered and that originally present in the sample is known. This may be established, in practice, by adding a yield tracer or yield monitor (Norton, 1966) to quantify the chemical recovery of the determinant. Various available tracers that have been used in ^{99}Tc determinations are given in Table 2.3.

TRACERS	HALF-LIFE	TYPE OF DECAY/ PROPERTIES
^{99m}Tc	6.02 hours	γ
^{95m}Tc	61 days	γ
^{97m}Tc	91 days	γ
^{97}Tc	2.6×10^{6} years	EC
Rhenium	Stable	Chemical Analogue

Table 2. 3 Various tracers available.

The yield tracer, in principle, 1) must behave chemically exactly the same as the determinant at each stage in the analysis, 2) chemical equilibrium between tracer and determinant must be established at the earliest possible point in the procedure, and 3) unique assay of tracer and determinant must be possible in the presence of one another. For this purpose, a stable form of technetium is not available, but fortunately, for technetium and many other radionuclides of environmental interest, nuclear technology has created additional radioisotopes which, though having different atomic weights, have the same atomic number and therefore identical chemical properties. Different isotopes of the same elements possess distinctive nuclear properties, and as such may be capable of being used as yield tracers (Harvey & Lovett, 1991).

^{95m}Tc (Ishanullah, 1991; Morita et al., 1991), ^{97m}Tc (Kaye et al., 1982), and ^{99m}Tc (Robb et al., 1985; Chen et al., 1989&1990) are often used as yield monitors. The use of ^{99m}Tc is limited due to its short half-life while the use of ^{95m}Tc is limited when using beta counting for ^{99}Tc determination due to impurities in the tracer. Disadvantages associated with the use of ^{97m}Tc is that the decay of ^{97m}Tc results in production of beta particles that also mask the original ^{99}Tc beta decay. Kaye et al. (1982) used ^{97m}Tc as a yield tracer for ^{99}Tc analysis with a low background GM counter. The measurement method involves taking two successive counts, one with only 0.83 mg cm^{-2} of mylar covering the sample, and a second with an additional amount of aluminium foil thick enough to stop the low-energy electrons from ^{97m}Tc (energies about 75 & 94 keV) but thin enough, so that a significant fraction of beta particles from ^{99}Tc (Emax=292 keV) are transmitted.

Matsuoka et al. (1990) and Harvey et al. (1991a) used rhenium as a non-isotopic tracer, as it behaves chemically like technetium. The use of rhenium as a yield tracer, however, is limited due to slight differences in anion-exchange behaviour. The counting efficiency of ^{99}Tc was also found to reduce as the mass of deposited rhenium increased. Golchert & Sedlet (1969) have avoided using rhenium as a yield tracer because in their opinion, the inevitable fractionation between rhenium and technetium would make it impossible to obtain accurate chemical yields (Anders, 1960).

The use of ^{97}Tc as a yield tracer, has become an important development in ^{99}Tc detection. ^{97}Tc is produced by neutron activation of enriched ^{96}Ru and may contain some ^{98}Tc ($t_{1/2}$=4.2x10^{6} y) but very little ^{99}Tc. Many studies involved with isotope dilution mass spectrometry (Kaye et al., 1978; Anderson, 1980; Anderson & Walker, 1980), ID-ICP-MS (Beals, 1995), have used ^{97}Tc as a yield tracer. The cost of production and time involved, however, limits the use of ^{97}Tc as a common yield tracer.

In the present study ^{99m}Tc and ^{95m}Tc were used as yield tracers. ^{99m}Tc was mainly used during method development work, as it is readily available and inexpensive to produce (^{99m}Tc was obtained from the West of Scotland Radionuclide Dispensary, Western Infirmary, Glasgow). The longer half-life of ^{95m}Tc, however, made it the more suitable tracer for the analysis of real samples (^{95m}Tc was obtained from the National Physical Laboratory, London). ^{106}Ru (half-life, 368 days) was used as a yield monitor for ruthenium decontamination studies, during method development work and was obtained from Amersham International. The detector used to measure these gamma emitters is a Germanium (Lithium) detector controlled by a Personal Computer running Maestro™ software for data acquisition and handling. The 141, 204 and 511 keV peaks were used for the analysis of ^{99m}Tc, ^{95m}Tc and ^{106}Ru, respectively.

2.2.3.2 Pre-concentration.

To prepare a sample suitable for ICP-MS analysis, technetium-99 present in the environmental sample must be separated from bulk matrix materials and concentrated into a small volume. Several different environmental matrices have been studied in this project.

The pre-concentration method for technetium from seawater is discussed first followed by biota (e.g., seaweed, mussel and winkles) and sediment.

Seawater samples:

Golchert & Sedlet used evaporation to preconcentrate ^{99}Tc from seawater samples. Losses of ^{99}Tc due to high temperature (>100°C) during evaporation reduced recovery, and thereby low levels of ^{99}Tc could not be detected in most samples. Good recovery of technetium was achieved using ion-exchange resin for preconcentration from large volume water samples (Patti et al., 1981; Riley & Siddiqui, 1982; Chen et al., 1990; Harvey et al, 1991a). Other methods used include reduction co-precipitation (Holm et al., 1984; Ballestra et al., 1987), selective precipitation (Till et al., 1979), and extraction using organic solvents (Chiu et al., 1990). However, recent works on ^{99}Tc in seawater suggest that anion-exchange provides good reproducible recovery of Tc (Ishanullah & East, 1990; Morita et al., 1991).

Anion-exchange.

For the preconcentration of technetium from large seawater samples an anion-exchange process has been selected. Ion-exchange methods have been widely employed for concentrating low levels of radionuclides from the environment. It is an exchange process of ions of like sign between a mobile phase and a stationary phase. Generally, the mobile phase is an aqueous solution of electrolyte while the stationary phase is a highly insoluble solid body with sites capable of exchanging ions. Typically, anion exchange resin is a polymer containing amino groups as an integral part of the polymer lattice and an equivalent amount of anions such as Cl^-, OH^- or SO_4^{2-} (Amphlett, 1964; Bassett et al., 1978).

In an ion-exchange procedure, the counter ions on the resin are replaced by sample ions that have the same charge. In the chloride form of resin, the counter ion on the resin is Cl^-. Usually the resin is used in an ionic form with a lower selectivity for the functional group than the sample ions to be exchanged. The sample ions are then exchanged onto the resin when introduced, and can be eluted by introducing an ion with higher affinity for the resin or a high concentration of an ion with equivalent or lower affinity. A general form of an anion exchange reaction is :

$$(\text{Resin } A^+)\, B^- + C^- \text{ (Solution)} = (\text{Resin } A^+)\, C^- + B^- \text{ (Solution)}.$$

The higher cross-linked resins, 1X8, 8% cross linked resin, are used for sorption, exchange, and separation of low molecular weight inorganic anions. In particular, higher cross-linked, strong anion exchange resins, are known to hold anions of technetium (TcO_4^-) well from basic aqueous solution (Harvey et al., 1991b). Commercially available, high grade anion exchange resin (AG-1X8, 100-200, chloride form) has been used for the preconcentration of Tc (Harvey et al., 1991a; Morita et al., 1991), however, commonly available anion exchange resin (Dowex-1X8, 50-100 mesh) is also known to be suitable for technetium preconcentration from seawater (Ishanullah, 1991). For the present study, Dowex-1X8, 50-100 mesh, chloride form has been selected and optimised for the preconcentration of technetium from large volume seawater samples.

Uptake of technetium.

The very low levels of technetium expected to be found in seawater samples necessitates the use of large sample volumes. Chen et al. (1990) have presented a method for collecting ^{99}Tc from 200-400 l of seawater by anion-exchange. Ishanullah & East (1990) have used up to 30 l of seawater. About 40 l of seawater were used by Harvey et al. (1991a) at a flow rate of 2 litre per hour. More recently, Chen et al. (1994) have used 500 l of seawater, at a flow rate of 145 ml per minute. During the development of the method, therefore, sample volumes of 50 l were used. To test the method, 50 litres of seawater collected from the Ayrshire Coast were filtered using 0.45 μm pore size cellulose nitrate membrane filters. The filtered seawater was spiked with yield tracers (^{99m}Tc and ^{106}Ru) and well mixed. A glass column was made indigenously (21cm x 24mm dia.) as shown in Figure 2.8 to accommodate 32 ml of the resin.

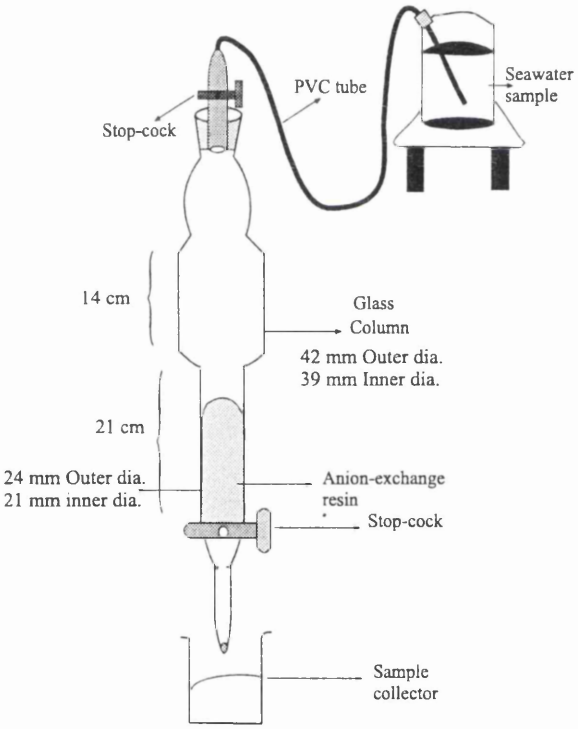


Figure 2. 8 Schematic diagram showing anion-exchange column set-up.

The required volume of resin was washed three times with de-ionised water. The water conditioned resin was then transferred into the above column. Both the top and bottom of the resin were plugged with fine glass wool to hold the resin firmly in the column. A transparent PVC tube (2m length) was connected to the top of the resin column (stop cock was used for flow control) and dipped into the sample container, which was kept above the column level. The sample flow rate was adjusted to 25-30 ml per minute.

The filtrate was collected and the percentage uptake of Tc and Ru on the column calculated (Table 2.4).

ELEMENT	% IN FILTRATE	% IN COLUMN
Tc	2	98
Ru	40	60

Table 2. 4 Levels of Tc and Ru - in column and filtrate.

Cleaning of resin column.

Before eluting Tc from the column, it is possible to further reduce levels of Ru and other matrix elements by the use of an appropriate washing agent. 0.1 - 1.0 M nitric acid concentrations have been used for gross decontamination during anion-exchange (Chen et al., 1990 & 1994). 1 M nitric acid washing is also thought to help reduce the salt concentration (Yamamoto et al., 1995) from the resin column thereby reducing matrix effects. In addition to acid solutions for cleaning, dilute alkaline (NaOH) solutions have also been used (Harvey et al., 1991a; Ishanullah, 1991; Chen et al.,1994)

For gross cleaning of the resin column, various concentrations of nitric acid were investigated. Nitric acid of 0.1, 1, 2, 4, 6, 8, 10 and 12 molar concentrations were tested. For this, 2 ml of resin spiked with ^{99m}Tc and ^{106}Ru were used. The percentages of technetium and ruthenium eluted are given in Figure 2.9.

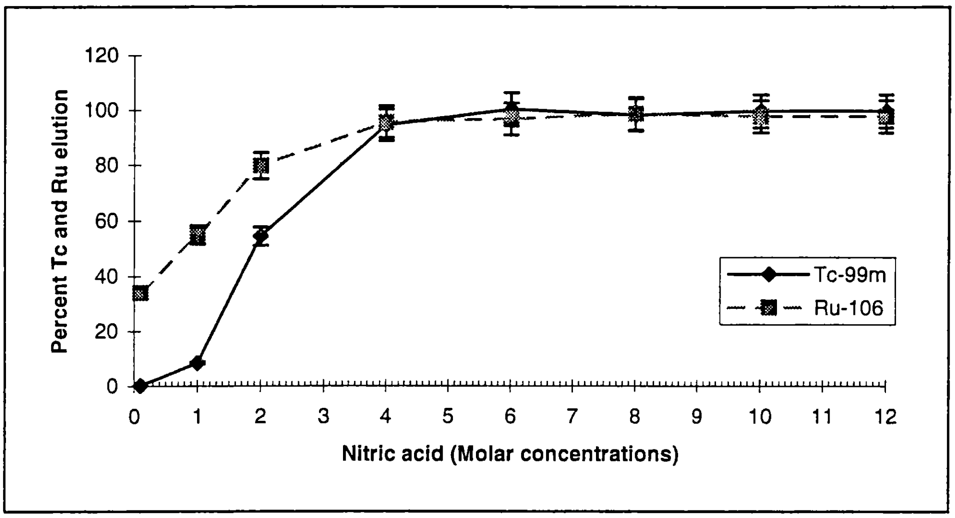


Figure 2. 9 Rinsing of anion-exchange column - Effect of nitric acid molarity.

0.1M HNO_3 did not remove any technetium while 1M HNO_3 and above did remove technetium from the resin. To minimise any loss of Tc during the analytical procedure, it was decided to use a molarity of 0.1 for washing the resin column, to provide gross decontamination over a wide range of anion and cations. The magnitude of ruthenium decontamination provided by the 0.1M nitric acid washing was significant (34±8%).

Since dilute NaOH solution has also been used in the literature for washing the resin column, the present study also tested 2M NaOH. Similar to the 0.1M nitric acid washing, 2M NaOH provided ruthenium decontamination of around 19±4%. However in the final analytical method, NaOH washing was avoided since it resulted in the formation of channels inside the resin column.

Elution of technetium from column.

For technetium elution, nitric acid has been widely used because acids like perchloric, hydrochloric, and sulphuric are likely to reduce technetium (+VII) to a lower valence state Tc(+IV). It is desirable to have a strong oxidising acid, to ensure conversion of all lower states to Tc(+VII) (Anders, 1960).

From Figure 2.9, it was clear that high acid concentrations (6-12M HNO_3) remove technetium efficiently from the resin. To verify further, two seawater sample (50 l each) were ion-exchanged with 32 ml of resin, and the technetium was eluted with 8M and 12M nitric acid. The observed results presented in Figure 2.10 showed that 400 ml of 8M gave about 93% recovery of Tc. However 250 ml of 12M HNO_3 was found to provide complete recovery (100%) of technetium and thus 12 M HNO_3 was chosen for the analytical procedure.

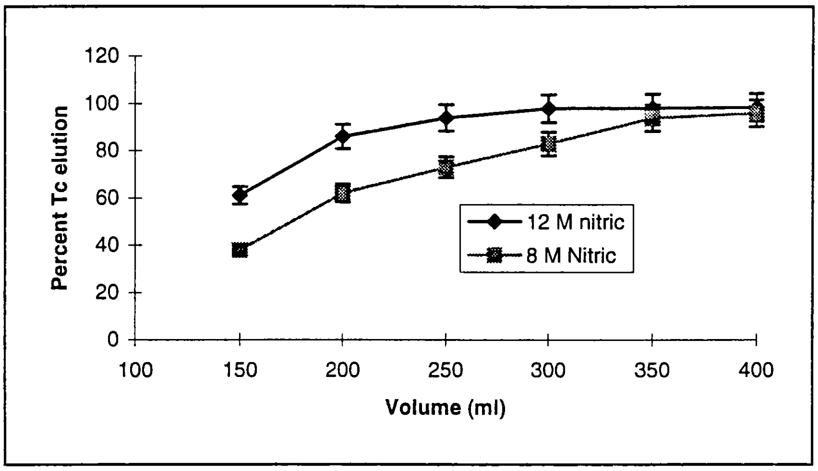


Figure 2. 10 Elution of technetium - Impact of 8M and 12M nitric acid.

Summary of the optimised Anion-exchange method for seawater.

Technetium in seawater is thought to exist in the heptavalent form, as pertechnetate (TcO_4^-). The seawater was filtered using 0.45 μm pore size cellulose nitrate membrane filters. The filtered seawater was spiked with yield tracer (^{99m}Tc and ^{106}Ru) and mixed well before passing through an anion - exchange resin column of size 21 cm length and 24 mm diameter filled with 32 ml of Dowex 1X8, 50-100 mesh, chloride form resin (Figure 2.8). The flow rate was adjusted to 25-30 ml min.$^{-1}$. After anion-exchange, the resin column was washed with 500 ml of deionised water and 500 ml of 0.1M HNO_3. The technetium was eluted using 12M HNO_3 (250 ml), and then carefully evaporated to reduce the acidity and volume. The recoveries of technetium and ruthenium during the anion-exchange processes are given in Table 2.5.

Tc Recovery	Ru Recovery
91.00±0.74	12±2.60

Table 2. 5 Final recoveries of Tc and Ru from anion-exchange method.

At the end of the anion-exchange process, about 90% of the ruthenium was removed while only 10% of the Tc was lost.

Biota samples:

Pre-treatment of biota samples (e.g., seaweed).

Difficult matrices are a common problem in separating trace amounts of radionuclides from biota samples. The most difficult part of technetium analysis is achieving complete sample ashing. The high volatility of pertechnetic acid usually prevents the use of vigorous conditions. Two main methods are mentioned in the literature i.e., dry ashing and wet digestion. In the dry ashing procedures, oxidation is accomplished by heating the sample to a relatively high temperature, usually between 400°C and 700°C, when atmospheric oxygen serves as the oxidising agent. In wet digestion procedures, the temperature is much lower, aqueous conditions are maintained throughout and the oxidation is carried out by oxidising agents in the solution.

Seaweed matrices are usually tackled using oxidising agents. Nitric acid has been universally used in both dry and wet procedures. In wet oxidation, it has been used in combination with H_2SO_4 to avoid any great loss of technetium during digestion processes. However, the hazards associated with the use of concentrated acids in wet digestion procedures result in the poor destruction of organic material. Riley and Siddiqui (1982) have used concentrated nitric acid to leach technetium from seaweed under reflux conditions. Hurtgen et al. (1988) used 9M HNO_3 under reflux conditions, but found that great care must be taken to get complete leaching of technetium from the samples.

In the dry ashing method of destruction, samples are first dried (110°C), charred (200-300°C) and ashed (450-700°C). For example, in the procedure described by Koide and Goldberg (1985) the algae samples were dried, charred and ashed in nickel crucibles, then fused with Na_2O_2 and melted at 550-600°C. The melts were dissolved in H_2O and HCl. Rioseco (1987) dissolved ashed samples in 5-10% HCl while Holm et al. (1984) used 3M H_2SO_4. Calcination was also used for analysing cellulose filter paper (to find air Tc concentrations) and floc (formed by Tc coagulation and precipitation with $Al_2(SO_4)_3$) samples (Garcia-Leon et al., 1984). In order to minimise Tc loss during ashing, samples have been treated with ammonia prior to ashing (Walker et al., 1980; Patti et al., 1981; Holm et al., 1984; Harvey et al., 1991a). Other workers selected the temperature carefully, not exceeding 450°C for ashing (Matsuoka et al., 1990; Harvey et al., 1991a). Recent methods, however, have combined ammonia and calcination treatments with ashing procedures (Hagan, 1994).

Most of the developmental work on the pre-concentration of biota samples was carried out on an homogenised bulk seaweed sample.

Optimisation - Ash procedures.

The temperatures selected for testing were 450, 550, 650, 750, 850 and 950°C using a muffle furnace. About 5g of dried seaweed powder was used for each sample. Duplicate samples were run at all the temperatures. One set was treated with ammonia. Treatment with ammonia prior to ashing is believed to reduce volatilisation of Tc by blocking the sites available for the formation of the highly volatile pertechnetic acid (Foti et al., 1972).

All the samples were spiked with technetium-99m tracer (which was gently evaporated to dryness) and placed in the muffle furnace. The temperature was increased each hour at 50°C increments up to the desired temperatures where it was left for 6 hours. After a cool-down period of 8 hours, the ashed samples were taken out and 25ml 8M nitric acid added. Approximately 5 ml of H_2O_2 were added and refluxed over a warm (~60°C) hot plate for 2-3 hours to ensure complete destruction of organic matter. The resultant solution was filtered (most of the time completely dissolved) through a Whatman No.42 filter. The final recoveries at different temperatures are shown in Figure 2.11. It is clear from the results that higher than 650°C ashing temperature, technetium loss would be inevitable irrespective of sample treatment with ammonia or not. Below this temperature, treatment with ammonia made very little difference. These samples were then processed for ICP-MS analysis. The technetium-99 concentrations obtained are depicted in Figure 2.12, along with the tracer yields obtained during ashing.

At higher temperatures (e.g., 850°C and above), technetium losses during ashing have increased the error in the calculated technetium concentrations. At lower temperatures (450 - 550°C) there was some indication of incomplete ashing resulting in low results. For this study, therefore, an ashing temperature of 700°C was selected.

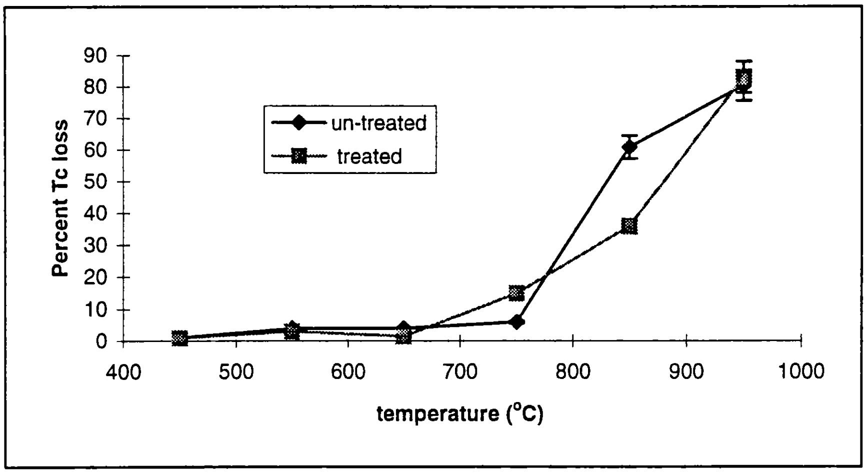


Figure 2. 11 Effect of ammonia treatment during ashing on technetium recovery.

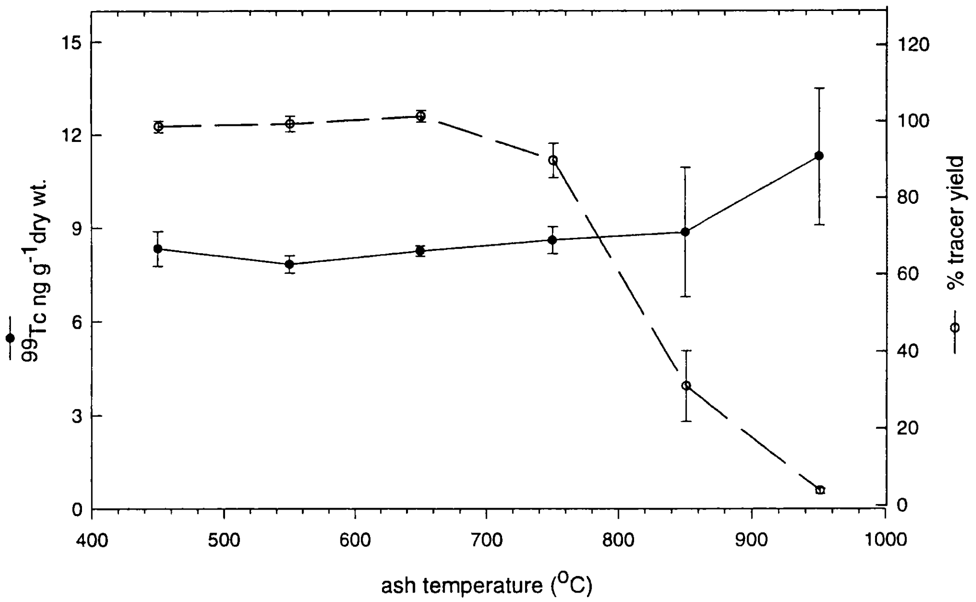


Figure 2. 12 Effect of ashing temperature on both recovery and chemical yield.

Sediments:

For the present study, the ashing procedure optimised for the biota samples was found to suit sediment samples also. Developmental work on the subsequent leaching procedure was, however, necessary.

About 20 g of dried sediment was spiked with a yield tracer (^{95m}Tc) and ashed. The ashed sediment samples were then taken out after a cool down period, transferred to 250 ml glass beaker and treated with 8 M HNO_3. About 50 ml of 8M nitric acid were used and 5 ml of H_2O_2 (30% v/v) were added to oxidise any technetium (IV) formed during ashing. The samples were refluxed over a hot plate. After 3 hours of refluxing, the samples were cooled and filtered through a Whatman filter paper (No.42) to remove the debris. The filtrate was collected and processed further to produce a sample suitable for ICP-MS.

The same samples were spiked with a second yield tracer (^{99m}Tc) and processed and leached for a second time to check the efficiency of the extraction method. A third extraction was done again using ^{99m}Tc. The results obtained are presented in Table 2.6.

EXTRACTION	SAMPLE 1	SAMPLE 2
I	119.88±13.49	73.09±8.22
II	32.78±3.69	26.98±3.03
III	3.11±0.35	13.93±1.57

Table 2. 6 Technetium-99 extraction from sediment
(^{99}Tc Bq kg^{-1} dry wt.) - Experiment.

From this above experiment, it is clear that a more vigorous extraction is needed to get complete technetium recovery in the first extraction step itself. To this end, 4 samples of sediment (50g) were leached under various conditions.

Sample A was placed in a 250 ml beaker and treated with 100 ml of 8M HNO_3 and 10 ml H_2O_2 (30% V/V). This was kept for 24 hour unstirred and heated intermittently. Sample B was placed in a 1000 ml glass beaker and treated with 100 ml 8M nitric acid and 10 ml H_2O_2, but subjected to continuous stirring on a hot plate at 45°C for 48 hours. Sample C was placed in a large crystallisation dish, providing more surface area for the sample to be stirred, with the same treatment as for Sample B. Sample D was placed in a 250 ml beaker, as Sample A, but kept for 48 hours before analysis.

All the above samples, A-D were processed and analysed for ^{99}Tc. The results obtained are given below in Table 2.7. Maximum technetium concentrations were obtained from Samples B & D which were leached for 48 hours. Stirring during leaching did not seem to have any major influence as Sample D (without continuous stirring) showed the highest ^{99}Tc concentration.

SAMPLE A	SAMPLE B	SAMPLE C	SAMPLE D
9.64 ±1.08	13.17± 1.48	10.32± 1.16	16.37±1.84

Table 2. 7 Technetium-99 extraction from sediment (^{99}Tc Bq kg^{-1} dry wt.) - Single leaching.

The results from Table 2.7 do show that different leaching procedures do produce relatively large differences in the final results obtained. Thus, it is important to use the same procedure throughout the study in order to produce comparable results. The procedure used, therefore, in this study was to place 50g of ashed sediment in a 1 litre beaker, add 100 ml 8M HNO_3 and 10 ml H_2O_2, and gently heat at 45°C for 48 hours.

2.2.3.3 Purification.

Ruthenium-99, with a natural abundance of 12.7% presents an isobaric interference in the determination of ^{99}Tc by ICP-MS. Thus samples containing ruthenium-99 must be purified before technetium-99 can be measured. As discussed previously, for seawater samples, simple resin washing with dilute nitric acid provides a limited amount of ruthenium decontamination. However, even for seawater samples, due to the high natural abundance of stable ruthenium further purification is necessary. The various decontamination procedures available are discussed along with the methods used in the present study.

Methods like selective precipitation, solvent extraction, ion-exchange etc., have been widely used to remove Tc from various contaminants. Rucker & Mullin (1980) removed uranium and its daughters from technetium by a simple hydroxide precipitation method. To remove most likely contaminants, Ballestra et al. (1987) combined iron hydroxide precipitation with a calcium carbonate precipitation step.

^{106}Ru, in environmental samples, provides the greatest interference in the beta counting of technetium-99. Using a ruthenium carrier, precipitation provides decontamination factors for ruthenium of up to 10^5 (Robb et al., 1985; Chen et al., 1990). Evaporation after precipitation has also been used for Ru decontamination (Chen et al., 1990). Due to unavoidable Tc losses encountered with precipitation and evaporation methods, selective extraction of technetium by organic solvents (e.g., cyclohexanone) leaving ruthenium in the aqueous phase was found to provide a better recovery of technetium with complete removal of ruthenium (Anderson, 1980; Anderson & Walker, 1980; Chen et al., 1989 & 1990; Morita et al., 1991). To achieve good decontamination from ruthenium, a new chromatographic resin (TEVA Spec®, EIChroM Industries, USA) has also been successfully used for technetium extraction (Sullivan et al., 1991; Davis et al., 1993; Beals, 1995).

Initial method development in the present study focused on a solvent extraction method (cyclohexanone and carbon tetrachloride extraction) for Ru decontamination. An alternative and successful method using TEVA Spec resin was later developed and optimised for a wide range of sample types. The experimental procedures used for these two methods are discussed in the following sections.

a) Solvent Extraction technique.

Solvent extraction is a partitioning process based on the selective distribution of substances in two immiscible phases, normally organic and aqueous. The liquid-liquid extraction or solvent extraction can be achieved either by extraction of the element to be separated into the organic phase or by extraction of the interfering elements leaving the elements to be separated in the aqueous phase. In the present method, using cyclohexanone, technetium is separated from ruthenium. Cyclohexanone has a low solubility in aqueous media which provides good phase separation and low volume changes during extraction (Boyd & Larson, 1960). Furthermore, it selectively extracts heptavalent technetium leaving ruthenium in the aqueous phase. Subsequently technetium was back-extracted from the organic into the aqueous phase by adding a non-polar organic diluent (CCl_4) plus H_2O, to the cyclohexanone (Foti et al., 1972). The extraction procedure used in the present study is given below, but was only adapted for the processing of seawater samples.

The nitric acid containing technetium (eluted from anion-exchange resin) was evaporated to near dryness to reduce the volume of acid as well as its nitrate levels, and re-dissolved in 1M HNO_3. The sample was then treated with 30%(v/v) H_2O_2 (2 ml for 25 ml of sample) before extraction of heptavalent Tc with cyclohexanone (3x15 ml). Ru was retained within aqueous phase. To enhance the oxidation/reduction process the sample was kept for at least 3 hr with occasional shaking before extraction. Subsequently, technetium was back-extracted into the aqueous phase using 10 ml deionised water plus 20 ml of CCl_4. This process was repeated 2 more times to ensure complete recovery of technetium.

The recovery of technetium and separation from ruthenium was essentially complete (Tables 2.8 & 2.9).

S. NO.	SOLVENT VOLUME	%TC RECOVERY	%RU RECOVERY
1	15 ml	74.9 ±2.0	<2±1
2	15 ml	24.4 ±1.2	<1±1
3	15 ml	5.9 ±0.6	<1±1
Total	45 ml	105.2 ±3.9	<4±3

Table 2. 8 Selective extraction of technetium using cyclohexanone.

S. NO.	CARBON TETRACHLORIDE + WATER	%RECOVERY OF TC
1	20+10=30 ml	48.3 ±1.6
2	20+10=30 ml	48.4 ±1.6
3	20+10=30 ml	3.0 ±0.5
Total	60+30=90 ml	99.8 ±3.7

Table 2. 9 Back-extraction of Tc into aqueous phase using $CCl_4 + H_2O$.

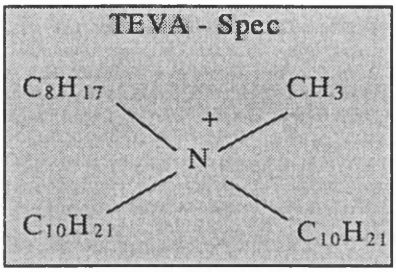
Although, solvent extraction was found to successfully remove technetium from ruthenium, use of organic solvents in regular analysis presents health hazards, and thus an alternative method (extraction chromatography) was investigated.

b) Extraction Chromatography - TEVA Spec® Extraction Technique.

Extraction chromatography (EC) is the separation technique in which an organic non-polar extractant is retained on an inert support (e.g., organic polymer etc.,) while a polar mobile phase is used as the eluting agent. EC was introduced by Carrit (1953), who used dithizone in carbon tetrachloride solution supported by granular cellulose acetate for the isolation of heavy metals from aqueous solutions. EC has several advantages over liquid-liquid extraction (solvent extraction) as well as other types of chromatographic methods. It is more selective than those using the most efficient ion-exchange procedures. The apparatus is very simple, only a small amount of extractant is needed and one column can be used several times. Thus EC is a very efficient method for the separation of chemically similar elements. In the present study, a new chromatographic extraction technique using EIChroM Industries' (USA) TEVA Spec resin was selected for the selective extraction of technetium over ruthenium from environmental samples.

TEVA Spec® resin.

The name TEVA itself denotes the purpose of the resin (i.e., for tetravalent actinides separations). The TEVA Spec chromatographic resin is commercially supplied by EIChroM Industries, Inc., Darien, IL. The resin has been developed at Argonne National Laboratory by Horowitz and Dietz. The resin has a high specificity, is suitable for room temperature operation, a high gravity flow, column compatibility for tandem arrangements and produces little waste at the end of procedures. The structure of the extractant present in TEVA Spec is:



TEVA Spec is coated with an aliphatic quaternary ammonium salt that enables separation of actinides (U, Th, Pu, Am, Np) from technetium (VII) in aqueous nitric acid solutions. The resin, manufactured as TEVA Spec, has 3 areas of application; 1) separation of tetravalent actinides, 2) technetium separation and 3) actinide/lanthanide separations.

As seen in Figure 2.13, TEVA Spec chromatographic extraction resin has a very high distribution coefficient (D) for retention of technetium at low acid concentrations. Thus, it was decided to investigate the potential of the resin for the separation of Tc from Ru.

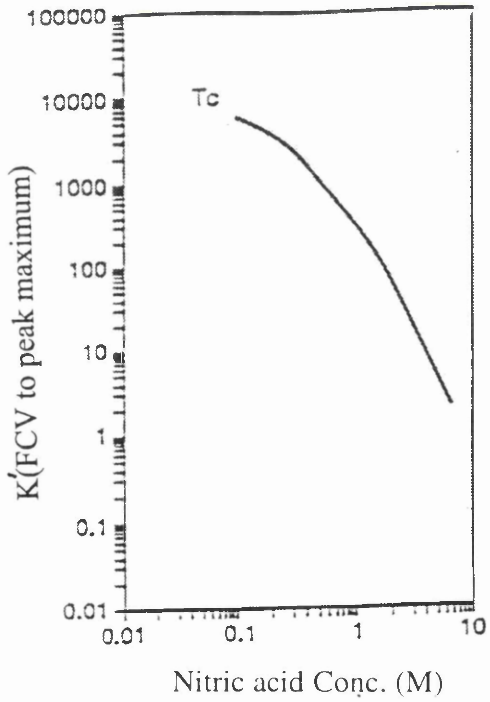


Figure 2. 13 Acid dependency of TEVA Spec resin (Beals, 1995).

Although TEVA Spec has been successfully used for this purpose by previous workers (Sullivan et al., 1991; Beals, 1995), this study was necessary to optimise resin use for our present purposes.

Preparation of TEVA Spec resin column.

TEVA Spec resin is commercially available in pre packed columns of 25 and 50 ml volume. To minimise the cost of the analytical method, small glass columns were produced indigenously and optimised. The glass column used in the experiment is shown in Figure 2.14. The bottom of the columns were plugged with fine glass wool for holding the resin. The top of the resin was also plugged to avoid any upward movement of the resin during acid rinsing procedures.

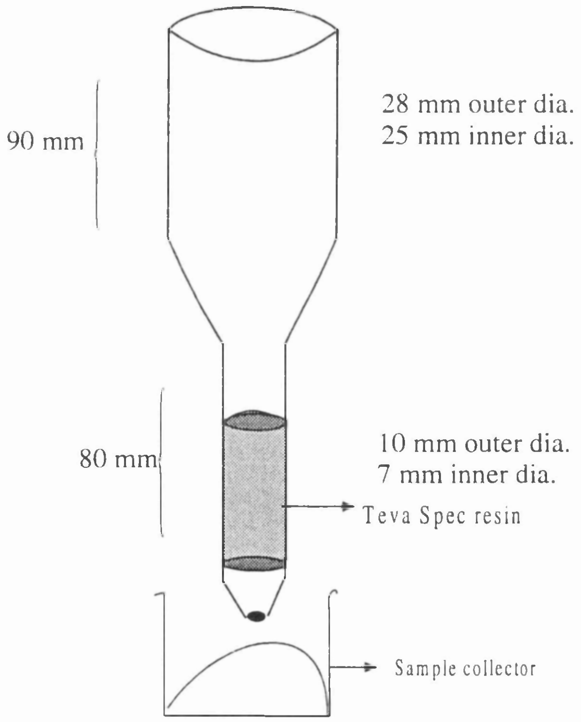


Figure 2. 14 Schematic diagram of glass column used in TEVA Spec extraction.

Column holders were used to keep the columns straight at all the time, and care always taken to avoid columns drying out.

Uptake of technetium.

Several experiments were set up to test the efficiency of Tc/Ru separation under batch extraction conditions, as recommended by Beals (1995). TEVA Spec® SPS (50-100 μ) resin (dry powder form) was used. To suit the present analytical method 150 ml was taken as the standard sample volume, and spiked with technetium-99m and ruthenium-106. The resins were placed in to sample beakers and stirred. The speed of the rod was kept to a minimum to avoid grinding of resins. After stirring, the resins were carefully collected by passing the stirred solution into the glass column made for this specific purpose.

The first experiment was performed to test the impact of sample molarity on technetium and ruthenium uptake. For this, a range (0.1 - 10M) of nitric acid molar solutions were tested. The uptake of technetium and ruthenium was calculated after 3 hours stirring. The results are presented in Figure 2.15.

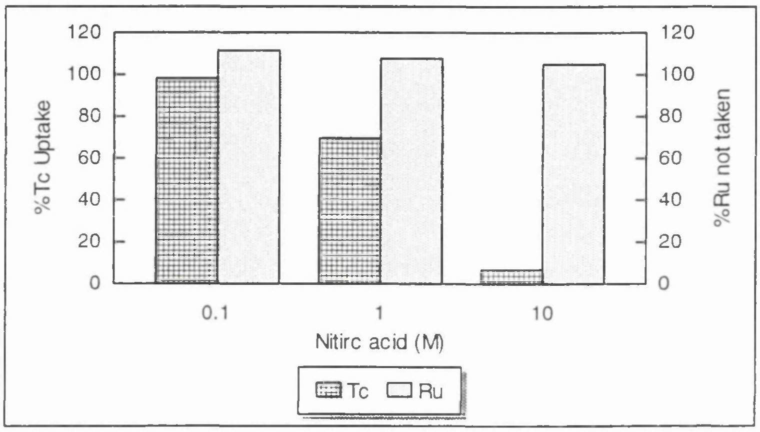


Figure 2. 15 Impact of sample molarity on technetium and ruthenium uptake.

In general, ruthenium was not taken-up by TEVA Spec resin at any of these molarities. In contrast, technetium was taken-up by the resin at all concentrations with a very high affinity at 0.1 M nitric acid. Tc uptake was reduced to 70% at 1 M, with an order of magnitude reduction at 10 M nitric acid. Thus, 0.1 M nitric acid was chosen as the most suitable medium.

In the next experiment, the minimum amount of resin required for a sample was investigated. Three sizes of TEVA Spec resin were tested (0.1, 0.3 and 0.5 g). After 3 hours stirring, the Tc and Ru uptake were both calculated and the results are presented in Figure 2.16.

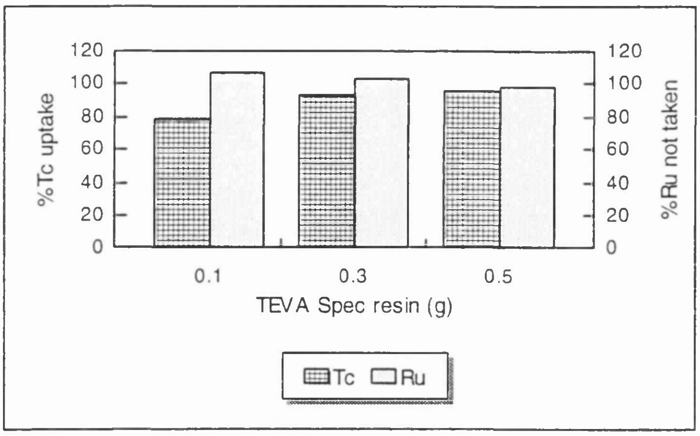


Figure 2. 16 Impact of resin volume on technetium and ruthenium uptake.

Technetium uptake was found to increase with resin size, however, the uptake was reasonably good at all the resin volumes. Technetium uptake was 93% with 0.3g of resin, with no ruthenium uptake. To minimise the cost incurred in the sample analysis, 0.3g of resin was taken as the standard amount of resin.

As a final step in the uptake experiment, various stirring times (3, 6 and 12 hours) were tested. The results are depicted in Figure 2.17.

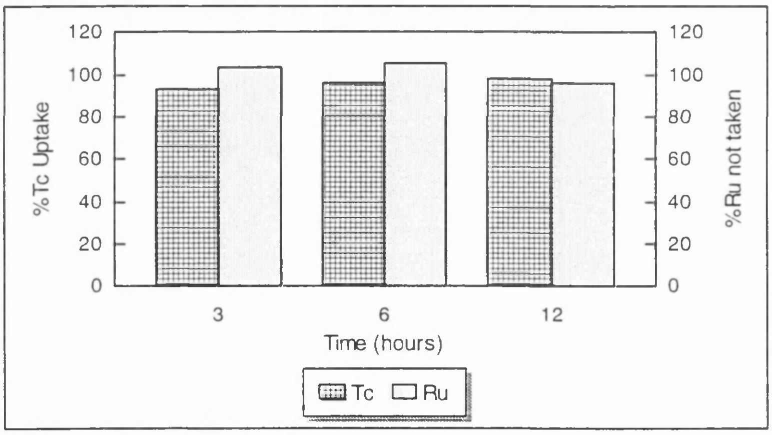


Figure 2. 17 Impact of stirring time on technetium and ruthenium uptake.

Technetium uptake did not vary much with stirring time, however, a little ruthenium was taken-up at 12 hours stirring time. The small difference observed between 3 and 6 hours was not considered to be significant and thus 3 hours was selected as the standard stirring time.

Cleaning of resin.

A broad range of nitric acid dilutions were tested for gross decontamination of the resin. 1, 5 and 10M HNO_3 solutions (20 ml) were used to rinse the column. The eluents were measured for technetium and ruthenium. No trace of ruthenium was found, however, 80-85% of Tc was removed from the column above 1 M HNO_3 (Figure 2.18). A small amount of Tc (<3%) was removed by the 1M HNO_3 rinse. Based on these results and earlier study (Beals, 1995), 1M HNO_3 (25ml) was selected for rinsing TEVA Spec resin column during regular sample preparation. The washing procedure removed any colour from the solution, which could cause suppression in ICP-MS analysis.

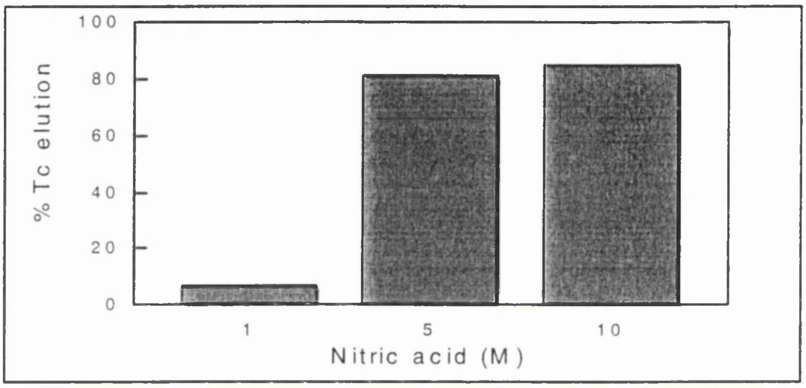


Figure 2. 18 Effect of nitric acid molarity on rinsing TEVA Spec resin.

Elution of technetium.

As observed in the experiment for technetium uptake, a high percentage of technetium was eluted from the resin by 10 M nitric acid. Use of a lower molarity in the final sample preparation was recommended for ICP-MS, however, in order to reduce the total dissolved solid level in the final solution (McCurdy, 1990). Thus 4M $HNO_3$was selected for elution. As elution was not complete with 20 ml of acid, a further experiment was carried out. The experimental conditions were similar to the one above, except that 4M nitric acid was used in all three columns but with 10ml, 20ml and 30ml volumes respectively. The percent recoveries for technetium are given in Figure 2.19.

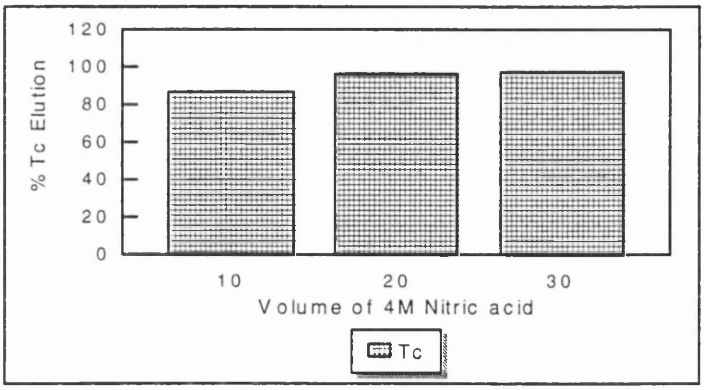


Figure 2. 19 Elution of technetium from TEVA Spec resin.

About 96 - 97% technetium was recovered using 20-30 ml of 4M nitric acid. Earlier workers (Beals, 1995) successfully used 30 ml of 4M nitric acid for technetium elution from the TEVA Spec resin. 30 ml of 4M nitric acid was selected for elution and used throughout the present study. The clear eluted sample was evaporated to near dryness and re-dissolved in 10 ml 2% nitric acid.

Summary.

It should be mentioned here that when real samples were analysed using the method described, traces of Ru were still found in the ICP-MS spectra (Figure 2.20). It should be noted that the peak at 101 is completely due to ^{101}Ru - natural abundance of 17.1%. Beals (1995) also found traces of ruthenium in some final solutions depending on the starting level of ruthenium in the sample. Hence it was necessary to add a further purification step. Based on the literature, it was decided to use $Fe(OH)_3$ scavenging before employing TEVA Spec resin extraction.

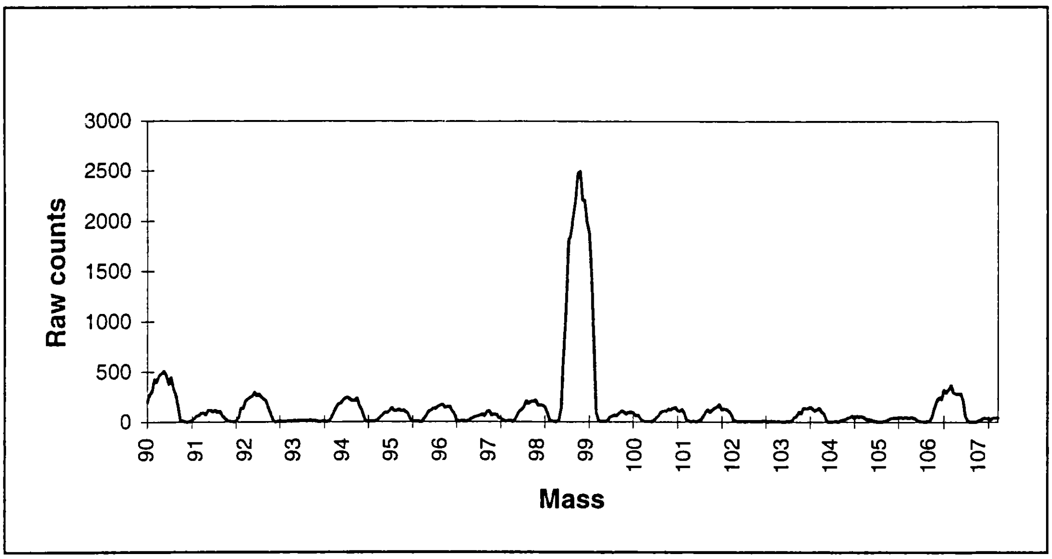


Figure 2. 20 ICP-MS spectrum showing ruthenium at mass 101(without NaOH precipitation).

Technetium pre-concentrated from environmental samples (seawater, soil/sediment and biota samples) in nitric acid was treated with 10M NaOH to produce a $Fe(OH)_3$ precipitate. To enhance precipitation in seawater samples, the addition of 3 ml of Fe(III) chloride (15%) was necessary. Experimental results confirmed that up to 75% of the ruthenium was removed by precipitation The precipitate formed is removed by centrifuging (2500$_{RPM}$ for 6 minutes). Samples run through the precipitation method followed by TEVA Spec extraction, were consistently devoid of ruthenium (Figures 2.21-2.24). The precipitation method was found to remove up to 15% of the Tc, however, depending on the sample matrix (for sediments the Tc loss would be higher).

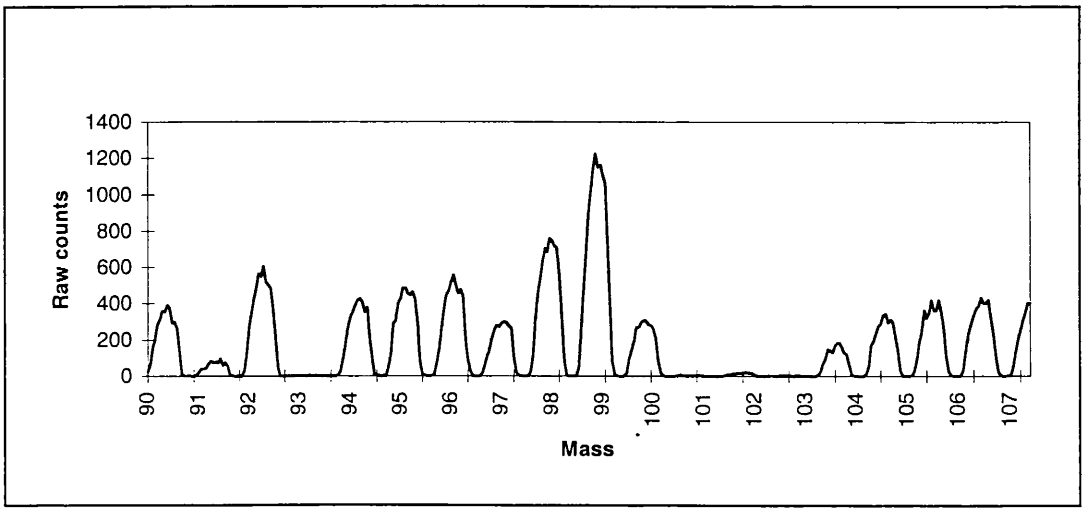


Figure 2. 21 ICP-MS spectrum of seawater sample after processing.

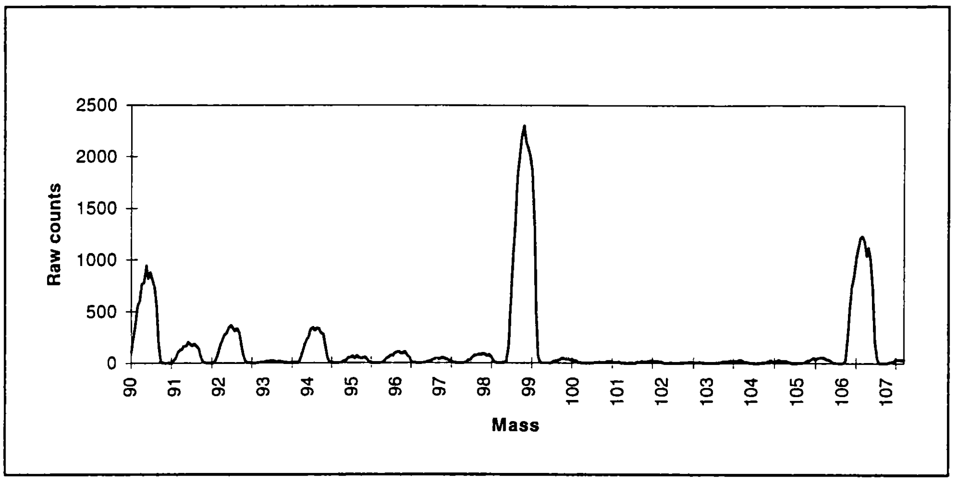


Figure 2. 22 ICP-MS spectrum of seaweed sample after processing.

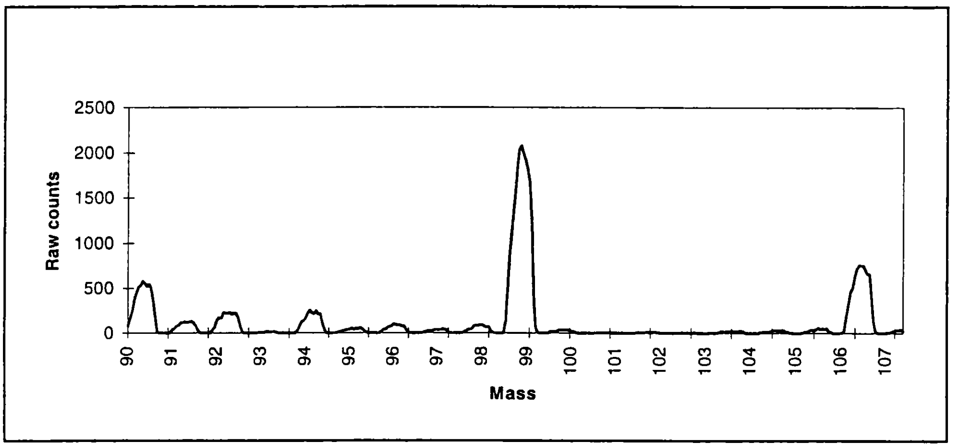


Figure 2. 23 ICP-MS spectrum of mussel sample after processing.

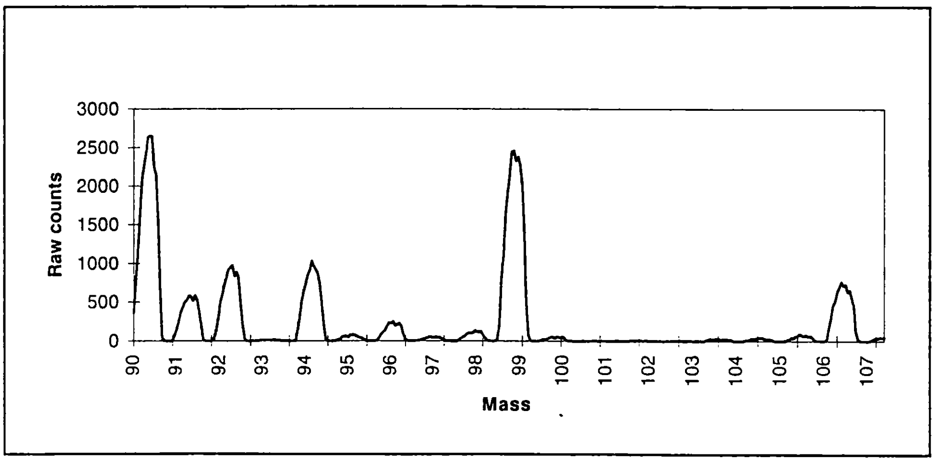


Figure 2. 24 ICP-MS spectrum of sediment sample after processing.

2.2.3.4 *ICP-MS Analysis.*

Operating conditions for measuring ^{99}Tc are shown in Table 2.10. The instrument installed at SURRC is a PlasmaQuad II STE (Fisons Instruments Elemental Analysis). For samples with very low levels of technetium, the acquire time per sample was increased to 60 s.

Instrument: PlasmaQuad II STE (Fisons Instruments Elemental Analysis)

Parameters	Value
RF power	1349 W
Reflected power	<5W
Nebuliser	DeGalan V-groove
Spray chamber	Scott-type double bypass (cooled to 12°C)
Sampling cone	Nickel, 1.0 mm orifice
Skimmer cone	Nickel, 0.75 mm orifice
Auxiliary gas flow	0.75 l/min.
Coolant gas flow	14.0 l/min.
Nebuliser flow rate	0.899 l/min.
Sampling depth	10 mm
Sample uptake rate	0.8 ml/min.
Acquisition parameters:	
Mass range	90 to 116 amu
Channel per amu	20
Dwell time	320 µsec.
Collector	Pulse counting
Acquire time	30 sec.
Acquire per sample	3

Table 2. 10 ICP-MS Operating Conditions.

Samples, including relevant processed blanks and an in house Standard Seaweed material (see later), were analysed in batches of up to 40. Calibration was carried out using a standard ^{99}Tc spike obtained from NPL laboratory and cross checked with an Amersham International ^{99}Tc standard. Both spikes were measured against each other and the linearity was found acceptable (Table 2.11). For routine sample analysis the NPL standard was used for calibration.

NPL ^{99}Tc Standard	Measured (ng g^{-1})	Calculated (ng g^{-1})	Ratio (M/C)
1	9.89	10.11	1.02
2	9.77	10.03	1.02
3	9.97	10.23	1.02

Table 2. 11 NPL Standard ^{99}Tc measured against Amersham Standard ^{99}Tc.

Contribution to the 99 peak from Ru can be corrected for by monitoring the counts in the peak at 101 (which is entirely due to Ru). In practice, however, no significant number of counts above background were ever detected at 101.

Other important parameters in the development of a reliable ICP-MS methodology are a) choice of internal standard and b) assessment of potential matrix effects. These 2 factors will now be considered before discussing c) reproducibility, d) detection limits and e) the results of intercalibration studies.

a) Internal Standard.

Internal correction can be used for several purposes: a) to monitor and correct for short term and long term fluctuations in signal, b) to calibrate for a second element and c) to correct for unspecified matrix effects. The effectiveness of an internal standard requires that it should behave similarly to the analyte in response.

To be an ideal internal standard, an element should not suffer from an isobaric overlap or polyatomic ion interference or generate them on the isotopes of interest. Two elements which are frequently used as internal standards, are In and Rh. Both lie in the central part of the mass range (^{115}In, ^{113}In and ^{103}Rh), occur at very low concentrations in many sample types, are almost 100% ionised (In = ~98.5% and Rh = ~93.8%), do not suffer from isobaric overlap and are either monoisotopic (Rh = 100%) or have one dominant isotope (^{115}In = 95.7%) (Jarvis et al., 1992). For the present study, ^{115}In was used as internal standard.

To justify the use of ^{115}In as internal standard, the relative signal change between the indium and technetium was measured along with several other elements. A known concentration (10 ng ml^{-1}) of ^{99}Tc was added to known concentrations (10 ng ml^{-1}) of ^{238}U, ^{209}Bi, ^{115}In, ^{59}Co and ^{9}Be. The ratios between technetium and all other elements were calculated and plotted against run numbers (Figure 2.25). The signal change between Tc and In (as represented by the ^{99}Tc/^{115}In ratio) was constant throughout the run while others showed large fluctuations.

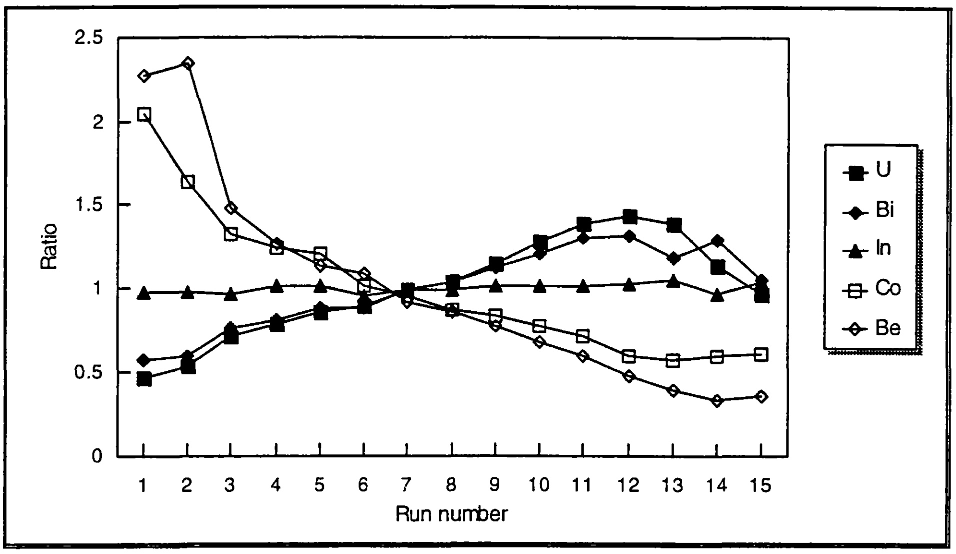


Figure 2. 25 Relative signal response of ICP-MS for ^{99}Tc at mass 99 with U, Bi, In, Co and Be.

b) Matrix effects.

Although the analytical procedure quantitatively removes Ru from the samples, interferences due to polyatomic or doubly charged species are still possible. Thus, experiments were run to assess the magnitude of i) general matrix effects and ii) specific inter-element interferences.

Standard Calibration method.

Serial dilutions of ^{99}Tc were routinely made to calibrate the instrument. In most cases, 2% nitric acid (the medium in which the final sample is in) was used as a base for dissolving the ^{99}Tc spike. To check on potential matrix effects, however, an experimental calibration curve was produced and compared with the normal calibration curve. The experimental calibration was carried out using the seaweed digest as a base solution for making serial dilutions of the ^{99}Tc standard.

Both 2% nitric acid and seaweed digest bases were run individually and the results are plotted in Figures 2.26 & 2.27 respectively.

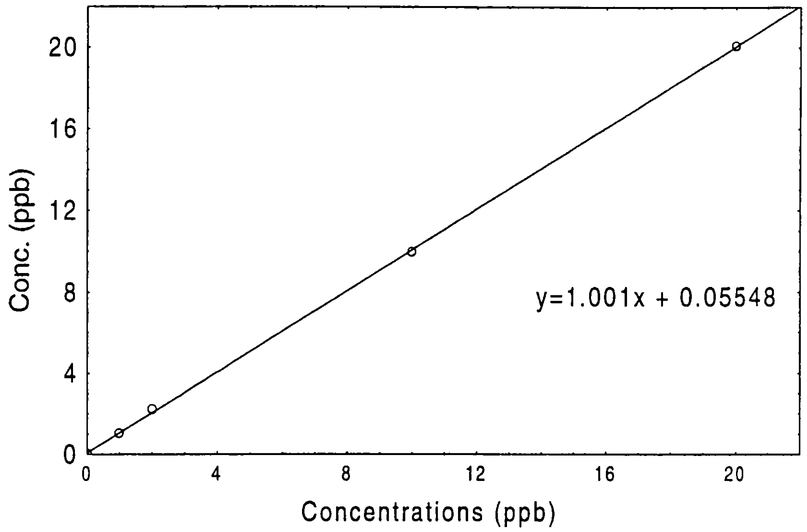


Figure 2. 26 Calibration using 2% Nitric acid.

There was no major deviation between the gradients of the two calibrations. From that it was confirmed that normal calibration using 2% nitric can be used without any correction for matrix effects.

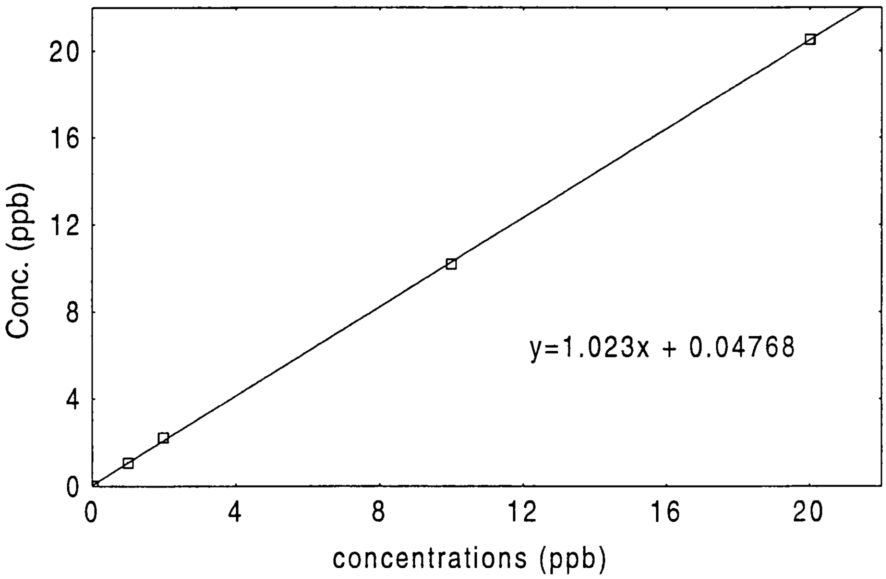


Figure 2. 27 Calibration using Seaweed digest.

Inter-element Interference.

Quadrupole mass spectrometers are compact and convenient to use with a high pressure source such as an ICP, but the resolution is insufficient to separate chemically different ions at the same nominal *m/z* value. Polyatomic ions are not overly abundant in the mass spectra observed from the ICP but can in some cases cause serious overlap interference with analyte ions. Different types of elements with potential interferences were selected for study (Table 2.12).

INTERFERING ELEMENTS	POSSIBLE INTERFERENCE
^{59}Co	$ArCo^+$
^{98}Mo	MoH^+
^{198}Pt	Pt^{2+}
^{62}Ni, ^{64}Ni	$NiCl^+$
^{64}Zn	$ZnCl^+$
^{198}Hg	Hg^{2+}

Table 2. 12 Possible inter-element interference at mass 99.

The possible elements which could cause an interference are Co, Ni, Hg, Mo, Zn and Pt. Solutions containing these elements at concentrations of 10 and 100 ng ml^{-1} were analysed. Environmental levels of these elements may be an order magnitude higher than 10 or 100 ng ml^{-1}, however, the same level can not be expected in our final processed samples as the chemistry followed in the present study is more specific for technetium. The calculated contributions at mass 99 are plotted against their respective elements and concentrations in Figure 2.28.

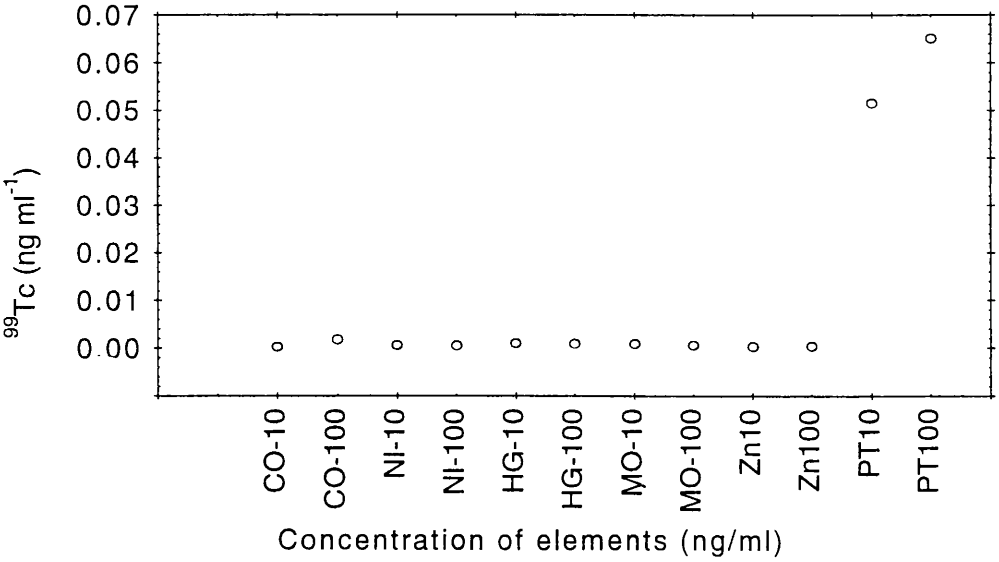


Figure 2. 28 Inter-element contributions at mass-99.

Measurable counts at mass 99 were only obtained from the Pt solutions. These solutions were in dilute HCl because Pt is not stable in dilute HNO_3. This matrix is known to adversely affect the ICP-MS background count rate, making it higher and more variable. Thus, the counts observed for Pt, may be an artefact of the unsuitable matrix as opposed to the formation of Pt^{2+} ions.

c) Reproducibility.

As the present study deals predominantly with seaweed samples, it was decided to take seaweed material as an in-house standard. In mid 1994, about 15-20 kg of fresh seaweed were collected from St. Bees Head. Samples were cleaned with running tap water. Any green or red sea weeds were removed carefully, and brown seaweed retained. The brown seaweed mostly comprise of the *Fucus* species. The selected brown seaweeds (~10 kg) were rinsed in de-ionised water and air dried. The air dried materials were placed in a preheated oven (~70°C) for 48 hours, and then put into a blender. The seaweed powder obtained from the blender was carefully sieved (~200-500 μm) and stored in a polythene bag. About 2 kg of powder were prepared and kept for regular analysis throughout the study period.

In each batch of ICP-MS samples, an In-house seaweed standard was prepared. The range of results obtained over the study period is shown in Figure 2.29. The standard deviation in-between runs was calculated as 11.5%.

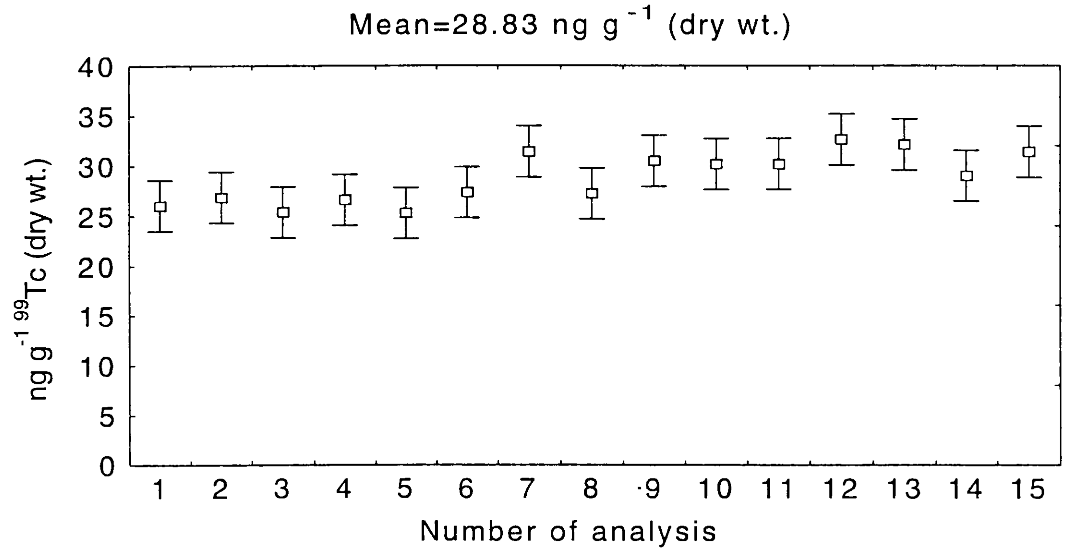


Figure 2. 29 In-house seaweed standard analysis during the present study.

d) Limit of Detection (LOD).

The limit of detection is defined as the mass of analyte giving an integrated ion signal equal to 3 sigma blank where σ blank is the standard deviation obtained for x repeats of a blank solution.

In ICP techniques, detection limits can be calculated using eleven determinations of the signal produced by a blank solution (Jarvis et al., 1992). In the present study, 2% HNO_3 blanks (12 numbers) were run and the signal produced at mass 99 is plotted (Figure 2.30). The limit of detection can be thus calculated as 2.016 pg ml^{-1} (3 times the mean standard deviation). For a 10g sample, this corresponded to 13 Bq kg^{-1}.

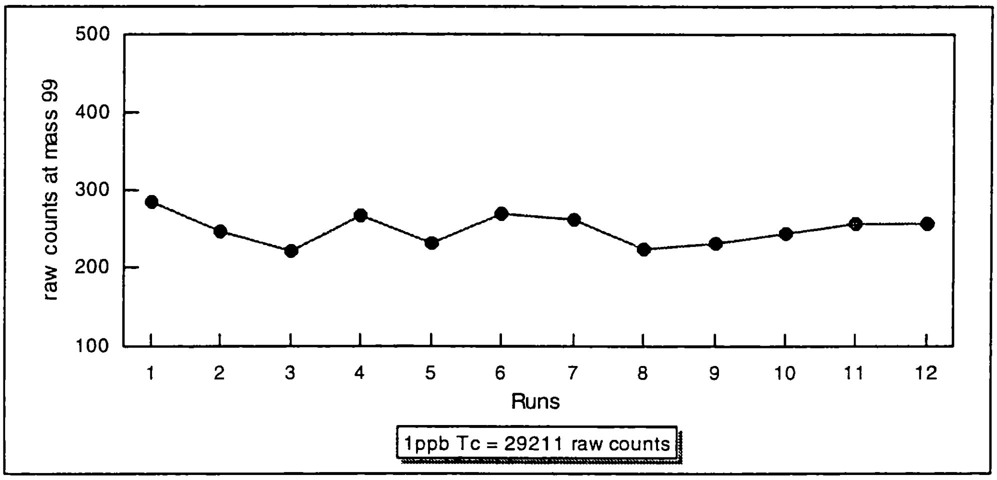


Figure 2. 30 Raw counts at mass 99 from 2% nitric acid blank runs.

e) Intercalibration studies.

Reference Material Analysis.

The analytical flow sheet for the determination of ^{99}Tc developed here is shown in Figure 2.31. The accuracy and precision of the method were studied by applying these techniques to the determination of ^{99}Tc in 'IAEA Reference material'. The International Atomic Energy Agency (IAEA) defines a material as 'Reference material' after completion of an inter comparison exercise. For technetium-99, IAEA released a Reference material, AG-B-1 (seaweed powder) during 1988 for an intercomparison exercise (Bates, 1988).

About 10g of AG-B-1 was processed using the analytical method developed. Due to non-availability of enough standard material, only one sample was prepared and analysed. The result is shown in Table (2.13).

CERTIFIED VALUE (mBq g^{-1} dry wt.)	PRESENT ANALYSIS (mBq g^{-1} dry wt.)
11.1 - 14.7	7.59±11.5%

Table 2. 13 IAEA intercomparison sample analysis.

The observed value is around 25% less than the minimum certified value. The variation could possibly be due to the very low level of ^{99}Tc present in the Reference material (AG-B-1). It is, in fact, below the detection limit of the current technique. Unfortunately, it was not possible to obtain enough of this material to make an accurate ^{99}Tc determination.

Informal Intercomparison Study.

In an attempt to validate the method, therefore, an intercalibration exercise was carried out with Westlakes Research Institute (WRI), who used a similar method for ^{99}Tc analysis. Good agreement between the 2 laboratories was obtained (Table 2.14).

Sample Number	SURRC	WRI
1	38.06	31.56
2	36.42	36.88
3	38.38	35.88
Mean ± 1σ	37.62±1.05	34.77±2.83

Table 2. 14 Intercomparison between SURRC & WRI (^{99}Tc ng g^{-1} dry wt.).

Repeat Analysis of seaweed.

The analytical method has been further checked by analysing seaweed samples previously analysed by Ishanullah (1991) at Scottish Universities Research & Reactor Centre. The values obtained using the present analytical method are very close to the previously measured values. The results obtained are presented in Table 2.15.

Seaweed taken from	Present study	Ishanullah (1991)
Sandyhills	1633±17	1780±90
Colwyn Bay	703±29	740±50
Ravenglass	9618±219	10180±530
Whitehaven harbour	2330±82	1980±60

Table 2. 15 Comparison of results of present study with previous study (^{99}Tc Bq kg^{-1} dry wt.)

In conclusion, due to the lack of a suitable standard reference materials it is not possible to completely validate the present method. Good agreement with data produced by 2 other groups has been obtained, although, in the long-term, participation in a wider inter-calibration exercise would be desirable.

2.2.3.5 Summary.

A simple and efficient analytical method for ^{99}Tc determination has been developed and optimised. Technetium from environmental samples (seawater, sediment and biota) is pre-concentrated first; from seawater by anion-exchange and from sediment and biota by using ashing and leaching methods. Iron hydroxide precipitation followed by the use of a new chromatographic resin (TEVA Spec®) provides adequate separation of Tc from Ru and other potential interferences. The sample is then presented to the ICP-MS in 2% HNO_3. A schematic diagram of the procedure is presented in Figure 2.31 and important parameters in the analytical method are given in Table 2.16. A detailed description of each step in the analytical method is given in Appendix I.

PARAMETERS	REMARKS
Chemical yield	45-70%
Decontamination Factor for Ru	10^5 - 10^6
Limit of Detection	2.01 pg ^{99}Tc ml^{-1} (1.28 mBq ml^{-1})

Table 2. 16 Analytical method - Important parameters.

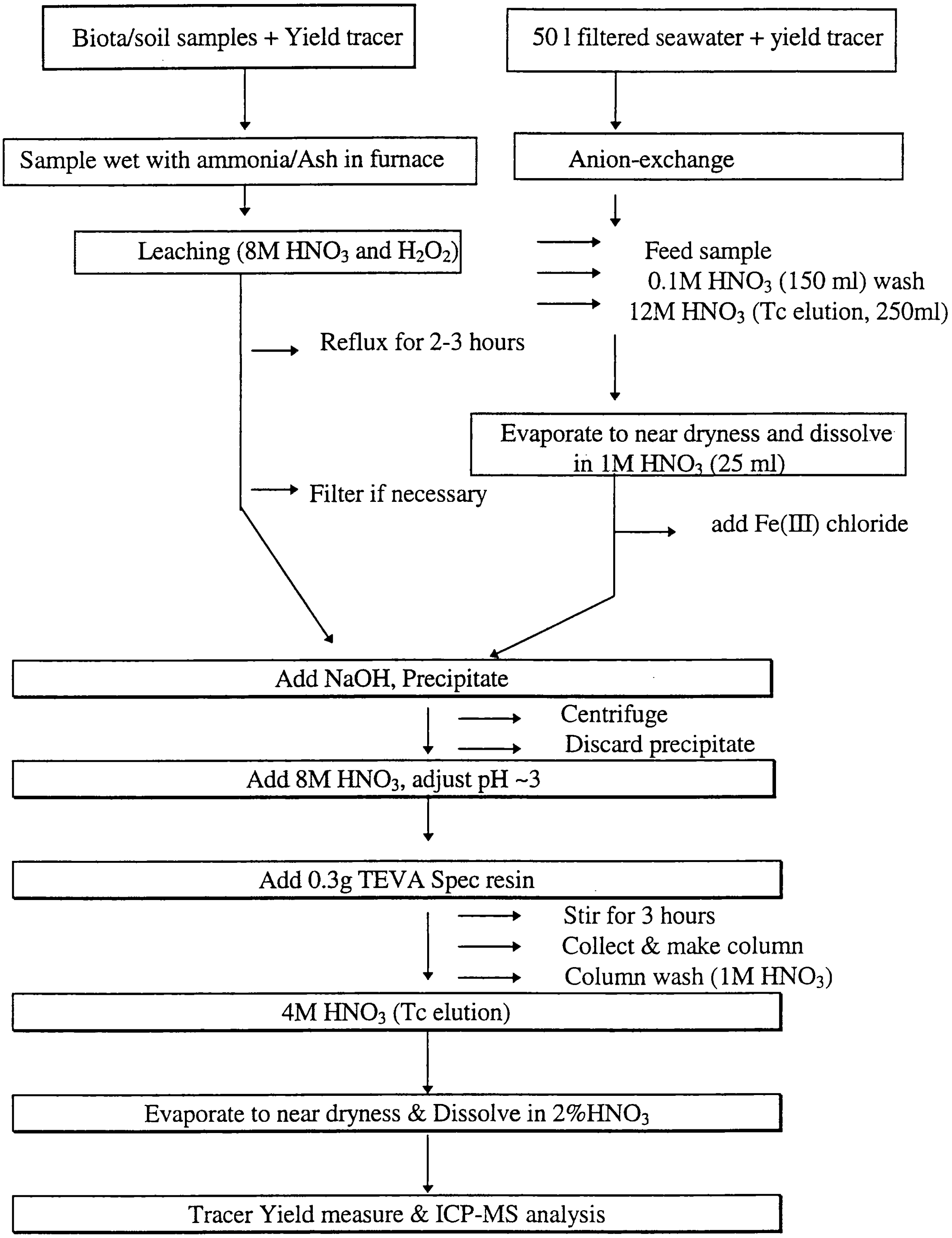


Figure 2. 31 Schematic diagram of analytical method.

2.3 LIQUID SCINTILLATION COUNTING - METHOD DEVELOPMENT.

The beta energy released from ^{99}Tc can be radiometrically measured by liquid scintillation counting. Although the present study principally involved the development of an analytical method based on ICP-MS, optimisation of the developed method for LSC was also investigated. Liquid scintillation counting would offer a cheaper mode of analysis provided the sample is devoid of any potential interference.

2.3.1 The LSC System.

The liquid scintillation process is shown in Figure 2.32. The basic objective of the technique is to arrange for beta particles to collide with solvent molecules. The energy resulting from the collisions excites the solvent molecules and is passed to other molecules until it is finally transferred to a solute molecule which converts the energy to visible light. The first step in this liquid scintillation process involves transfer of the energy from the beta decay process to aromatic solvent molecules. This results in an activated solvent molecule which almost quantitatively retains the energy from the beta decay. Since activated solvent molecules can not be detected easily, the energy must be transferred further. The second step in the process is to transfer the energy from the activated solvent molecule to organic scintillator molecules which are in solution with the radioactive sample and the solvent. A scintillator is a substance which emits a weak light flash, or scintillation, of short duration whenever energy is transferred. This scintillator molecule becomes activated to a higher energy state. This molecule then returns to the ground state and the excess energy is converted directly to flashes of light. The intensity of the light flashes is directly proportional (10 photons/keV) to the energy of the nuclear decay which created the flashes of light.

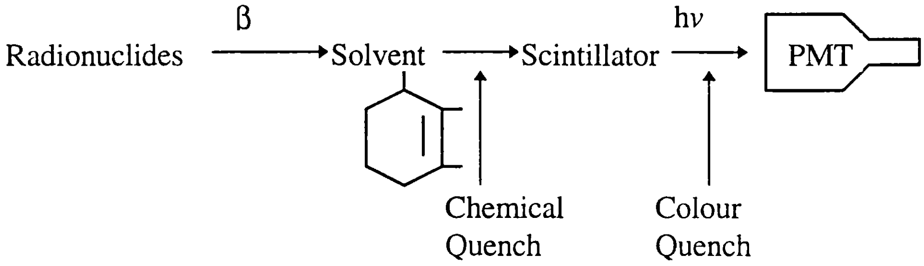


Figure 2. 32 Liquid Scintillation Process.

The intensity of the scintillation depends on the energy of the particle dissipated in the scintillator by the particle. Liquid scintillators are used for the efficient, routine measurement of beta emitters, particularly those of low energy. They are especially well suited for the measurement of large samples with high sensitivity. For this, the sample must be dissolved or at least uniformly dispersed in the scintillation liquid. A variety of liquid-scintillation systems are commercially available.

2.3.1.1 Scintillation Cocktails.

In the past, photomultiplier tubes were responsive only to certain wavelengths of light, hence, scintillation cocktails came into use. These cocktails are produced to replace primary and secondary scintillators. Although modern bialkali photomultiplier tubes respond to a wider range of wavelengths of light, the tradition of using two scintillators has been maintained as the cocktail has been found to be both efficient and convenient to use. Cook et al. (1990) found that the composition of a "scintillation cocktail" play an important role in the optical efficiency of modern instruments. For the present study, a cocktail called "Ultima Gold^{TM} LLT" supplied by Packard Co., USA, has been selected and optimised. The performance of Ultima Gold cocktail with various environmental samples was examined and documented by Thomson et al. (1994). It has the basic characteristics of an extremely low background, high detection efficiency and excellent sample acceptance.

2.3.1.2 The Detection System.

The detection system of most modern liquid scintillation spectrometers consists of photomultiplier tubes and a centrally mounted optimising reflector. The light from the scintillators can be converted into electrons by photosensitive devices known as "photomultiplier" tubes (PMTs, usually two). The block diagram of a typical LSC showing its different features is shown in Figure 2.33.

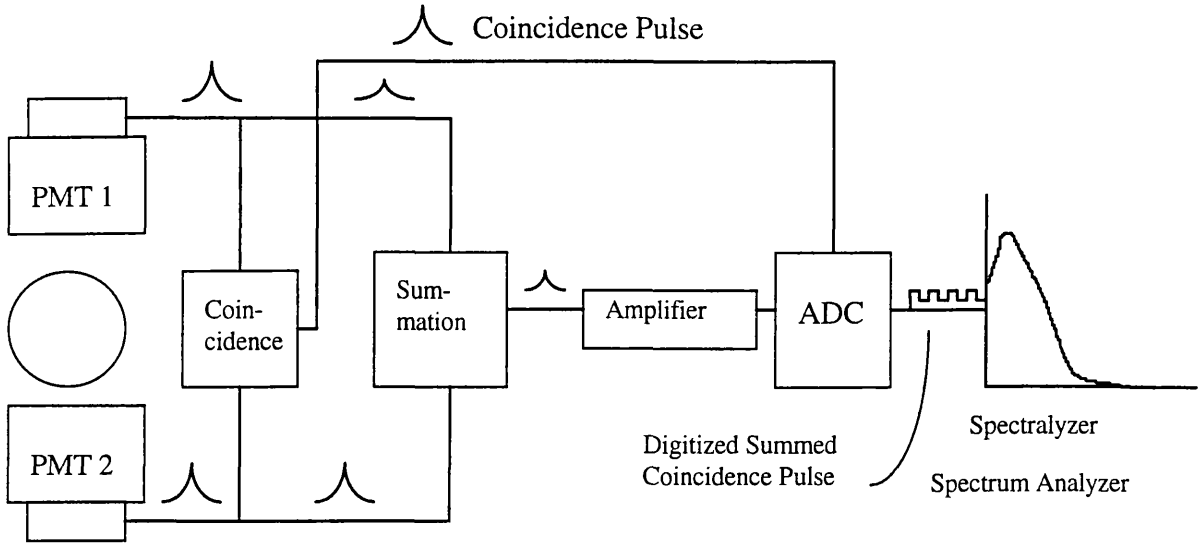


Figure 2. 33 Block diagram showing LS system.

A photosensitive material coated uniformly on the inner surface of the PMTs converts the absorbed photons of light into electrical energy by the release of photoelectrons which are negatively charged. These photoelectrons are attracted to a positive electrode within the PMT resulting in the production of more electrons. These secondary electrons are attracted to a second electrode where a similar process occurs.

The electrons are accelerated through a series of dynodes that produce between two and six electrons for each electron input. The overall multiplication may amount to a 10^5 fold increase over eleven stages, to form electrical pulses of sufficient strength to be detected by the counter electronics (Gibson & Lally, 1971; Willard et al., 1981).

PMTs are linear devices, therefore, the amplitude of the electrical pulse is directly proportional to the number of photons detected at the photocathode. By this means, the scintillation is detected and converted to an electrical pulse. By monitoring the occurrence of these electrical pulses in a given time period, an indication of the number of scintillations, hence, beta emissions, which are taking place in the sample is obtained. As PMTs are sensitive, the application of a voltage between the electrodes produces small noise pulses which contribute to the background of the system. The use of two PMTs and coincidence circuitry was introduced to reduce this component of background.

The introduction of logarithmic amplification eliminated the need for individual channel amplifiers etc., and by 1980, further advances resulted in counters with pulse height energy spectrum analysis facilities (Mullet-Channel Analysis), which allowed windowless counting, in conjunction with linear amplification. The pulse height energy distribution spectrum is collected at a fixed gain over an energy range, normally 0 - 2000 keV, allowing the interpretation of any portion of the spectrum simultaneous to sample counting.

In the present study, a Packard Tri-carb Model 2550 TR/LL LSA has been used. The latest generation of Packard Instrument Company liquid scintillation spectrometers employs a concept termed Time Resolved Liquid Scintillation Counting (TR-LSC) i.e. pulse shape / duration analysis.

2.3.1.3 Quench monitoring.

The counting efficiency of the solvent - solute system can be affected by both chemical and colour quenching. The beta energy itself may be absorbed before it can produce photons of light by chemical quenching while colour quenching occurs when the photons move through the medium and change the wavelength of the light reaching the PMTs, thus reducing the response. The resulting decrease in the number of photons produced per keV reaching the PMTs reduces the pulse amplitude, and results in a shift of the whole spectrum to lower energies.

The quench indicating parameter (QIP) is a feature of the Packard Tri-Carb LSC that utilises an externally placed gamma source (^{133}Ba) positioned near the scintillation sample to derive a quench value from the induced energy distribution produced by the interaction of ^{133}Ba gamma rays with the scintillation medium of the sample. In the Packard Liquid Scintillation Analyser, the QIP can range from zero (for a totally quenched sample) to 1000 (for unquenched sample).

SIS (Spectral index of Sample) is a second quench parameter. It is also an additional feature of Tri-Carb LSA. At a given level of quenching, each radionuclide has a definite mean pulse height distribution and hence a unique SIS value. The SIS of the sample (derived from the average energy) is the most sensitive quench indicating parameter. An attractive feature is that this index is count rate independent. It does not shift with increasing or decreasing activity.

In addition to SIS, another method often used in the Tri-Carb LSA to monitor the extent of quenching in each individual sample is the external standard technique which uses the movement of the external standard spectrum as an indicator of quenching. An external source of gamma radiation (e.g., 10 μCi of ^{226}Ra) can be placed adjacent to the sample vial. The electrons thus produced in the scintillation solution due to the Compton collision process, can be detected and used to produce an external standard spectrum. Analysis of this external standard spectrum produces an index which can be related to the measuring efficiency in the region of interest. This index is termed the SIE (Spectral Index of the External Standard).

The tSIE is used in the present study as the primary quench indicator, which denotes the transformed SIE.

2.3.2 Counting conditions.

A new feature in the 2550 series which reduces background count rates is burst counting circuitry, which can differentiate between the non quenchable component of background from quenchable events on the basis of the number (burst) of very small pulses (afterpulses) which follow prompt pulse events (Valenta, 1986). The non quenchable component of background has prompt pulse events which are accompanied by a number of these trailing afterpulses of much smaller amplitude (similar to single photoelectrons) while the prompt pulses of quenchable events (particularly the soft betas) have fewer or none. This difference in afterpulsing characteristics is the basis of the background reduction feature (van Cauter, 1986; Noakes et al., 1988). As an additional feature of the 2550 series, this burst delay can be varied from 75 to 800 nanoseconds (nsec). The ability to vary this delay has the potential to make this instrument much less cocktail dependent during pulse shape and duration analysis (Cook et al., 1992).

The samples were prepared using the analytical method developed for ICP-MS analysis in the present study. At the end of the chemical procedure, the samples were taken in to glass vials (15 ml capacity) with 2ml 2% nitric acid and 5 ml scintillation cocktail (Ultima Gold LLT™). Samples were counted for a minimum of 100 minutes and 450 nsec was selected as the burst delay time. To reduce background counts, a 10-87 keV counting window was selected for technetium-99 which decays with an average energy of 85 keV. Under these counting conditions for a spiked sample an efficiency of 69% (at tSIE of 350) was obtained with a background count rate of 2 counts per minute. All errors quoted are at the 1 σ level.

2.3.3 Quenching.

In order to investigate the effect of quenching on efficiency, varying amounts of quenching agents (2% HNO_3 and a mixture of nitromethane + benzene) were added to vials containing a known amount of ^{99}Tc activity. All samples were counted for 100 minutes. The activity (CPM) and the tSIE were measured. The results are presented in Table 2.17. The percent efficiency (E) was calculated for each sample and plotted against tSIE (Figure 2.34).

Initially as quenching increased (tSIE reduced from 447 to 341), there was a slight increase in efficiency. However, further quenching, by adding the nitromethane + benzene mixture (tSIE up to 217), ended with a reduction in efficiency as a greater number of counts fell below the low energy window (<10 keV). The variation in efficiency with tSIE, however, was small. In practice, no significant variation in tSIEs were observed within analytical runs in this work, although variations between runs were noticeable. Thus, the absolute efficiency for each run was determined by counting a known activity of ^{99}Tc under standard conditions.

Vol. of HNO_3 (ml)	Vol. of Nitromethane + Benzene mixture	Efficiency (%)	tSIE
0.5	0	70.6	447
0.7	0	72.1	429
0.9	0	71.9	415
1.0	0	72.3	406
1.1	0	71.7	404
1.3	0	72.6	384
1.5	0	72.5	371
0.5	0.8	73.6	361
0.7	0.8	74.5	341
0.9	0.8	73.5	314
1.0	0.8	73.9	310
1.1	0.8	72.6	291
1.3	0.8	70.5	237
1.5	0.8	68.9	217

Table 2. 17 Effect of quenching on ^{99}Tc counting efficiency (%) and tSIE.

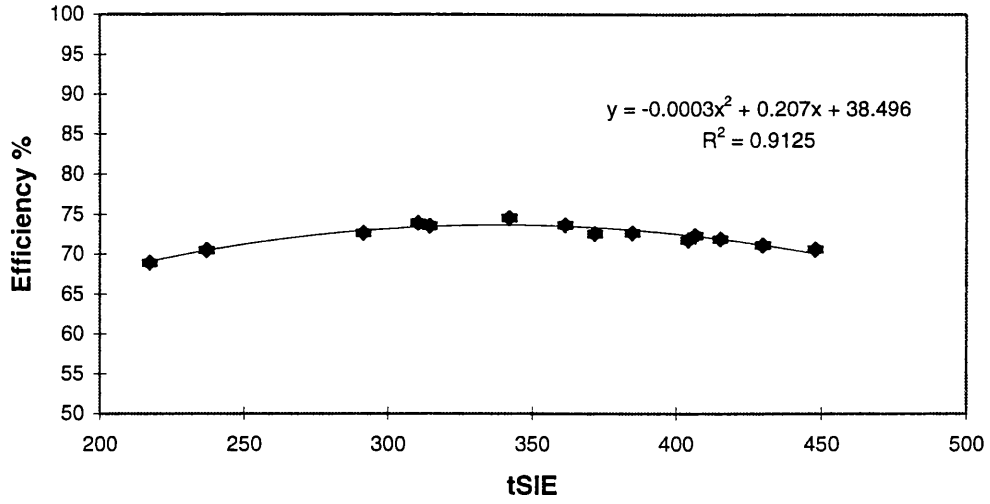


Figure 2. 34 ^{99}Tc Counting efficiency (%) versus tSIE - Quench curve.

2.3.4 ^{3}H effect.

The influence of tritium (^{3}H) on technetium-99 beta counting was tested. Four separate samples were counted: a blank, a ^{3}H spike, a ^{99}Tc spike, and a sample spiked with both ^{3}H and ^{99}Tc. The results for both open (0-2000 keV) and optimum (10-87 keV) windows are presented in Table 2.18. In the open window, ^{3}H interferes with ^{99}Tc counting. In the optimised window, however, there appears to be no significant interference. The count rates obtained for the blank and the ^{3}H spike are similar, as are the ^{99}Tc and the ^{3}H + ^{99}Tc sample. The spectra obtained from the experiment are shown in Figure 2.35 (open window) and Figure 2.36 (optimum window). The tritium peak is prominently seen in the lower region (0-10 keV) and thus can be avoided by selecting the optimum window for technetium counting.

Sample	CPM (0-2000 keV)	CPM (10-87 keV)
Blank	10±0.31	2±0.14
^{99}Tc	724±2.69	560±2.37
^{3}H	220±1.48	2±0.14
^{99}Tc+^{3}H	822±2.87	551±2.35

Table 2. 18 Tritium counting with technetium spike.

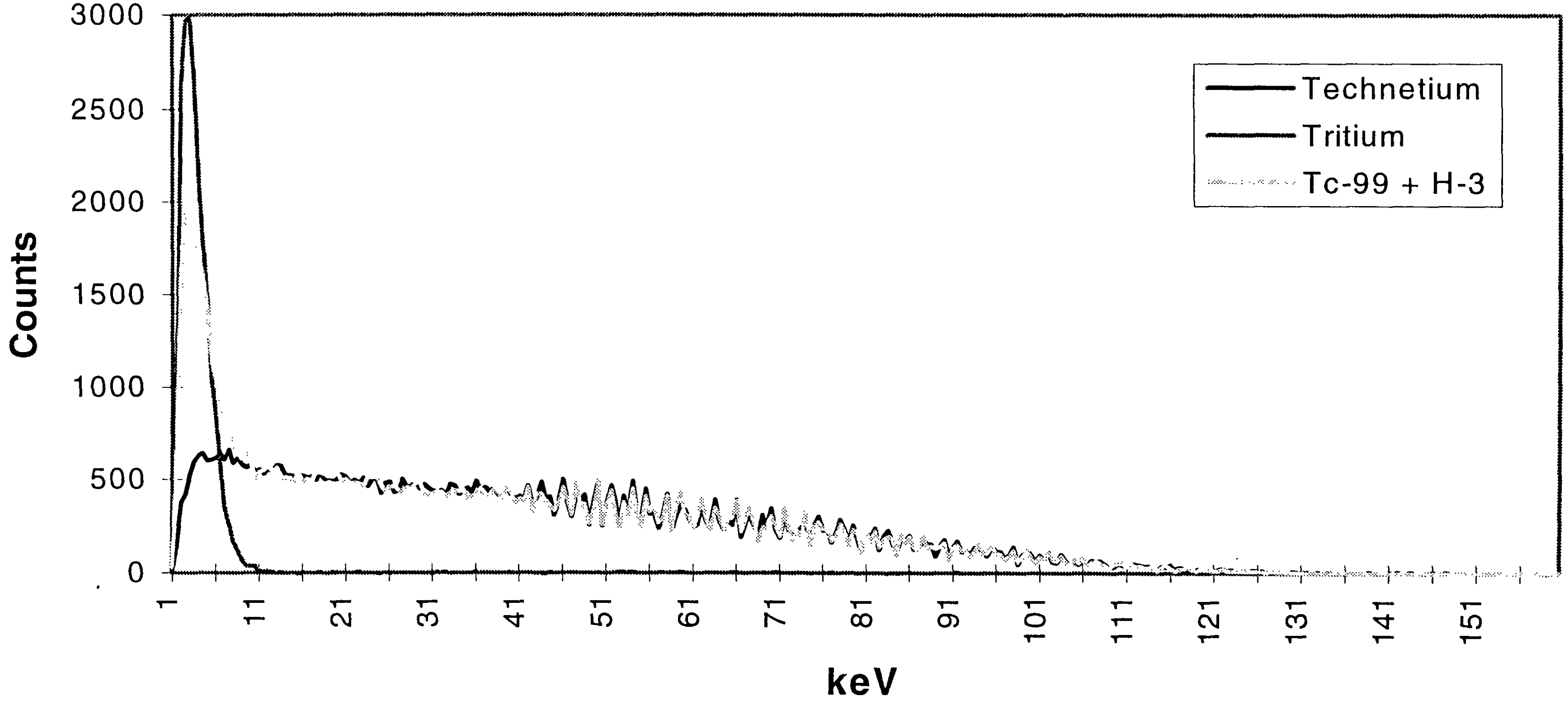


Figure 2. 35 Spectrum showing technetium and tritium counts with open window (0-160 keV).

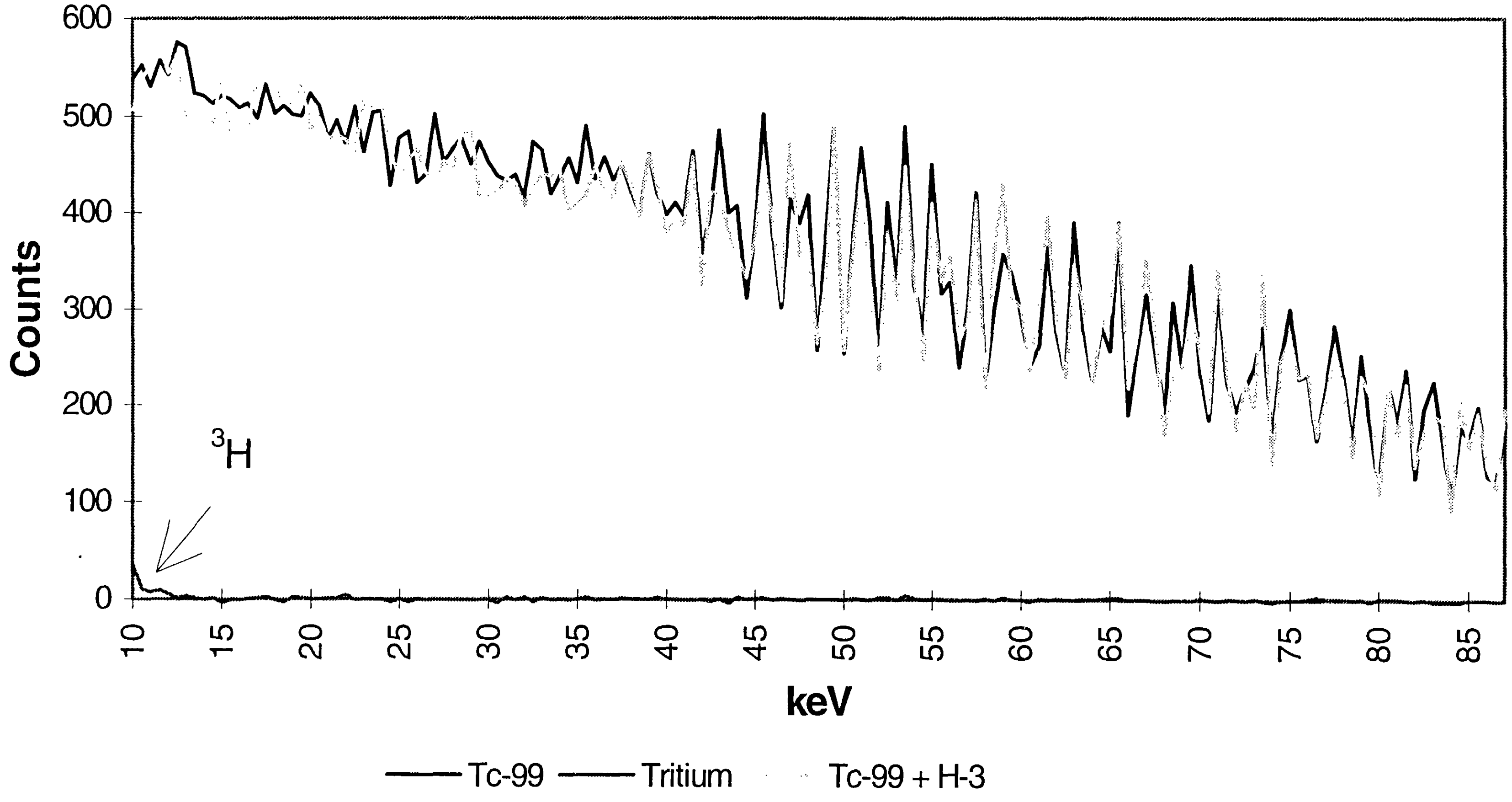


Figure 2. 36 Spectrum showing less tritium counts with optimum window (10-87 keV).

2.3.5 Dual counting of samples in LSC.

Generally the gamma ray from the yield tracer (^{99m}Tc or ^{95m}Tc) has been directly measured on a Ge(Li) detector to determine the chemical yield after the sample was processed. The processed sample is then measured for ^{99}Tc. LSC, however, can be used as a single instrument for technetium analysis thus obviating the need of gamma counting for yield calculations. Both yield tracers (^{95m}Tc and ^{99m}Tc) were tested. This involved counting the yield tracer by LSC first (for short time) and subsequent counting for technetium-99 (for longer time). From the first tracer count, the chemical yield can be determined. The total sample activity can then be calculated using the chemical yield.

2.3.5.1 Experiments using ^{95m}Tc as yield tracer in dual counting method.

To test the use of ^{95m}Tc as a yield tracer in LSC counting, serial dilutions of the tracer (20, 30, 40, 50 Bq) were measured by both Ge(Li) and LSC. The obtained count rates from both Ge(Li) and LSC are plotted against each other in Figure 2.37. At 95% confidence level counts from LSC showed linearity with counts from Ge(Li) counter.

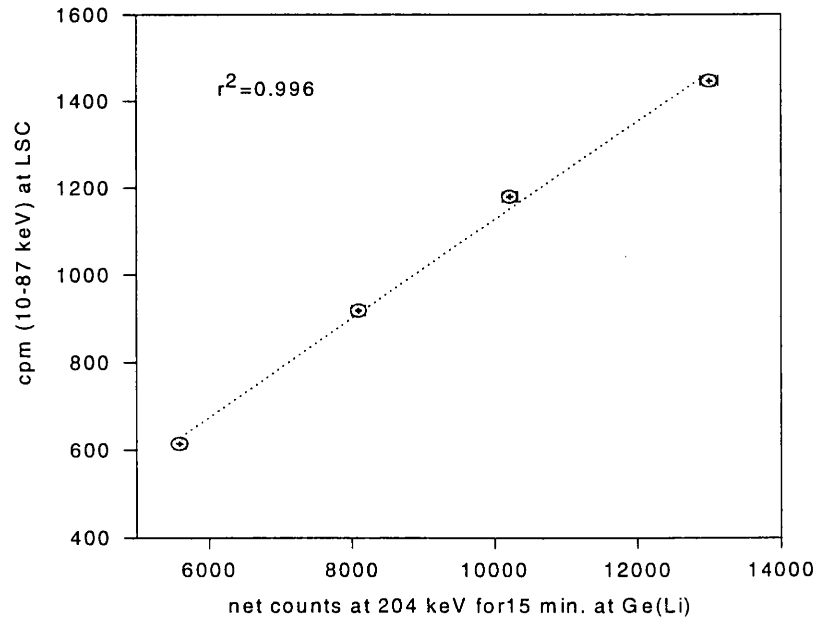


Figure 2. 37 Plot showing linearity between tracer (^{95m}Tc) counts obtained from Ge(Li) and LSC (at 95% confidence level) methods.

In the next experiment, ~16 Bq of ^{95m}Tc and 25 Bq of ^{99}Tc spikes were counted individually. These activities represent average amounts that would normally be present /

added to real samples. The obtained counts per minute in the region of interest is presented in Table 2.19.

Isotopes	(10-87 keV) CPM
^{95m}Tc	323±5.68
^{99}Tc	864±9.30

Table 2. 19 Tracer (^{95m}Tc) contribution at 10-87 keV.

The above measurement was made on the first day of sample preparation. After allowing decay for a month, a second measurement was made. The results are presented in Table 2.20.

Isotopes	(10-87 keV) CPM
^{95m}Tc	253±5.03
^{99}Tc	865±9.30

Table 2. 20 Tracer (^{95m}Tc) contribution at 10-87 keV after a month decay period.

Although a slight decrease in the ^{95m}Tc count rate is observed, it still makes a very significant contribution to the ^{99}Tc window. Thus, it was concluded that the use of ^{95m}Tc as a tracer for LSC was inappropriate.

2.3.5.2 Experiments using ^{99m}Tc as yield tracer in dual counting method.

To test the use of ^{99m}Tc as a yield tracer in LSC counting, 4 MBq ^{99m}Tc and 25 Bq of ^{99}Tc spikes were counted individually. The results obtained are given in Table 2.21.

Isotopes	(10-87 keV) CPM
^{99m}Tc	3395±18.43
^{99}Tc	859±9.27

Table 2. 21 Tracer (^{99m}Tc) contribution at 10-87 keV.

The above measurement was made on the first day of sample preparation. After allowing decay for a month, a second measurement was made. The results are presented in Table 2.22.

Isotopes	(10-87 keV) CPM
^{99m}Tc	2±0.45
^{99}Tc	859±9.27

Table 2. 22 Tracer (^{99m}Tc) contribution at 10-87 keV after a month decay period.

Initially ^{99m}Tc was found to significantly contribute (3395 counts per minute) to the technetium-99 window (10-87 keV). However, once decayed for a month, the contribution from ^{99m}Tc is negligible (<2 counts per minute).

Although, after allowing for a sufficient decay time, ^{99m}Tc did not interfere with the counting of ^{99}Tc, the latter will interfere with the determination of ^{99m}Tc. Thus, the ^{99m}Tc count rate (obtained from the initial count) must have the contribution from ^{99}Tc subtracted. The ^{99}Tc contribution can, of course, be simply obtained from the second count. Tracer yield (%) for 3 real samples, obtained by both Ge(Li) and LSC are given in Table 2.23.

SAMPLE	Ge(Li)	LSC (2550 TR)
1	55.21±3.37%	54.39±0.99%
2	58.91±1.70%	58.12±0.93%
3	56.99±1.74%	55.65±0.97%

Table 2. 23 Tracer yield (%) obtained from LSC and Ge(Li) methods.

Good agreement between the two methods was obtained. Hence ^{99m}Tc can be successfully used with LSC as a yield tracer.

Summary.

From the above results, the optimum conditions for sample counting were established. Glass vials with a 2 ml sample volume + 5 ml cocktail were selected for sample preparation. 2% HNO_3 was selected as sample base. To enhance the counting efficiency but at the same time maintain a reasonably low background count, low level count mode with a 450 nsec burst delay time was selected. A sample counting period of 100 minutes was used. Colour quenching is not expected in the final sample solution as the very effective separation (co-precipitation and TEVA Spec Extraction) methods produce a colourless sample. Jordon et al. (1995) have analysed low levels of technetium-99 (0.242±0.007 Bq g^{-1} wet wt.) present near Chernobyl without the need for colour quench correction. Potential interferences from tritium were excluded by careful choice of the counting window (10-87 keV). The efficiency ranged between 69 and 81% for the optimum window (10-87 keV). The effect of quenching on efficiency (%) for ^{99}Tc beta counting was small within runs. The use of ^{99m}Tc as a yield tracer was found satisfactory.

2.3.6 Comparison of LSC and ICP-MS.

2.3.6.1 Analysis of Seaweeds.

In house Standard Seaweed samples were prepared using the analytical method developed using ^{99m}Tc as yield tracer and measured using LSC. The values obtained are given in Table 2.24.

SAMPLE	^{99}Tc (kBq kg^{-1} dry wt.)
1	21.27
2	22.49
3	20.14
4	19.08
5	19.94
6	20.15
Mean	**20.51±1.19**

Table 2. 24 Analysis of ^{99}Tc in seaweed samples by LSC method.

The mean value obtained by LSC is very similar to the mean value of 21.82±1.93 Bq g^{-1} obtained by ICP-MS.

2.3.6.2 Analysis of Sediments.

Again to compare both ICP-MS and LSC methods, 3 sediment samples have been processed using the analytical method developed and measured by both ICP-MS and LSC. The values obtained are given in Table 2.25, and they are very close to each other, especially when the very low levels present in these samples are taken into account.

Sample	ICP-MS	LSC
A	10.46±1.17	8.37±0.94
B	14.73±1.66	16.30±1.83
C	8.54±0.96	7.21±0.81

Table 2. 25 Analysis of ^{99}Tc (^{99}Tc Bq kg^{-1} dry wt.) in sediment by ICP-MS and LSC methods.

2.3.6.3 Detection limits in both LSC and ICP-MS.

The detection limit reported for LSC using 100 minute counting times is 6 Bq kg^{-1} (calculated based on Currie (1968). The detection limit can be improved by longer counting time if necessary. In ICP-MS the detection limit reported is 13 Bq kg^{-1}, although it can be varied by altering the final sample volume. For example, sediments having very low^{99}Tc activities (mBq levels) could be prepared in a smaller volume (5 ml instead of 10 ml in final sample) and thus the detection limit would be reduced.

2.4 CONCLUSIONS.

An analytical method for the determination of ^{99}Tc, devoid of ruthenium, has been developed and optimised.

Technetium present in seawater has been preconcentrated using a simple anion-exchange method. By this method more than 90% of ruthenium present in the seawater sample was removed while only 10% technetium was lost. Ashing (at 700°C for 6 hours) under ammoniacal conditions and subsequent leaching (at 60°C for 2-3 hours) helps to concentrate technetium from other commonly encountered environmental matrices (e.g., seaweeds, mussels, winkles etc.). More than 90% of the technetium was recovered during ashing. Sediment samples were subjected to a similar ashing process, however, leaching continued for 48 hours to make sure most of the sediment bound technetium was removed. By use of a simple ferric iron hydroxide precipitation, using 10M NaOH, most of the remaining ruthenium (75%) present in the sample was removed. To remove any final traces of ruthenium, the supernatant, following precipitation, was subjected to two types of extraction method. First, a solvent extraction method (cyclohexanone plus carbon tetrachloride) was found to recover technetium (>99%) from the sample completely devoid of ruthenium. However the solvent extraction method was superseded in the present analytical method by a new extraction chromatography method using the chromatographic resin, TEVA Spec® (supplied from EIChroM Industries, USA). Tc is quantitatively taken up by the resin from 0.1M HNO_3, whereas Ru remains in solution. In summary, an average of 45-70% technetium recovery combined with a decontamination factor of 10^5-10^6 for ruthenium was achieved.

Various potential problems (e.g., matrix effects, polyatomic formation) in ICP-MS analysis have been tested. No major effect was observed at mass 99 from these interferences. The detection limit obtained, under standard operating conditions, was 13 Bq kg^{-1}.

An informal intercomparison with Westlakes Research Institute, Cumbria was carried out, along with the repeat analysis of samples previously analysed at SURRC (Ishanullah, 1991). Both exercises have proved the accuracy and precision of the analytical method. Regular checks on the analytical method during the course of the study period, were performed on an in-house standard seaweed material. Based on 15 analyses, a standard deviation of 11.5% was observed (1σ level) and quoted subsequently as the error associated during real sample analysis.

The second part of the analytical method development concentrated on liquid scintillation counting. The chemistry used is the same as for the ICP-MS method, except for the choice of yield tracer used. Both ^{95m}Tc and ^{99m}Tc can be used as yield tracers during ICP-MS analysis. However, only ^{99m}Tc could be used in LSC as ^{95m}Tc was found to raise the background contribution (~27%) in the ^{99}Tc window. Further investigation would be required to use ^{95m}Tc as a yield tracer in LSC.

The scintillation cocktail, Ultima Gold LLT (supplied from Packard Co.,) was used along with the low level counting mode with a 450nsec 'delay before burst' (an advanced feature of Packard 2550 series LSA). Potential interferences from ^{3}H were excluded by careful choice of the counting window (10-87 keV) and the effect of quenching was small. The detection limit obtained, under standard operating conditions, was 6 Bq kg^{-1}.

In summary, the analytical method has been proved to remove ruthenium completely from technetium using a combination of iron hydroxide precipitation and ion-exchange chromatography methods. The iron hydroxide method removes up to 75% of ruthenium from the sample with the remaining ruthenium being successfully removed by TEVA Spec® resin. The analytical method thus developed has been applied to analyse ^{99}Tc in a wide range of sample types (e.g., seaweeds, mussels, winkles, sediment) and results obtained are discussed in Chapter 3.

CHAPTER 3: TECHNETIUM-99 IN THE IRISH SEA

3.1 STUDY AREA.

The Irish Sea is a semi-enclosed body of water bounded by St. David's Head in the South and the Mull of Galloway in the North. It receives Atlantic water influences and inputs through both entrances, however, the bulk of the oceanic input (1000 km^3 y^{-1}) comes from the south (Jefferies et al., 1982). Due to the strong tides present, there is a vertically homogenous water column in most areas of the Irish Sea (Dickson, 1987). Water circulation in the Irish Sea is dominated by a northerly flow, however, around Sellafield it is southerly (Howarth, 1984) (Figure 3.1).

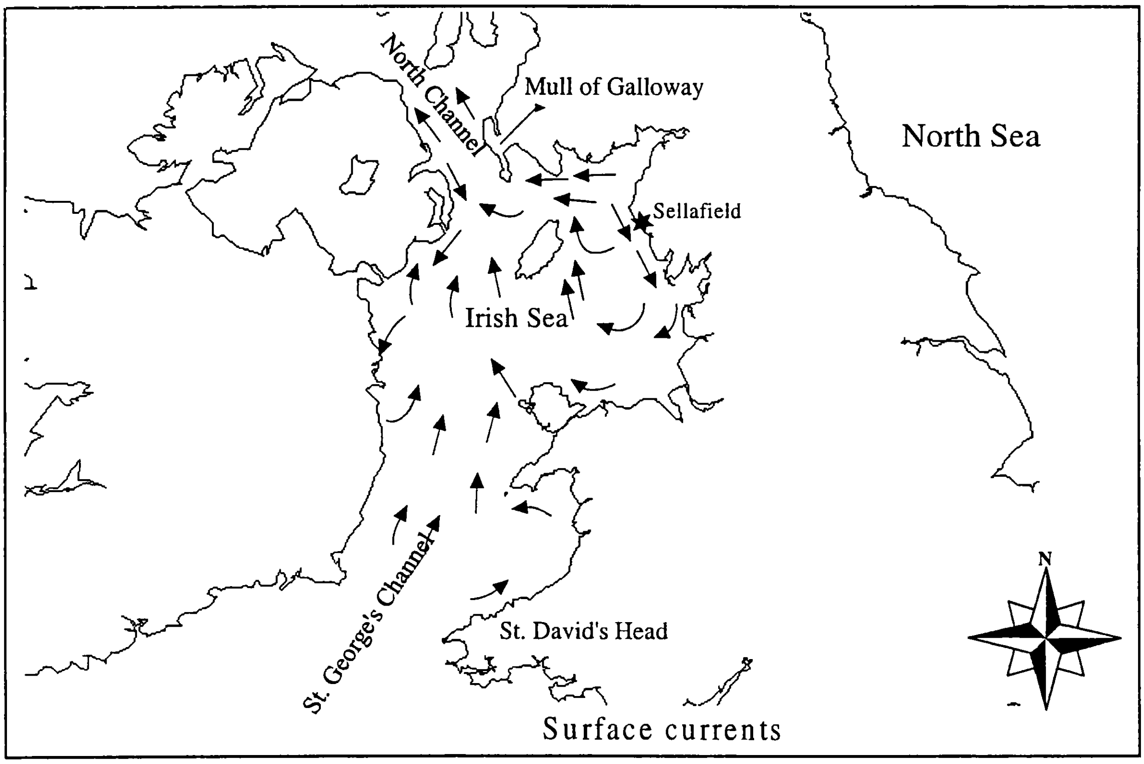


Figure 3. 1 Map showing the predominant residual surface currents in the Irish Sea.

Sellafield is situated on the Cumbrian coast and discharges radioactive waste through a pipeline which terminates 2.1 km beyond the low water mark.

3.2 SAMPLING STRATEGY, RESULTS AND DISCUSSION.

A wide range of samples (seaweed, mussels, winkles, sediment/soil) of marine origin were collected in the surrounding zones of the Irish Sea. The sampling sites are shown in Figure 3.2.

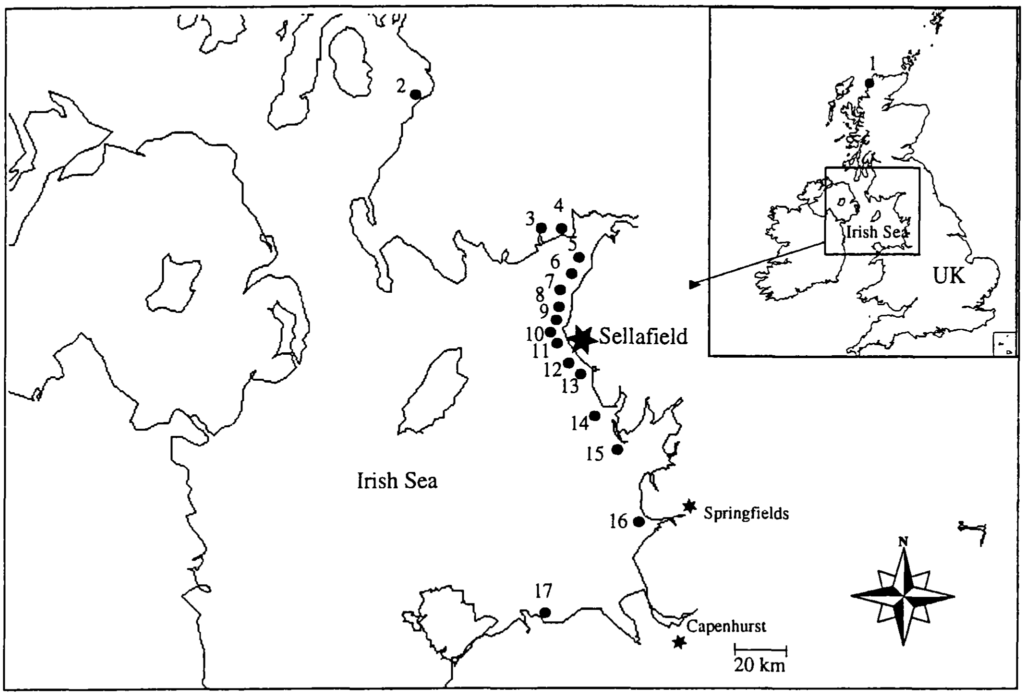


Figure 3. 2 The study area and sampling sites - Irish Sea.

Seaweeds were hand picked, washed on site in seawater and brought to the laboratory in plastic bags. In the laboratory, they were washed under running tap water, rinsed with de-ionised water and then put in an oven pre-heated to 70°C. After two days, the brittle seaweed was ground using a blender. The seaweed powder obtained was stored in a sealed polythene bag. Approximately 10g of seaweed powder was taken for analysis.

Mussels and winkle samples were hand-picked and frozen for storage on return to the laboratory. As required, the samples were de-frosted and the outer shells separated from the body tissues. The body tissues of mussels and winkles were then placed in an oven pre-heated to 70°C for two to three days. The dried tissues were taken from the oven and ground into powder using a clean blender. The powdered tissues of mussels and winkles were stored in sealed polythene bags. Sample sizes of approximately 10g were used for each analysis.

Surface sediment samples were collected using a trowel and air dried on return to the laboratory. The air dried sediments were crushed and then dried in an oven at 70°C for 24 hours. The oven dried sediments were stored in polyethylene bags. Approximately 50g were used for each analysis.

Saltmarsh plant samples were cut above ground and washed. In the laboratory, the plants were thoroughly rinsed and the adhering sediment was carefully removed prior to drying in an oven (as described for seaweeds). The dried plants were then ground and stored for analysis.

The analytical methods described in Chapter 2 were used and all analyses were carried out by ICP-MS. All errors quoted represent either the standard deviation between the 15 analyses of IHSM (11.5%) or the error associated with individual ICP-MS measurement, whichever was greater. All concentrations are based on dry weight, unless otherwise stated, and reported with 1 sigma error.

3.2.1 Inter-species variations.

3.2.1.1 Variation within seaweeds.

Different types of samples have been used for monitoring technetium-99 concentrations in the environment. Routine monitoring in the past has mainly utilised seaweeds (*Fucus vesiculosus, Ascophyllum nodosum and Porphyra umbilicalis*) (Dutton & Ibbett, 1973; MAFF, 1995) and lobsters (MAFF, 1994). Technetium-99 levels in seaweeds, however, have been observed to vary significantly between species (Caravalho & Fowler, 1985; Bonotto et al., 1988).

To investigate these variations a broad range of seaweeds types were collected from the Irish Sea coast during July 1995 and analysed for technetium-99. The seaweeds collected were primarily brown seaweeds but a green algae (*Enteromorpha linza*) and red algae (*Chondrus crispus*) were also collected. The brown algae collected are: *Pelvetia canaliculata* (Figure 3.3), *Fucus spiralis* (Figure 3.4) *Dictyopteris membranacea* (Figure 3.5), *Ascophyllum nodosum* (Figure 3.6), *Fucus vesiculosus* (Figure 3.7 & 3.8) and *Fucus serratus* (Figure 3.9). The most well known, *Fucus vesiculosus*, is more commonly known as *Bladder wrack* and is widely distributed throughout Europe and North America.

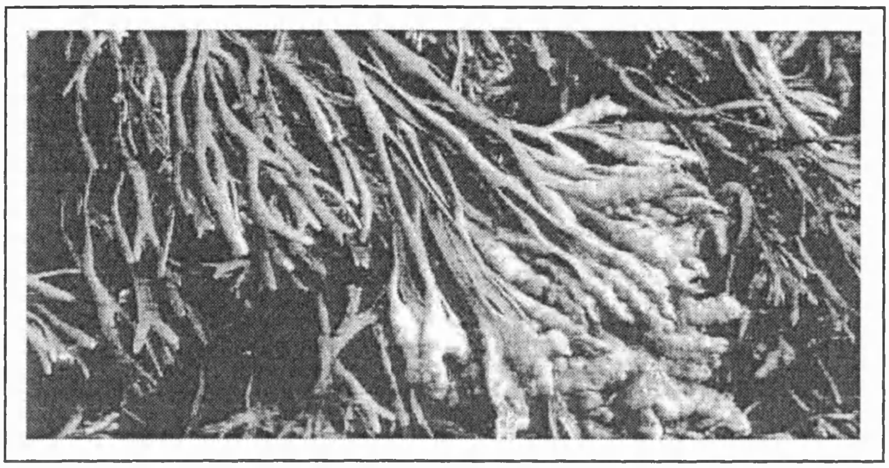


Figure 3. 3 *Pelvetia canaliculata* - a brown alga.

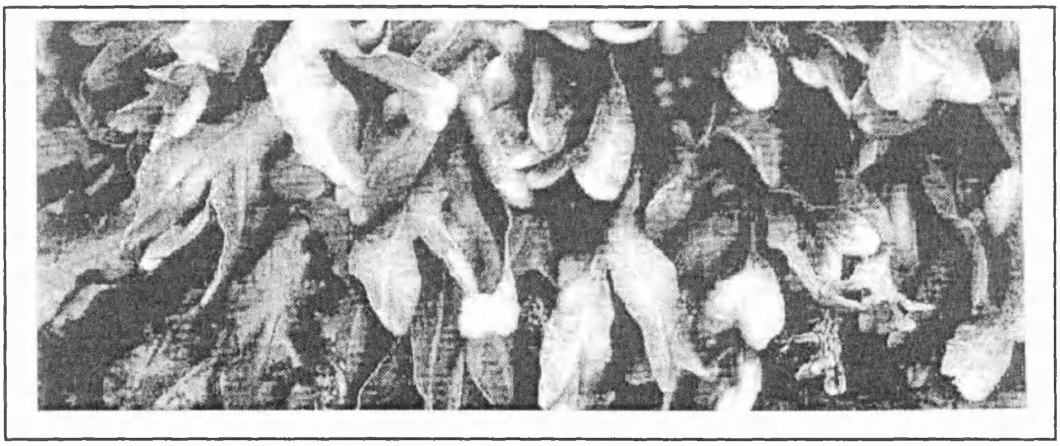


Figure 3. 4 *Fucus spiralis* - a brown alga.

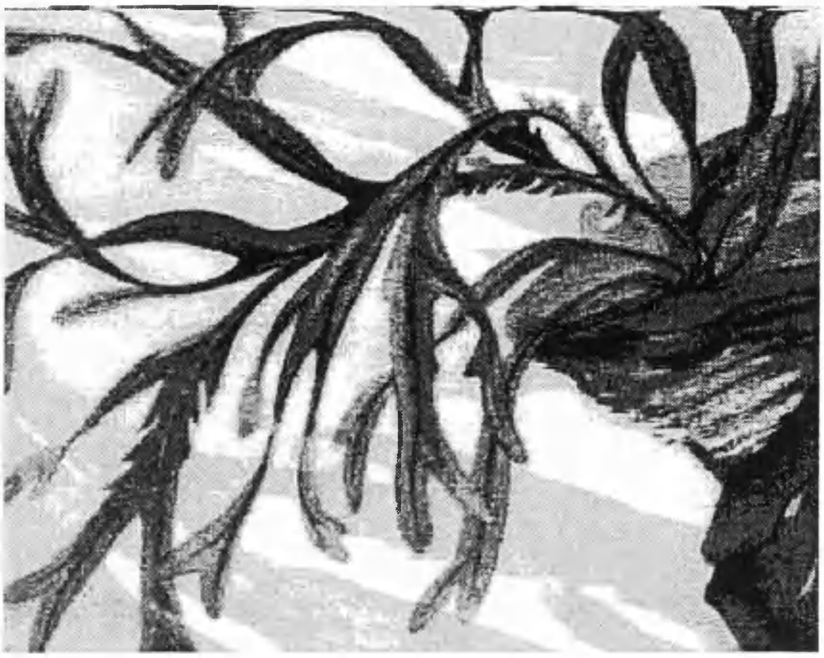


Figure 3. 5 *Dictyopteris membranacea* - a brown alga.

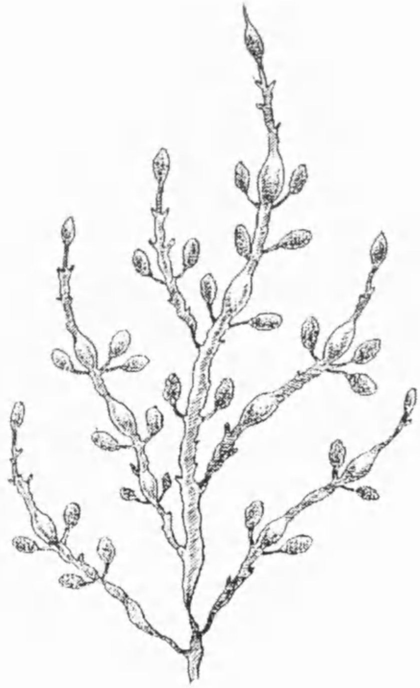


Figure 3. 6 *Ascophyllum nodosum* - a brown alga.

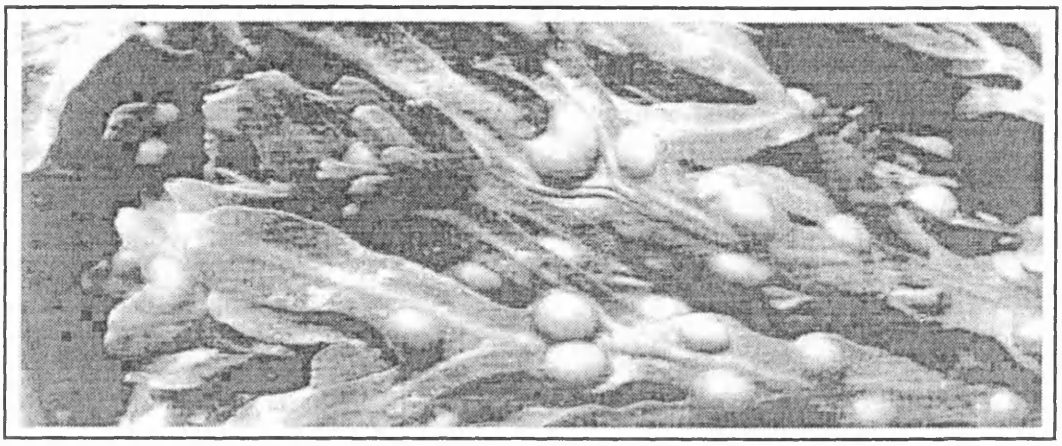


Figure 3. 7 *Fucus vesiculosus* - a brown alga.

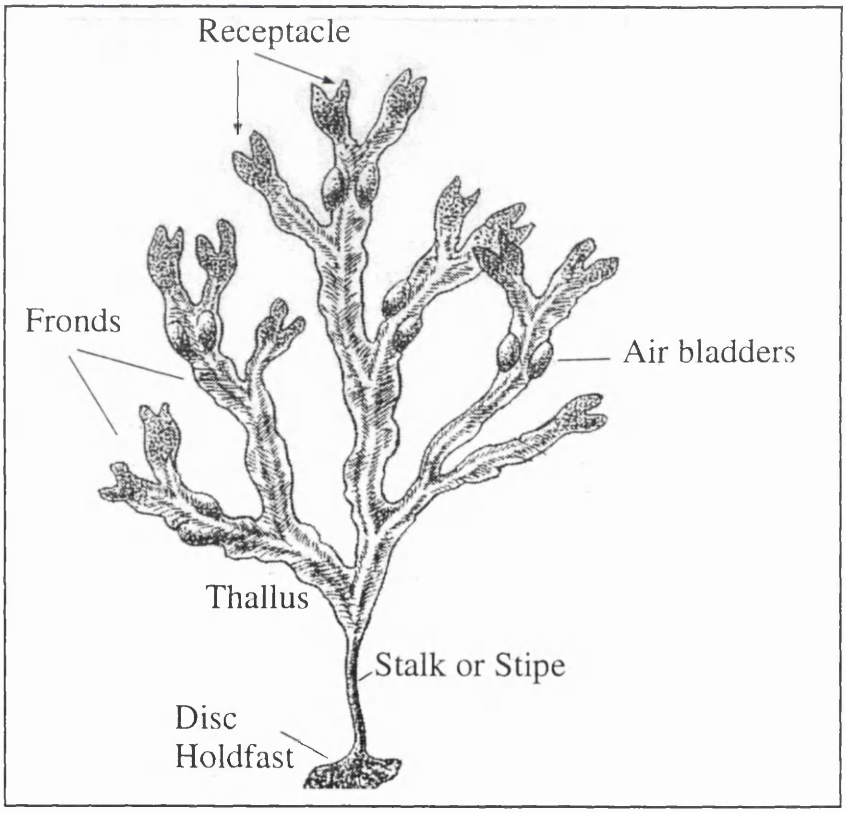


Figure 3. 8 Parts of a typical seaweed (e.g. *Fucus vesiculosus*).

Figure 3. 9 *Fucus serratus* - a brown alga.

^{99}Tc levels found in the different seaweeds are presented in Table 3.1. The results obtained ranged from 0.31 kBq kg^{-1} (dry wt.) for a *Enteromorpha linza* seaweed collected at Whitehaven to 215 kBq kg^{-1} (dry wt.) for a *Dictyopteris membranacea* seaweed collected from Ravenglass. The results from four sites (St. Bees Head, Seascale, Ravenglass and Whitehaven harbour) at which several seaweed species were collected are shown in Figures 3.10 - 3.13.

Location/Key	**Sample**	**^{99}Tc (kBq kg^{-1} dry wt.)**
St. Bees Head (10)	*Enteromorpha linza* (G)	1.43±0.2
	Ascophyllum nodosum (B)	119.0±14
	Fucus spiralis (B)	86.8±10
	Fucus vesiculosus (B)	136.4±16
Seascale (12)	*Dictyopteris membranacea* (B)	115.1±13
	Fucus serratus (B)	158.8±18
	Fucus spiralis (B)	144.2±17
	Fucus vesiculosus (B)	213.7±25
Ravenglass (13)	*Enteromorpha linza* (G)	1.23±0.14
	Dictyopteris membranacea (B)	215±25
	Fucus spiralis (B)	142.2±16
	Chondrus crispus (R)	0.90±0.10
Whitehaven (9)	*Enteromorpha linza* (G)	0.31±0.03
	Ascophyllum nodosum (B)	43±5
	Fucus vesiculosus (B)	75.6±9
Haverigg (14)	*Fucus spiralis* (B)	23.9±3
Maryport (5)	*Ascophyllum nodosum* (B)	29.6±4
	Fucus spiralis (B)	19.7±2
Prestwick (2)	*Fucus spiralis* (B)	1.9±0.23
Rockcliffe (3)	*Pelvetia canaliculata* (B)	14.4±2
	Fucus spiralis (B)	10.2±1
St. Lytham Jetty (16)	*Fucus spiralis* (B)	16.23±2

Table 3. 1 ^{99}Tc activities in various seaweeds (July 1995).

(G = Green alga, B = Brown alga, R = Red alga)

In general, brown seaweeds (e.g., *Fucus species*) had higher technetium-99 levels than green or red seaweeds. At Ravenglass, another member of brown *algae (Dictyopteris membranacea)* accumulated the highest level of technetium-99. At all the other three sites *Fucus vesiculosus* showed the highest levels of technetium-99.

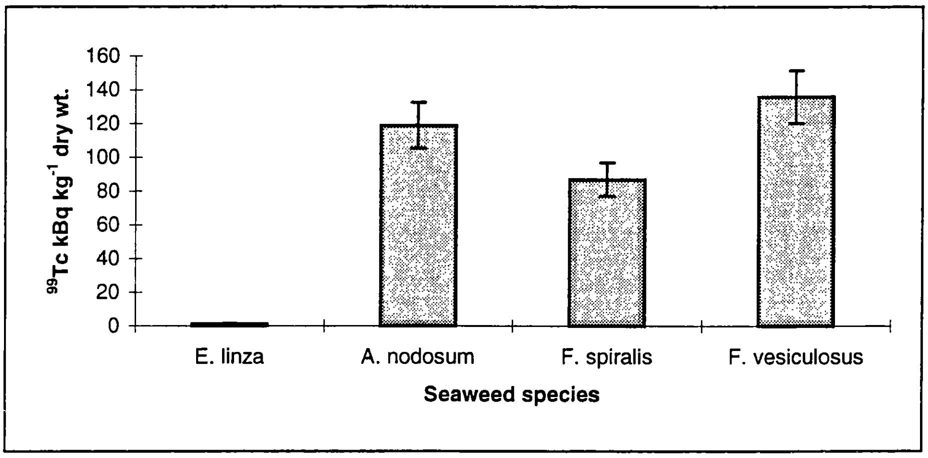


Figure 3. 10 Inter-seaweed species variations in ^{99}Tc accumulation - St. Bees Head.

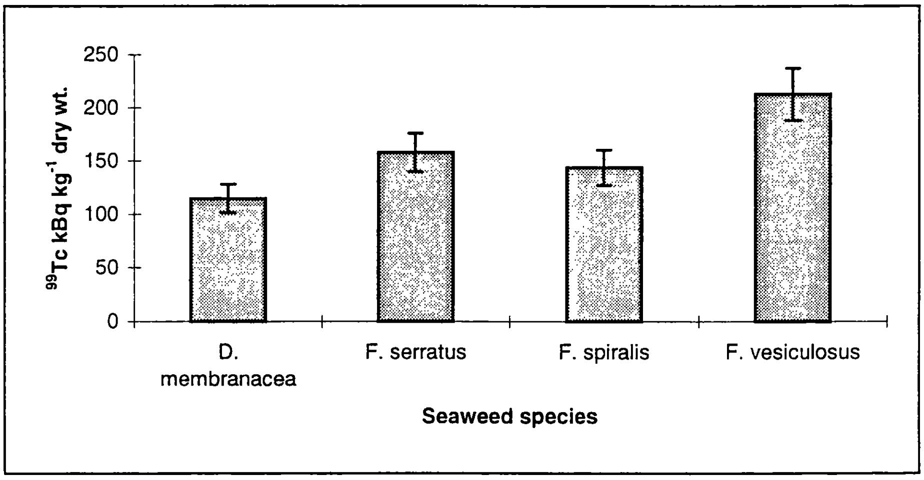


Figure 3. 11 Inter-seaweed species variations in ^{99}Tc accumulation - Seascale.

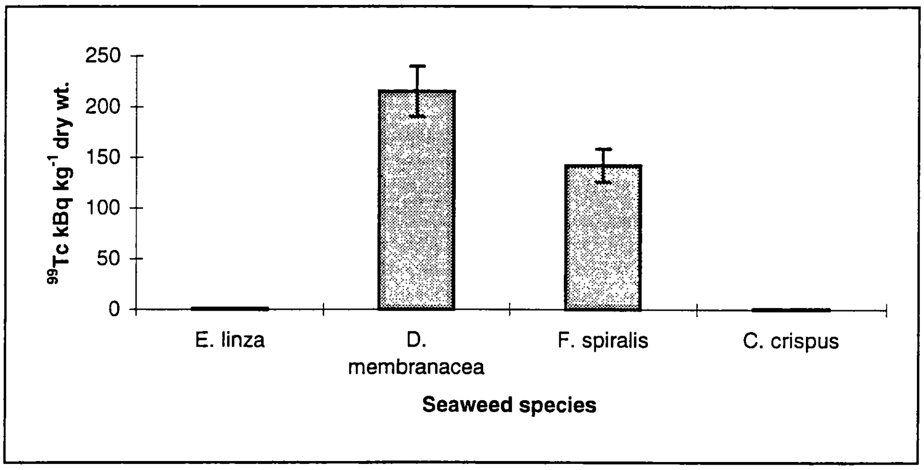


Figure 3. 12 Inter-seaweed species variation in ^{99}Tc accumulation - Ravenglass.

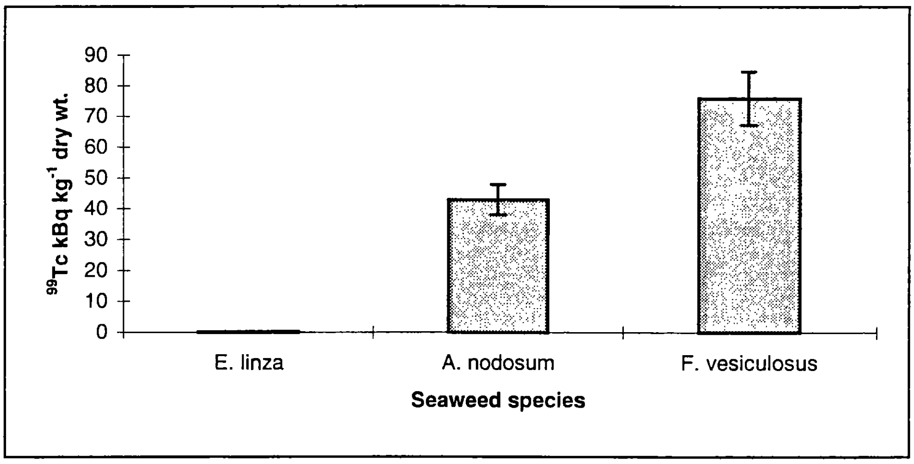


Figure 3. 13 Inter-seaweed species variations in ^{99}Tc accumulation - Whitehaven.

The absolute level of ^{99}Tc in seaweeds varied greatly from site to site. For example, *Fucus spiralis* collected from Seascale (2 km south of the Sellafield outfall) had a ^{99}Tc activity of 144 kBq kg^{-1} (dry weight), an order of magnitude higher than the activity of 16 kBq kg^{-1} (dry weight) observed in this species at St. Lytham (80 km south of Sellafield). Thus, it is hard to draw conclusions from a comparison of the ^{99}Tc levels in different species collected at different sites. To overcome this problem, the relative activities of technetium-

99 normalised to *Fucus spiralis* (a common seaweed collected from most of the sites) have been collected and are presented in Table 3.2. The average value for each seaweed is shown in Figure 3.14.

Seaweed / Sites	St. Bees	Seascale	Ravenglass	Maryport	Rockcliffe	Average
A. nodosum	1.37			1.50		1.44
F. vesiculosus	1.57	1.48				1.53
F. serratus		1.10				1.10
D. membranacea		0.80	1.50			1.15
P. canaliculata					1.41	1.41
C. crispus			0.006			0.006
E. linza	0.016		0.008			0.013

Table 3. 2 ^{99}Tc activity in seaweeds relative to *Fucus spiralis.*

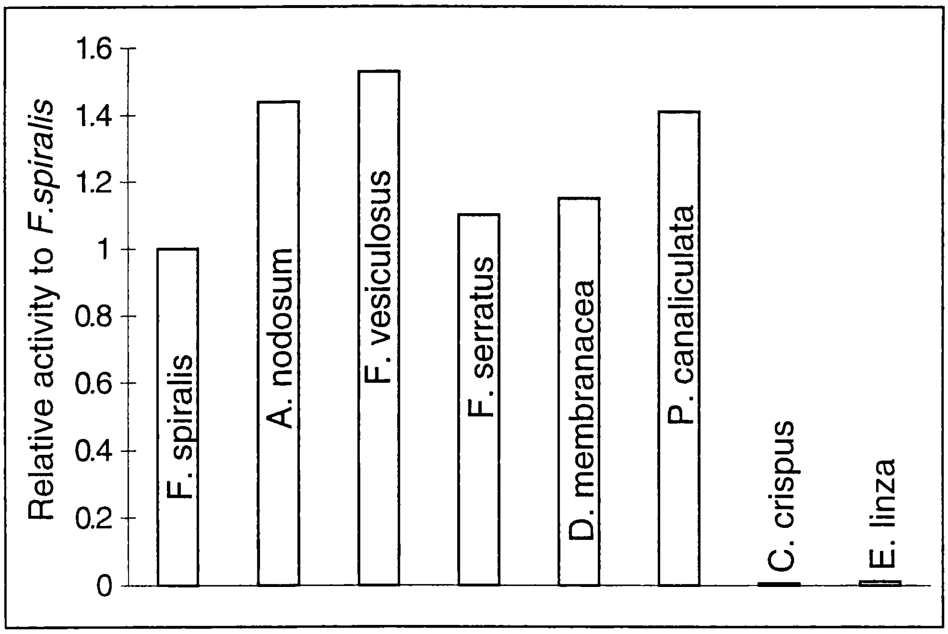


Figure 3. 14 Composite diagram showing ^{99}Tc activities in seaweeds.

The relative activity found for red seaweed (*Chondrus crispus*) was 2 - 3 orders of magnitude less than that observed for brown seaweeds. However, it was fairly similar to that observed for green seaweed (*Enteromorpha linza*). In contrast, brown algae (irrespective of species) were found to show a far higher affinity towards technetium-99.

According to the data presented in Figure 3.14 *Fucus vesiculosus* showed higher activities than all other seaweeds. However, it was only slightly higher than *Ascophyllum nodosum* (1.44) and *Pelvetia canaliculata* (1.41). The order of ^{99}Tc accumulation can be presented as follows:

Fucus vesiculosus > Ascophyllum nodosum > Pelvetia canacliculata >> Dictyopteris memberanacea > Fucus serratus > Fucus spiralis.

Holm et al. (1986b) normalised the ^{99}Tc activity in a variety of seaweeds collected from temperate and Arctic waters of the North Atlantic to *Fucus vesiculosus*. The results obtained are presented in Table 3.3.

SEAWEED	RELATIVE ACTIVITY
Fucus serratus	0.56±0.15
Fucus spiralis	0.54±0.05
Ascophyllum nodosum	2.1±0.09
Pelvetia canaliculata	1.2±0.4

Table 3. 3 ^{99}Tc activity relative to *Fucus vesiculosus* (*Holm et al.* 1986b).

Although the results are not in perfect agreement with those obtained in this study, it is interesting to note that, as in the results of the present study, *Fucus vesiculosus*, *Ascophyllum nodosum*, *Pelvetia canaliculata* all had significantly higher ^{99}Tc concentrations than *Fucus serratus* or *Fucus spiralis*.

Investigations into technetium-99 and its biological behaviour have been carried out in aquatic plants (mostly algae) and animals by various workers (Dutton & Ibbett, 1973; Pentreath et al., 1980; Jeanmaire et al., 1981; Fisher, 1982; Bonotto et al., 1983; 1984a; 1984b; Masson et al., 1983; Topcuoglu & Fowler, 1984; Benco et al., 1986). In the 1970's, a study took place on the shores of Cap de la Hague, close to a French nuclear reprocessing plant (Germain et al., 1979; Jeanmaire et al., 1981). For this, the brown alga, *Fucus serratus* was mainly analysed over the period 1974 to 1979 along with other seaweeds (Table 3.4). When a variety of seaweeds were collected in 05/77, the ^{99}Tc levels decreased in the order *Ascophyllum nodosum > Pelvetia canaliculata > Fucus serratus >> Chondrus crispus > Enteromorpha linza*, largely in agreement with the results of the present study.

Samples	Species	Date of Sampling	^{99}Tc concentration (Bq kg^{-1} wet weight)
Brown algae	*Fucus serratus*	11/74	22.20
	Fucus serratus	02/76	48.10
	Fucus serratus	05/77	45.50
	Fucus serratus	08/77	56.61
	Fucus serratus	05/78	78.80
	Fucus serratus	06/78	62.16
	Fucus serratus	07/78	77.70
	Fucus serratus	01/79	68.45
	Pelvetia canaliculata	05/77	61.42
	Ascophyllum nodosum	05/77	125.80
	Fucus vesiculosus	05/79	<0.74
Red algae	*Chondrus crispus*	05/77	2.96
Green algae	*Enteromorpha sp.*	05/77	1.85

Table 3. 4 ^{99}Tc concentrations in seaweeds from French Coast (Jeanmaire et al., 1981).

In the same period, Dutton & Ibbett (1973) measured ^{99}Tc in some marine biological materials in the Irish Sea close to the liquid discharge point for Sellafield. It was the first time *Fucus vesiculosus* was demonstrated to accumulate technetium-99 (14.8 kBq kg^{-1} fresh wt.). Similar to this study, Dutton & Ibbett (1973) also observed low technetium-99 levels in red algae (*Porphyra umbilicalis*) (25.9 Bq kg^{-1} fresh wt.). Unfortunately, this study was unable to locate *Porphyra umbilicalis* even though MAFF (1995) has provided results from 1994 at St. Bees Head (4.8 Bq kg^{-1} fresh wt.).

Concentration factors (CF= Concentration of ^{99}Tc in seaweeds to Concentration of ^{99}Tc in seawater) calculated by earlier studies for a variety of seaweeds are given in Table 3.5.

Species	CFs	Reference
Green algae		
Enteromorpha intestinalis	<1	Schulte et al., 1981
Red algae		
Chondrus crispus	4	Aprosi & Masson, 1981
Porphyra umbilicalis	0.1 - 0.5	Bonotto et al., 1988
Brown algae		
Ascophyllum nodosum	9,000	Bonotto et al., 1988
Dictyopteris membranacea	21	Benco et al., 1986
Fucus serratus	500	Aprosi & Masson, 1981
Fucus serratus	50,000*	Masson et al., 1989
Fucus serratus	1500	Masson et al., 1981
Fucus serratus	$>10^4$	Birks, 1975
Fucus serratus	12,000	Bonotto et al., 1988
Fucus serratus	$5.1\text{x}10^4$*	Hurtgen et al., 1988
Fucus vesiculosus	$9\text{x}10^4$ - 10^5*	Aarkrog et al., 1986

Table 3. 5 Technetium uptake (CFs) by green, red and brown algae (*data based on Field studies) in Laboratory studies - earlier studies.

A notable difference has been observed between laboratory derived CF and field CF studies. For *Fucus serratus*, a CF of 50,000 was observed in samples taken around the Cap de la Hague nuclear reprocessing plant (Masson et al., 1989). In contrast, a CF of only 1,500 was observed in a laboratory study (Masson et al., 1981). Similar high CFs were found in the field for *Fucus vesiculosus* (dry wt.) ($9\text{x}10^4$ - 10^5) by Aarkrog et al. (1986). The very high CFs observed for brown algae suggest that integrated accumulation occurs during their entire life span (Masson et al., 1989).

Using a value of 1.2 Bq l^{-1} for the average seawater concentration at Ravenglass in 1995 (Busby et al., 1996, in press), CFs for the seaweeds collected from this site during this study can be determined. The results obtained are presented in Table 3.6. The CF observed for *Dictyopteris membranacea* ($1.8\text{x}10^5$) is far higher than the value presented in Table 3.5 (21).

Seaweed species	Concentration Factor*
Enteromorpha linza	$1.0\mathrm{x}10^3$
Dictyopteris membranacea	$1.8\mathrm{x}10^5$
Fucus spiralis	$1.2\mathrm{x}10^5$
Chondrus crispus	$7.5\mathrm{x}10^2$

Table 3. 6 Technetium-99 uptake (CFs) by green, red and brown seaweeds at Ravenglass site (*CFs = dry wt. basis) - present study.

Similarly, the CF observed for the green seaweed (*Enteromorpha linza*) is two orders of magnitude higher than the CF observed in the laboratory study (Schulte et al., 1981). Direct comparison between laboratory work and field data, in particular CFs, are not well suited. The CF calculated in laboratory normally employs limited time and space, while accumulation in the field from the ambient environment is integrated over longer periods.

Technetium uptake, in seaweeds, is thought to be primarily an active process. This process is controlled metabolically and can be affected by variations in physico-chemical parameters (Caravalho & Fowler, 1985; van der Ben et al., 1990).

In order to explain the variations observed between species therefore we have to look at the biology / habitat / life cycles of the various species. Most of the brown seaweeds possess similar characteristics in their morphology and reproduction. The plant is a flat, expanded sheet of cellular tissue (the thallus) that narrows towards the base, forming the 'stipe' or stalk, which is attached to the plant's habitat by the disc-shaped 'holdfast'. The thallus cells are in crowded rows with thick jelly-like cell walls, giving the plant flexibility and a degree of protection against turbulent wave action. The thallus and its branches each have a prominent midrib, on either side of which are numerous oval-shaped air-filled bladders, which develop each spring. The ends of the thallus branches are divided into lobed fronds, which during reproduction divide into forks, many of which bear swollen, minutely granular or warty, bulbous fruiting bodies known as 'receptacles' (Figure 3.15).

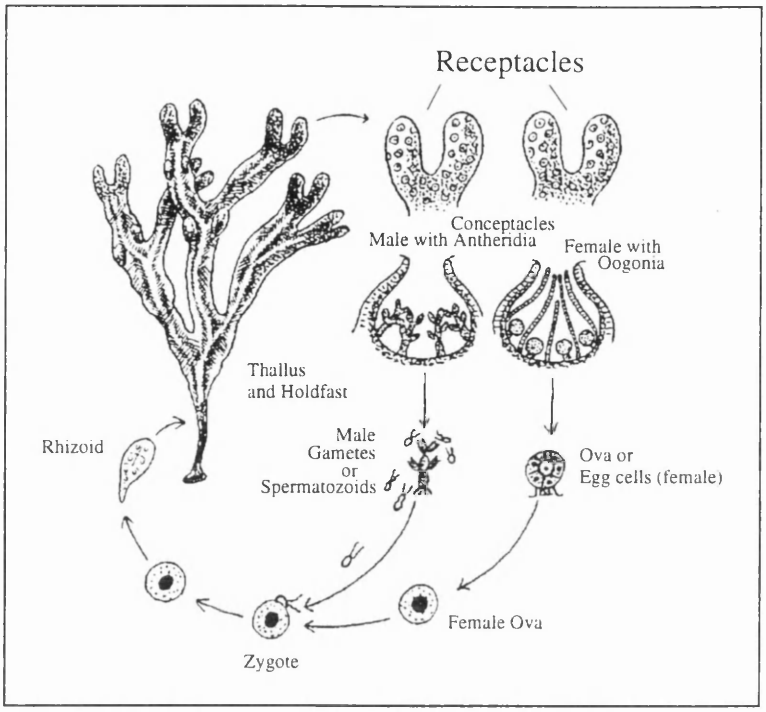


Figure 3. 15 Life cycle in seaweeds.

For example, in Bladder Wrack (*Fucus vesiculosus*) male and female reproductive organs are on separate plants. Each receptacle is like a tiny cup, and has a lining of hairs, the paraphyses, which secrete the mucilage with which the conceptacles are filled.

The green seaweeds (e.g., *Enteromorpha sps*) have a short hollow stalk attached to small disc holdfast and a single narrow or spiral deflated frond (Figure 3.16).

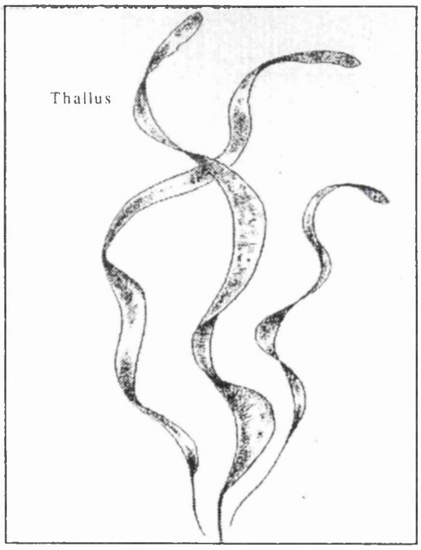


Figure 3. 16 *Enteromorpha linza* - a green alga.

The red alga, *Chondrus crispus* posses similar characters to green alga; growing up to 6 inches (15 cm) long, with fronds varying in width from 0.5 to 1 inch (1.2 - 2.5 cm) (Major, 1977). The green seaweeds, *Enteromorpha sps*, are found on rocks, stones, shells and on other seaweeds. They can withstand low salinities and can live in fresh-water outflows. They are bright green and grow up to 20 inches (50 cm).

An autoradiographic study carried out by Bonnoto et al. (1988) clearly demonstrated that technetium is distributed heterogeneously in seaweeds. In brown algae, the higher metabolic activity in the apices, which contain young tissues, accumulates technetium well. For example in *Fucus vesiculosus* and *Fucus spiralis*, the apical parts with fertile receptacles were found responsible for the high accumulation of technetium while *Ascophyllum nodosum* had more technetium in the apical region of the lateral branches.The low levels of technetium accumulation in the red and green algae thus could be attributed to their different morphology and physiology from brown algae. The brown algae (e.g., *Fucus vesiculosus*) have higher CFs because they possess more branches (having more apical meristems) with thick fertile receptacles than algae possessing thin flat rounded bodies (for example, *Enteromorpha linza* (Figure 3.16) with a single apical meristem (not laterally branched). Although, C*hondrus crispus* (Figure 3.17), a red alga shows thallus similar to brown algae, have accumulated less technetium.

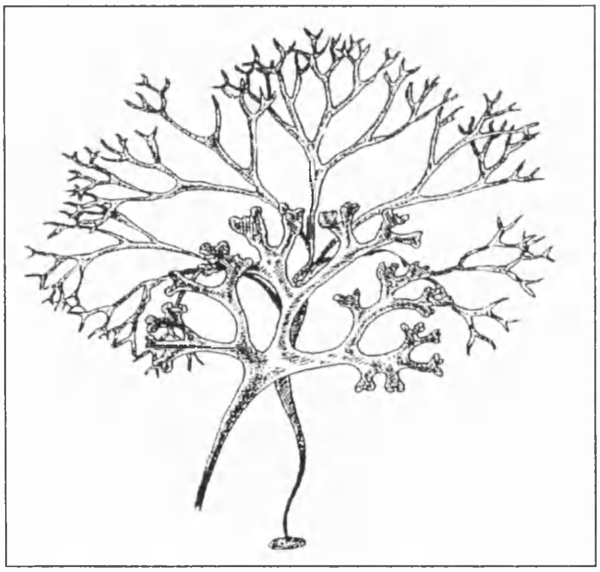


Figure 3. 17 *Chondrus crispus* - a red alga.

The variation observed between seaweeds could also be partially due to their life span. Green seaweeds tend to survive, at maximum for a year whilst red seaweeds are perennial.

Both green and red seaweeds are regularly cleared by grazing animals (e.g. *Littorina, Patella*). In contrast, brown seaweeds can survive for longer times in their natural habitat, allowing more time to accumulate ^{99}Tc. A summary of the life span of common macroscopic brown algae is given in Table 3.7, based on population studies made in the natural environment.

Plant	**Life span (max.)**	**Comment**
Pelvetia canaliculata	3-5 years	fruits after 2-3 years, then degeneration
Fucus spiralis	4 years	average age 1½ years
Fucus vesiculosus	3 years or more	average age 1 year
Fucus serratus	3-4 years	average age 2 years
Ascophyllum nodosum	15 years	average age 12-13 years

Table 3. 7 Observations on the life span of macroscopic algae (Source: A.D. Boney, 1966).

Explaining the differences in ^{99}Tc accumulation among the brown algae sampled is, however, more problematic.

Based on the affinity shown by the brown seaweeds towards technetium-99, they can be divided in to two distinct groups. The first group, in descending order of accumulation are *Fucus vesiculosus* > *Ascophyllum nodosum* > *Pelvetia canaliculata* while the rest (*Dictyopteris membranacea* > *Fucus serratus* > *Fucus spiralis*) form the second group. All members of the first group members are of the Fucaceae family. *Pelvetia canaliculata* (Channelled Wrack) grows in dense tufts from about the level of high-water mark down as far as, and sometimes into, the zone of *Fucus spiralis* (Spiral Wrack). *Ascophyllum nodosum* (Knotted Wrack) occupies the middle region of the shore, usually a little higher than *Fucus vesiculosus.* The most common, *Fucus vesiculosus* also inhabits the middle regions of the shore, occupying the zone immediately above the *Fucus serratus* (Toothed Wrack).

Members of the second group, though, come from two distinct families (*Dictyopteris membranacea* from Dictyotaceae and the others from Fucaceae), but come under the same order Fucales, which includes both family members. *Fucus spiralis* grows on the upper part of the beach, immediately below the *Pelvetia* zone and above the zone occupied by *Fucus vesiculosus* and *Ascophyllum nodosum.* *Fucus serratus* is a most distinct seaweed; it is found in great masses on shelving rocky shores just above low tide level, and below the zone occupied by *Fucus vesiculosus* and *Ascophyllum*. *Dictyopteris membranacea*, is a common Mediterranean species with a limited southern distribution in the British Isles. It is not a common British Seaweed, occurring only sporadically, in the region of low spring tides or in the sub littoral.

Thus, it is observed that brown seaweeds which accumulate the higher levels of ^{99}Tc tend to occupy the upper regions of the shore. This, however, does not entirely explain the pattern observed (e.g. *Fucus spiralis* does not fit comfortably within this order).

3.2.2 Temporal variations in ^{99}Tc.

Inter-tidal biota samples, seaweeds (*Fucus sp.*), mussels (*Mytilus edulis.*) and winkles (*Littorina littorea.*) from Whitehaven and Ravenglass were analysed to identify temporal variations in technetium-99 levels, if any, due to the ^{99}Tc discharges from Sellafield. Samples spanning the time period 1989-1995 were analysed for both sites. The technetium-99 concentrations measured are presented in Table 3.8 (Whitehaven) and Table 3.9 (Ravenglass).

DATE	SEAWEEDS	MUSSELS	WINKLES
Oct-1989	2.33±0.3	NA	NA
Nov-1992	4.8±0.6	NA	NA
Mar-1993	5.2±0.6	NA	NA
Aug-1993	3.04±0.4	NA	NA
Feb-1994	4.6±0.5	0.03±0.01	BDL
Jul-1994	24.14±2.8	0.13±0.01	0.07±0.01
Dec-1994	21.5±2.5	0.15±0.02	0.05±0.01
Jul-1995	75.6±8.7	0.46±0.06	0.14±0.02

Table 3. 8 Temporal technetium-99 (kBq kg^{-1} dry wt.) distribution in seaweed, mussel and winkle at Whitehaven site (NA = not analysed; BDL=below detection limit).

DATE	SEAWEEDS	MUSSELS	WINKLES
Oct-1989	9.6±1.1	NA	NA
Nov-1992	1.8±0.2	NA	NA
Aug-1993	2.7±0.3	NA	NA
Feb-1994	3.84±0.4	0.38±0.04	0.08±0.01
Jul-1994	14.43±2	0.55±0.06	0.73±0.1
Dec-1994	82.1±9	2.12±0.24	0.83±0.1
Jul-1995	142.3±16	3.11±0.36	0.39±0.4

Table 3. 9 Temporal technetium-99 (kBq kg^{-1} dry wt.) distribution in seaweed, mussel and winkles at Ravenglass site (NA = not analysed).

In general, Ravenglass (Table 3.9) samples had higher concentrations of technetium-99 than samples taken from Whitehaven harbour (Table 3.8). This higher level at Ravenglass is in agreement with the general dispersion pattern. Ravenglass (11 km, South) is closer to the discharge location than Whitehaven (16 km, North) and lies in the direction of the predominant mean residual current off Sellafield (Howarth, 1984).

In Whitehaven harbour, the ^{99}Tc concentration in seaweed samples ranged from 2.3±0.1 to 75.6±8.7 kBq kg^{-1}. Seaweeds taken in 1989 had the lowest technetium-99 levels while maximum concentrations were observed in July 1995. During the study period levels of ^{99}Tc in the seaweeds were observed to increase by 40 times overall (Figure 3.18). The same trend was also observed in the mussel samples with the concentration of ^{99}Tc ranging from 0.03±0.01 to 0.46±0.06 kBq kg^{-1} during the study period (1994-1995) (Figure 3.19). The accumulation of technetium in winkles (Figure 3.20) was more varied although a significant increase between 1994 and 1995 levels was also observed.

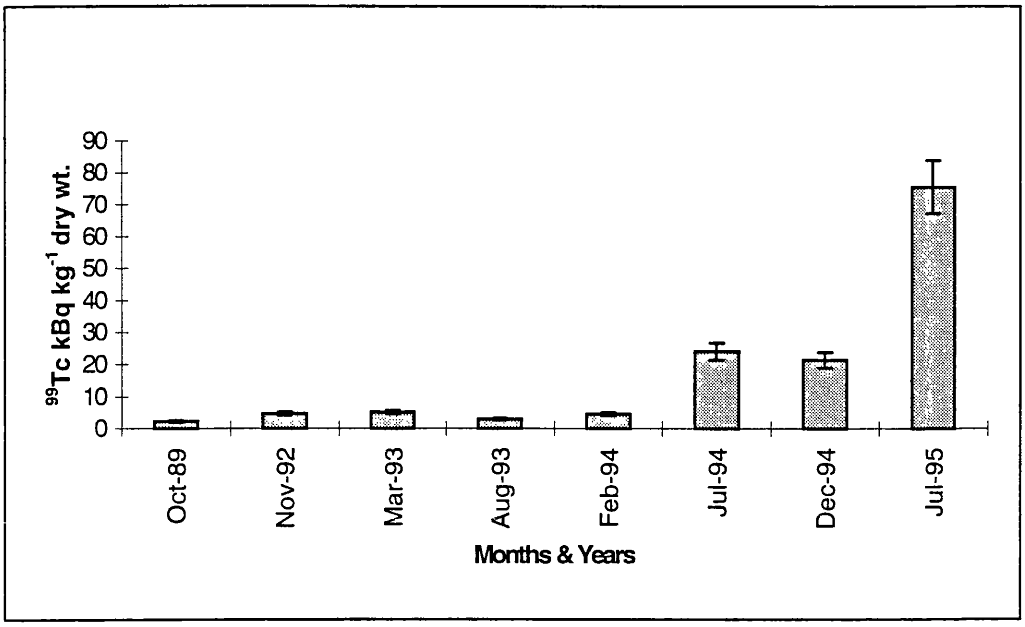


Figure 3. 18 ^{99}Tc activities in seaweeds-temporal variations (Whitehaven).

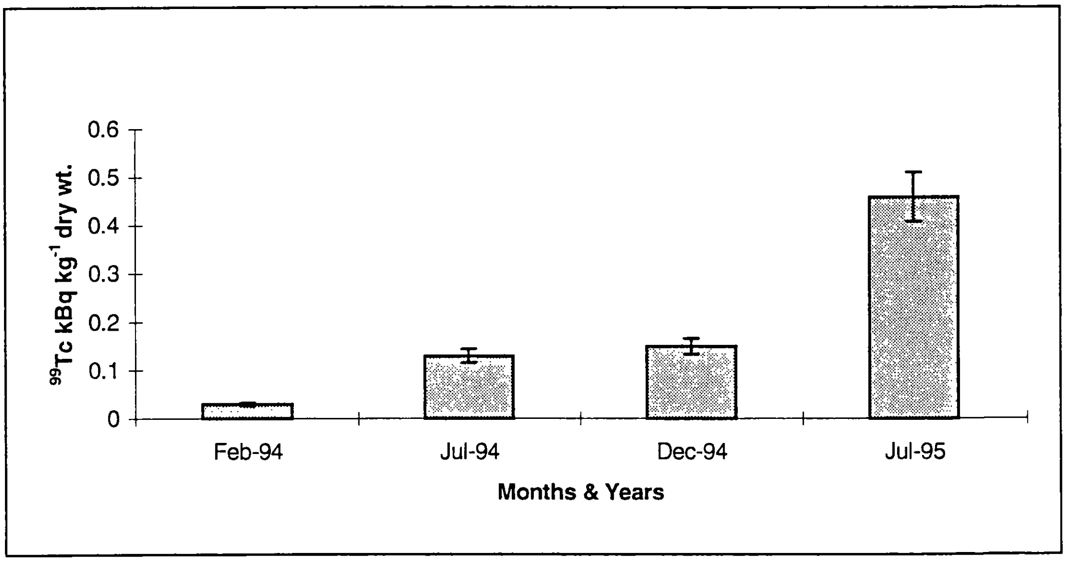


Figure 3. 19 ^{99}Tc activities in mussels - temporal variation (Whitehaven).

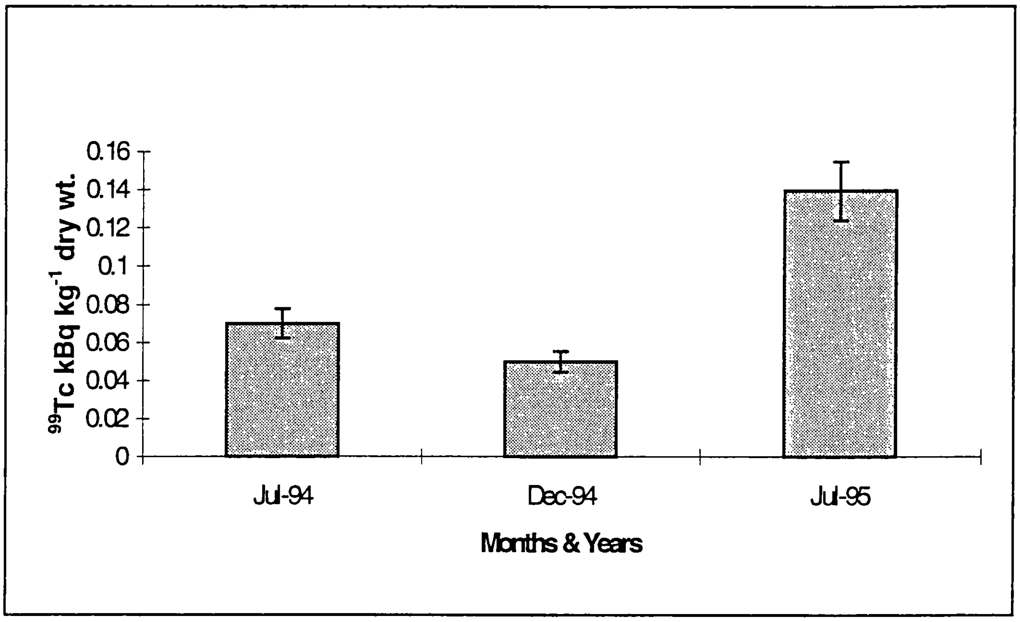


Figure 3. 20 ^{99}Tc activities in winkles - temporal variation (Whitehaven).

In Ravenglass seaweeds, the technetium-99 concentrations ranged from 1.78±0.2 to 142.3±16 kBq kg^{-1} (Figure 3.21). The sample taken in October 1989 (9.6±1.1 kBq kg^{-1} dry wt.) is in good agreement with the low levels found by Nicholson et al. (1992) in seaweeds at Ravenglass of 8.9 kBq kg^{-1} dry wt. (September 1989) and 5.8 kBq kg^{-1} dry wt. (April 1990).

The minimum seaweed concentration was found in the sample taken in November 1992, while the maximum was found in the July 1995 sample, similar to Whitehaven. In July 1994, the ^{99}Tc level in seaweed was 5 times greater than in August 1993 and continued to increase by an order magnitude (142 kBq kg^{-1}) to July 1995. In mussels, the technetium-99 concentration ranged from 0.38±0.04 to 3.11±0.4 kBq kg^{-1} (Figure 3.22). The minimum concentration was observed during February 1994, while the maximum was observed during July 1995, as in the seaweeds. In winkles, the technetium concentration was observed to fluctuate with the highest level in December 1994 (0.83±0.1 kBq kg^{-1}) (Figure 3.23). In contrast to the seaweed and mussel samples, winkles analysed during July 1995 showed a decrease in the level of technetium-99 (0.39±0.04 kBq kg^{-1}).

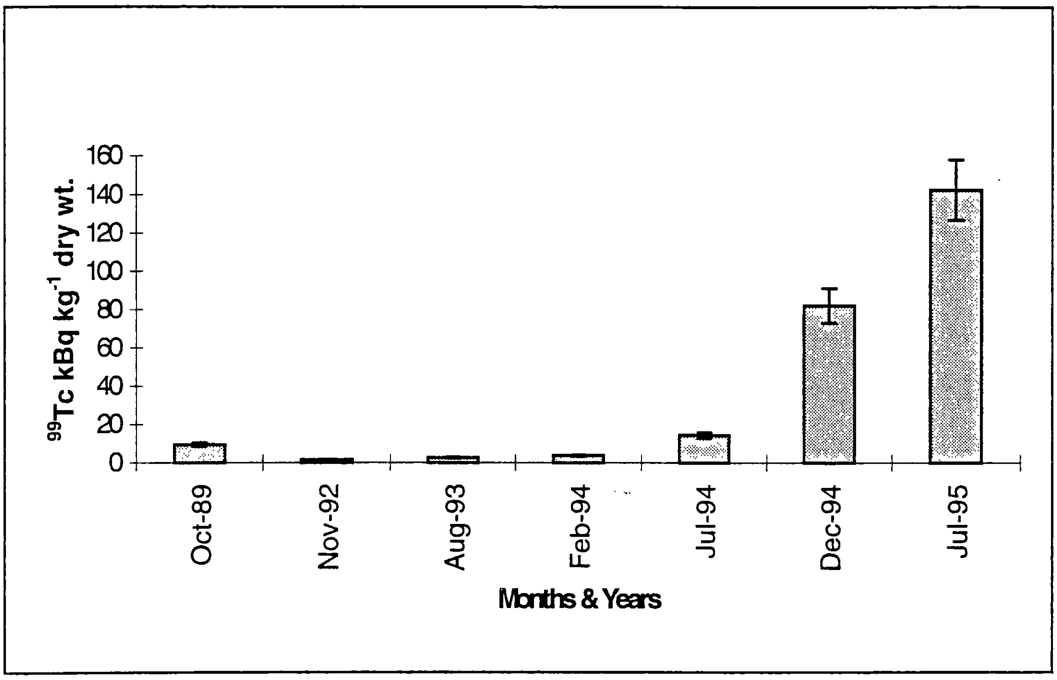


Figure 3. 21 ^{99}Tc activities in seaweeds - temporal variations (Ravenglass).

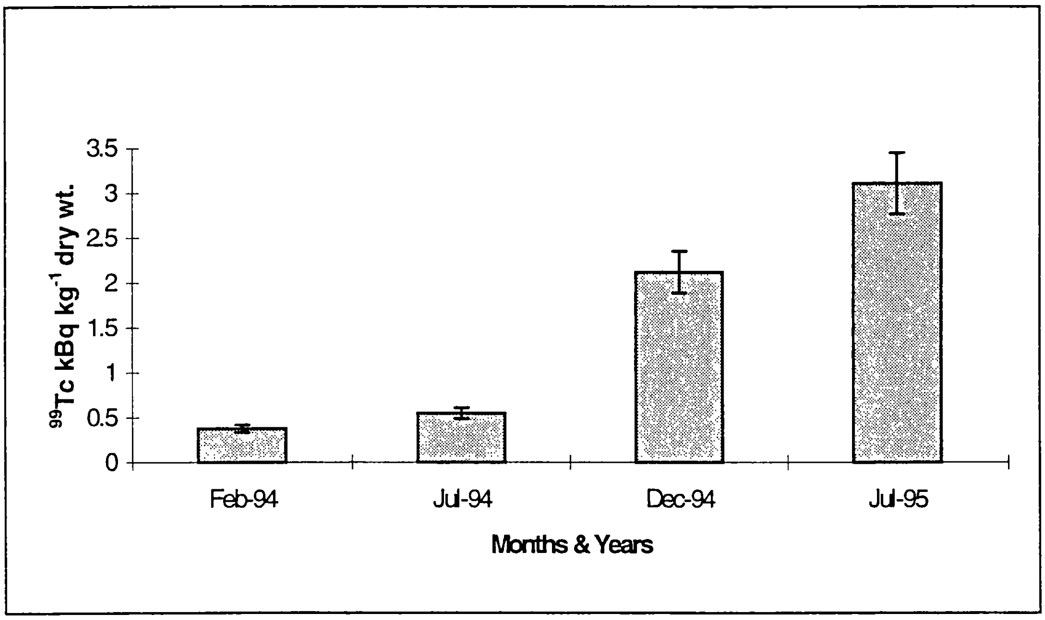


Figure 3. 22 ^{99}Tc activities in mussels - temporal variation (Ravenglass).

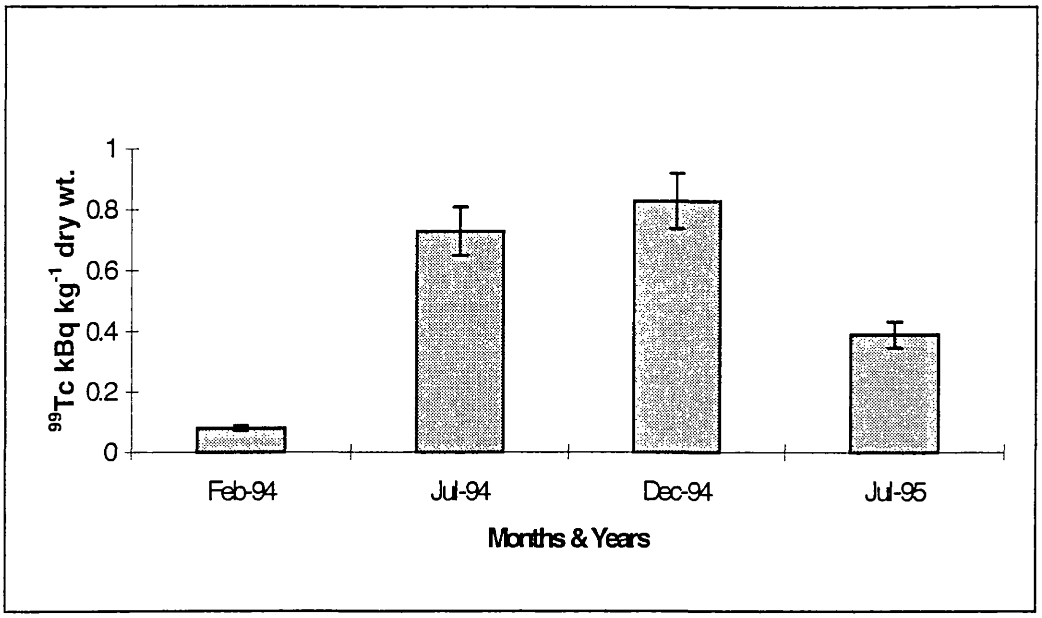


Figure 3. 23 ^{99}Tc activities in winkles - temporal variations (Ravenglass).

In comparison, the ^{99}Tc levels in the different marine species, seaweeds, mussels and winkles from Whitehaven and Ravenglass sites are presented in Figures 3.24 & 3.25 respectively.

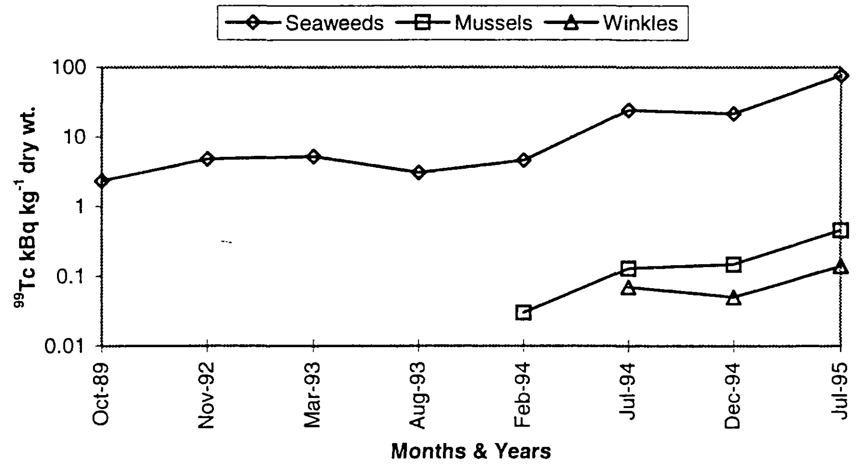


Figure 3. 24 ^{99}Tc activities in seaweeds, mussels and winkles - Whitehaven.

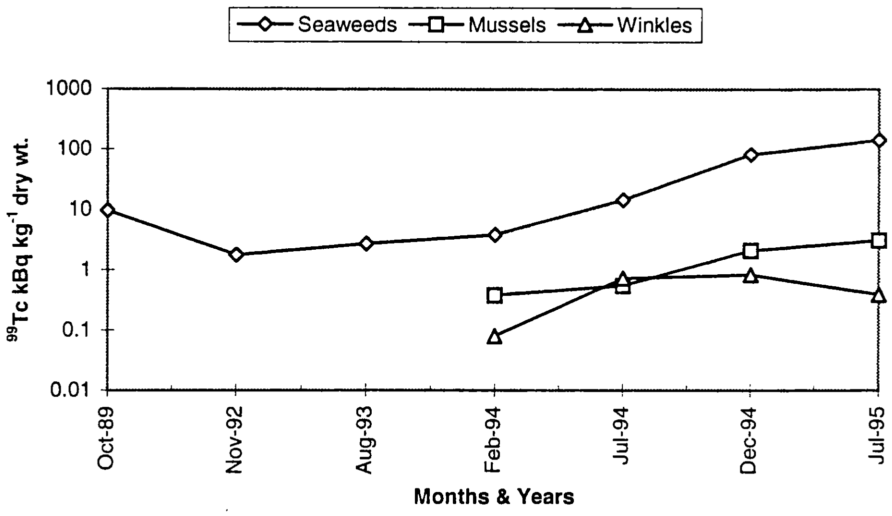


Figure 3. 25 ^{99}Tc activities in seaweeds, mussels and winkles - Ravenglass.

The samples collected in Oct-89, Nov-92, Mar-&Aug-93 and Feb-94 represent the situation before EARP, whilst those collected after that date are assumed to have been exposed to the higher discharge regime. The dramatic increase in environmental levels of ^{99}Tc is best represented by the seaweed data, due to the greater frequency of sampling. The increase in the seaweed is, however, mirrored in the rise of ^{99}Tc activities in both mussels and winkles.

This increases in technetium-99 activities from March 1994 have resulted from EARP reprocessing back-logged wastes stored on site for many years (as discussed in Chapter 1). The technetium-99 concentrations in the environment, in general, were found to be an order magnitude higher in 1995 than in previous years. This agrees with the reported ^{99}Tc discharges, which also increased by an order magnitude compared to previous years.

Figure 3.24 and 3.25 clearly demonstrates that brown seaweeds accumulates ^{99}Tc to a far greater extent than either mussels or winkles. Furthermore, these results also suggest that mussels have accumulated higher levels of ^{99}Tc than winkles at both Whitehaven and Ravenglass. Lower levels still, were observed in sediments collected from Whitehaven (33±3.6 and 84±13.7 Bq kg^{-1} dry wt. during July 1994 and 1995 respectively). As the K_d of ^{99}Tc is expected to be around 10^2 - 10^3 very little ^{99}Tc should be associated with oxic sediments (Nicholson et al., 1992).

Concentration factors (wet wt. basis) of 24000, 500 and 100 are obtained for the seaweed (*Fucus spiralis*), mussels and winkles, respectively (assuming a wet/dry ratio of 5, 5.3 and 2.8 (McDonald et al., 1992). The concentration factors quoted should be used with caution as it is unlikely that the Irish Sea system is yet in a state of equilibrium, especially given the pulsed nature of the ^{99}Tc discharges (Busby et al., 1996, in press). Nevertheless, these concentration factors do sit comfortably within the large range of values available in the literature of 10^3 - 10^5 (brown seaweeds), 10^0 - 10^4 (mussels) and 10^2 - 10^5 (winkles) (Beasley and Lorz, 1986; Beasley et al., 1982; Topcuoglu and Fowler, 1984; Masson et al., 1989; Swift, 1989). In general, the lower end of the range refer to laboratory studies and the upper end to field-based studies.

To help explain the ^{99}Tc accumulation pattern in molluscs, knowledge of their biology is essential and is discussed here based on Boyle (1981). The basic structure of a mollusc, a morphotype, is shown as a cross-section in Figure 3.26.

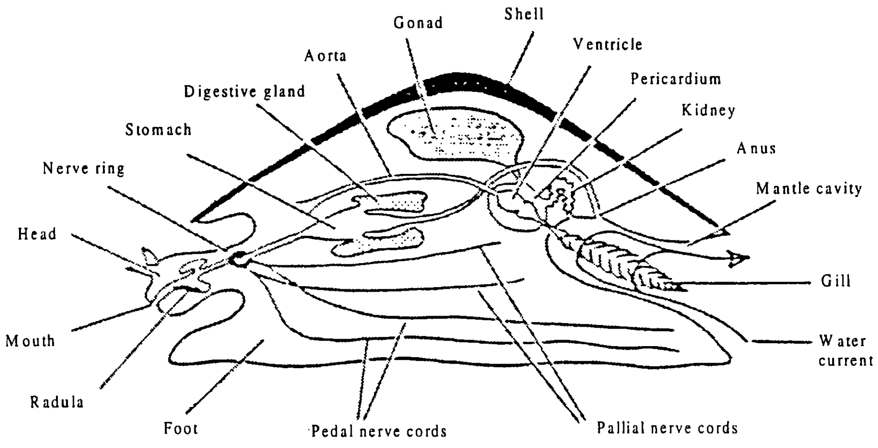


Figure 3. 26 Morphotype (Mollusca) - Cross section.

This basic mollusc has a single, conical calcareous shell surmounting a broad foot which the animal uses to move. The outer shell is made by secretion by an epithelial layer, the mantle, which covers the dorsal surface of the body. The mantle takes calcium carbonate from its environment and organises it into crystal layers within a proteinaceous matrix. The mantle edge is an important muscular region and encloses the cavity through which the animal is exposed to the environment. Feeding, is facilitated through this cavity using gills and sense organs present inside the mantle cavity. Virtually all of their activities take place through the mantle cavity including digestive (gut), reproductive and excretory functions. Based on the mantle cavity structural modifications, inside the phylum Mollusca, different classes are now described.

Winkles (e.g., *Littorina littorea*, Figure 3.27), another member of the Phylum Mollusca, under class Gastropoda, order Mesogastropoda, are detritus feeders. They feed via their mouth which opens into a complex buccal cavity enclosing a ribbon of teeth, known as radula. The radula helps in feeding by basic forward and backward movement, thus collecting particles of food into the gut. The food is then digested by the digestive gland. For reference, the structure of radula of a typical gastropod is given in Figure 3.28.

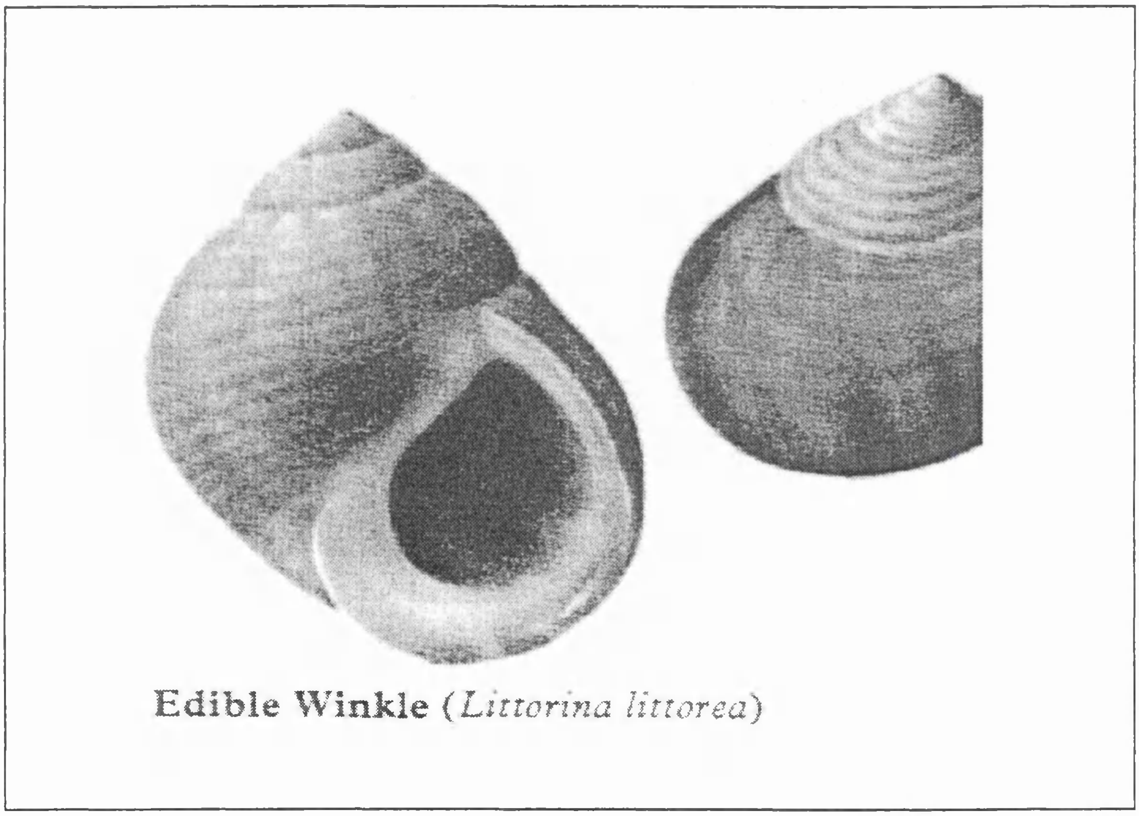


Figure 3. 27 Periwinkle - *Littorina littorea*.

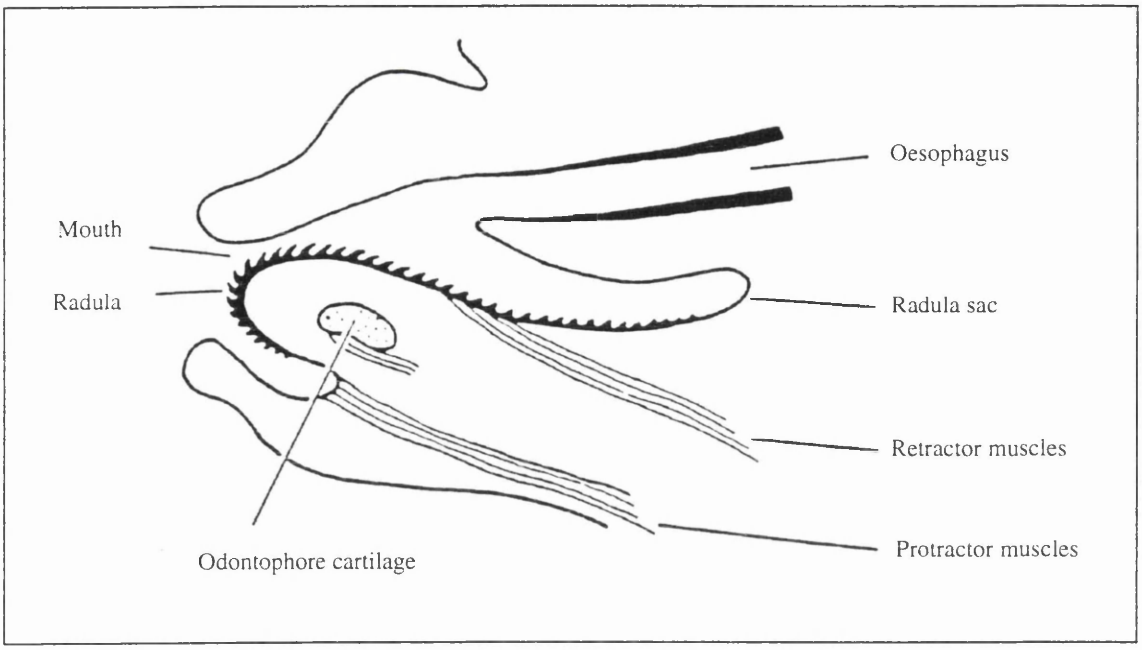


Figure 3. 28 Radula (Winkles).

Mussels (e.g., *Mytilus edulis*) are bivalvia, i.e. having two halves and are highly modified among Molluscs, belonging to class Lamellibrachiata and subclass Lamellibrachia. Mussels have no heads, and hence no 'radula' as in winkles. Typically, mussels have two symmetrical mantle flaps which enclose the whole body tissue (Figure 3.29).

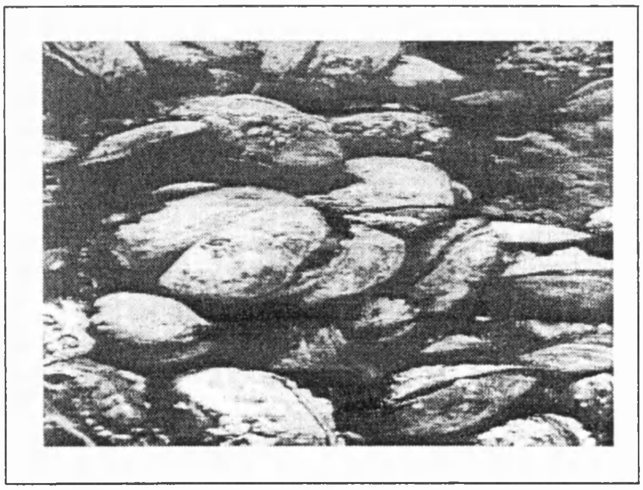
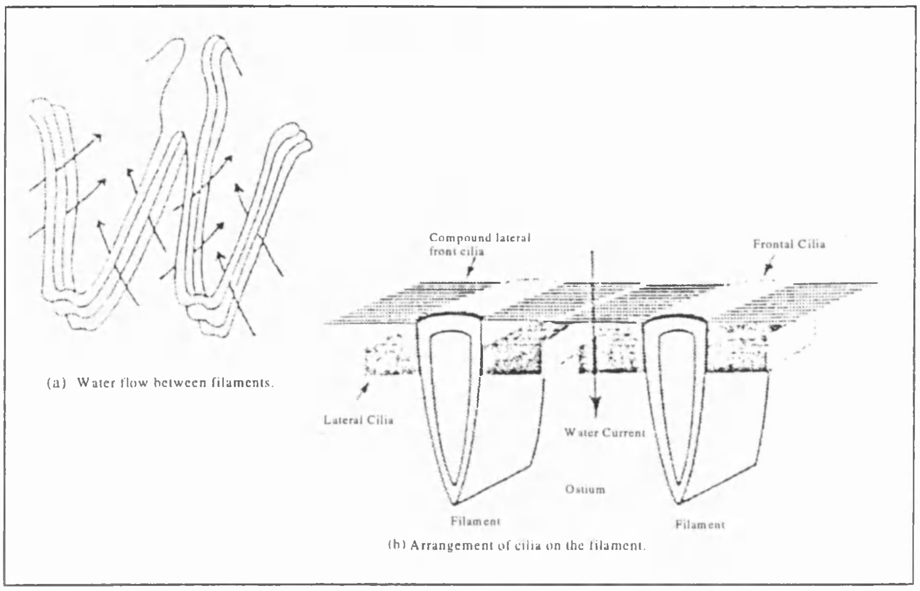


Figure 3. 29 Mussels - Bed.

These secrete right and left shells which are hinged at the dorsal line and can be closed tightly using the adductor muscles. The gills present in bivalves help mussels in respiration and extract food particles from water by way of a filtering mechanism (passing water through the mantle cavity). Figure 3.30 shows the two rows of gill filaments which hang down into the mantle, each pair are thought to be in a "W" shape.



(a) Water flow between filaments.

(b) Arrangement of cilia on the filament.

Figure 3. 30 Gills (Mussels).

The descending and ascending "arms" of each of these filaments join together by means of ciliary or tissue bridges, called cilia. In the *Mytilus edulis*, the cilia are fused together and are called cirii. There are several types of cilia which are responsible for different aspects of filter feeding. The lateral cilia generate a water current through the gills, while the frontal cilia transport the food particles through the mantle to collect in food tracts in the gill margins. These margins are grooves which stop at the mouth where a continuous "rope" of food and mucus is taken into the gut.

A detailed laboratory study using ^{95m}Tc contaminated seawater has suggested that technetium accumulation in winkles is a slow process (210 days to reach equilibrium) (Swift, 1989). Very low uptakes of technetium have also been observed in *Mytilus edulis* (Verthe et al., 1986). Concentration factors measured in the laboratory for ^{99}Tc in winkles or mussels have been very low (<2) in many cases (Fowler et al., 1981; Beasley et al., 1982; Verthe et al., 1985). Swift (1989), on the other hand, quoted a CF of 45. CFs as high as 640 (for winkles) and 330 (for mussels) were recently observed at Ravenglass (Busby et al., 1996, in press).

From laboratory studies, there is no evidence of that there is any difference in ^{99}Tc accumulation by mussels/winkles caused by their biology. This suggest that differences observed in the field are perhaps due to either the ^{99}Tc levels in what they eat (e.g. brown / red / green seaweeds) or may be an age effect. Winkles are detritus feeders (graze on phytoplankton, live and dead seaweeds) while mussel are filter feeders (grasp food particles through their gills mainly). As discussed in Chapter 1, phytoplankton are found to accumulate very little technetium. Technetium accumulation by seaweeds is also found to vary greatly between species (Section 3.2.1.1). Technetium accumulation by green and red seaweeds is far less than by brown seaweeds. So, if winkles feed primarily on green and red seaweeds (soft and highly palatable), their technetium levels will be lower than if they fed on brown seaweeds. *Littorina littorea*, for example, prefers the green algae *Enteromorpha* and *Ulva* to the Fucoids (brown algae) or to the red algae (Little and Kitching, 1996). Interestingly, some winkles (e.g., *Littorina puteolus*) are known to feed preferentially on carrageen (*Chondrus crispus*), a red seaweed (Step, 1945) and others (e.g., *Littorina littoralis, Littorina obtusata, Littorina mariae*) are found to feed on soft fronds of brown seaweeds (e.g., *Fucus vesiculosus, Fucus spiralis, Ascophyllum nodosum*) (Bakker, 1959; Purchon, 1968, Norton et al., 1990). Thus, the differential feeding habits of winkles and mussels may explain the variations in ^{99}Tc levels observed in this study.

3.2.3 Spatial variations in ^{99}Tc.

Seaweed samples collected during September/October 1989, July 1994 and July 1995 from various places along the west coast of Britain were analysed to determine the spatial variation of ^{99}Tc. The observed spatial variations in ^{99}Tc activities are presented in Tables 3.10, 3.11 & 3.12. Distances from Sellafield to sampling sites are also shown. These distances are direct measurements along the coast from Sellafield and do not represent the actual route of water currents in the area.

DATE	LOCATION/KEY	DISTANCE (km)	^{99}Tc ACTIVITY
22/9/89	Colwyn Bay (17)	125 (S)	0.7±0.1
03/10/89	Ravenglass (13)	11 (S)	9.6±1.1
04/10/89	Whitehaven harbour (9)	15 (N)	2.3±0.3
04/10/89	Sandyhills (4)	70 (N)	1.6±0.2
27/09/89	Poolewe (1)	606 (N)	0.2±0.02

Table 3. 10 ^{99}Tc activity (kBq.kg^{-1} dry wt.) in seaweeds - 1989.

DATE	LOCATION/KEY	DISTANCE (km)	^{99}TC ACTIVITY
26/07/94	Isle of Walney (15)	38 (S)	8.2±0.9
26/07/94	Haverigg (14)	30 (S)	2.8±0.3
26/07/94	Ravenglass (13)	11 (S)	25.24±2.9
27/07/94	Seascale (12)	2 (S)	40±4.6
27/07/94	Nethertown (11)	5 (N)	25.5±2.9
27/07/94	St. Bees Head (10)	10 (N)	11.9±1.4
27/07/94	Whitehaven harbour (9)	15 (N)	19.8±2.3
27/07/94	Parton (8)	16 (N)	28.2±3.2
27/07/94	Harrington (7)	20 (N)	14.9±1.7
27/07/94	Workington (6)	30 (N)	26.43±3
27/07/94	Maryport (5)	38 (N)	14.4±1.7

Table 3. 11 ^{99}Tc activity (kBq kg^{-1} dry wt.) in seaweeds - 1994.

DATE	LOCATION/KEY	DISTANCE (km)	^{99}Tc ACTIVITY
05/07/95	St. Lytham (16)	80 (S)	16.23±1.9
05/07/95	Haverigg (14)	30 (S)	23.9±2.8
05/07/95	Ravenglass (13)	11 (S)	142.3±16
05/07/95	Seascale (12)	2 (S)	213.7±25
06/07/95	St. Bees Head (10)	10 (N)	136.44±16
06/07/95	Whitehaven harbour (9)	15 (N)	75.6±9
06/07/95	Maryport (5)	38.5 (N)	19.7±2.3
06/07/95	Rockcliffe (3)	77 (N)	10.2±1.2
06/07/95	Prestwick (2)	206 (N)	1.9±0.22

Table 3. 12 ^{99}Tc activity (kBq kg^{-1} dry wt.) in seaweeds - 1995.

Generally, the ^{99}Tc concentrations are higher nearer to the Sellafield outfall and decrease with increasing distance north and south. The following paragraph discusses the hydrography of the Irish Sea, which influences the dispersion of ^{99}Tc.

The main body of the Irish Sea has a width of 75 - 200 km, decreasing to 30 km in the North Channel and has an overall approximate volume of 2400 km^3. In the west, a deep channel 300 km long and 30 - 50 km wide opens to the Celtic Sea in the south and the Malin Shelf in the north, by St. George's and North Channel respectively. Flows of

Atlantic water into the Irish Sea have been extensively studied using caesium distributions, with fluxes of 2.2 km^3 d^{-1} for inflow *via* St. George's Channel (Bowden, 1950) and 2.7 - 8 km^3 d^{-1} for outflow *via* the North Channel (Jefferies et al,, 1982; McKay and Baxter, 1985). Dickson and Boelens (1988) have postulated that flow through the North Channel occurs in both directions, with fluxes of 10.3 km^3 d^{-1} and 3.0 km^3 d^{-1} for the northward and southward flows respectively. They have also produced a map of the predominant residual surface currents (Figure 3.1) which are in agreement with direct current measurements and radioactive tracer distributions. All these indicate a northward flow of Irish Sea water through the North Channel with some southward flow of Atlantic water. However, in the Eastern Irish Sea, a southward drift of surface water along the Cumbrian coastline from St. Bees Head is present.

Figure 3.31 illustrates the dispersion pattern of technetium-99 before EARP (1989).

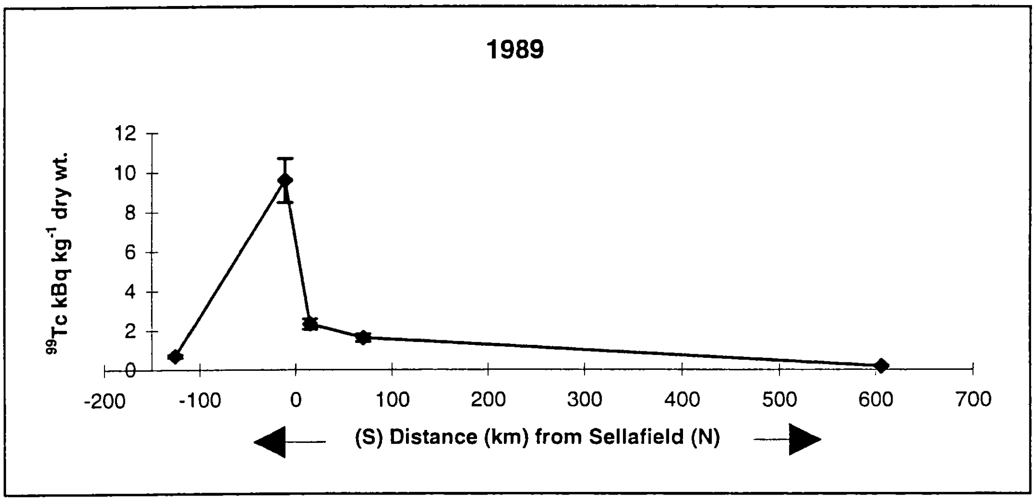


Figure 3. 31 ^{99}Tc activity in seaweeds - spatial variations (1989).

Figures 3.32 and 3.33 illustrates the dispersion pattern of technetium-99 from samples taken after EARP discharges.

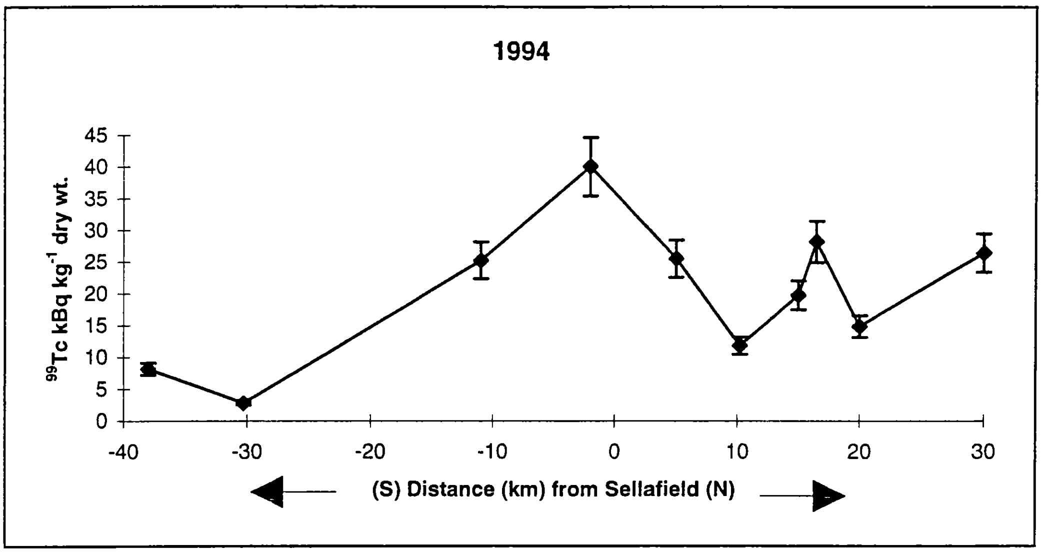


Figure 3. 32 ^{99}Tc activity in seaweeds - spatial variations (1994).

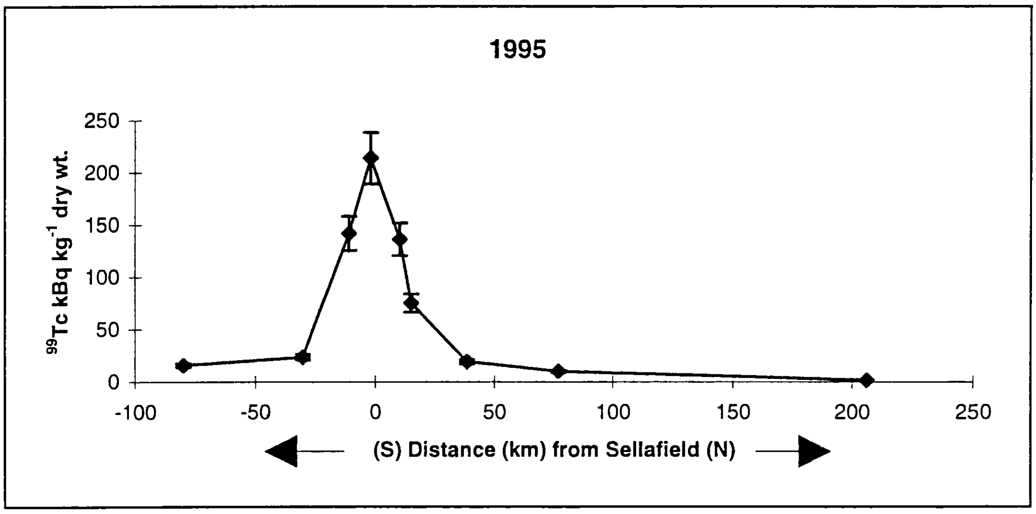


Figure 3. 33 ^{99}Tc activity in seaweeds - spatial variations (1995).

The seaweeds analysed were mainly composed of *Fucus vesiculosus*, however, there was a small chance that other brown seaweeds may be mixed in with these. To correct for this, if necessary, the brown seaweed *Fucus spiralis*, was collected during July 1995 at most sampling sites. The observed spatial variations are given in Figure 3.34 and it appears very similar to Figure 3.33 for general seaweeds during the same period.

Clear peaks, at the sites closest to Sellafield, are seen in 1989 and 1995 but not in 1994. It was thought that this may be due to sampling different types of brown seaweeds - but data in Figure 3.34 show that this is not necessarily the case. This suggests that it may be due to incomplete mixing of newly discharged slugs of ^{99}Tc from EARP.

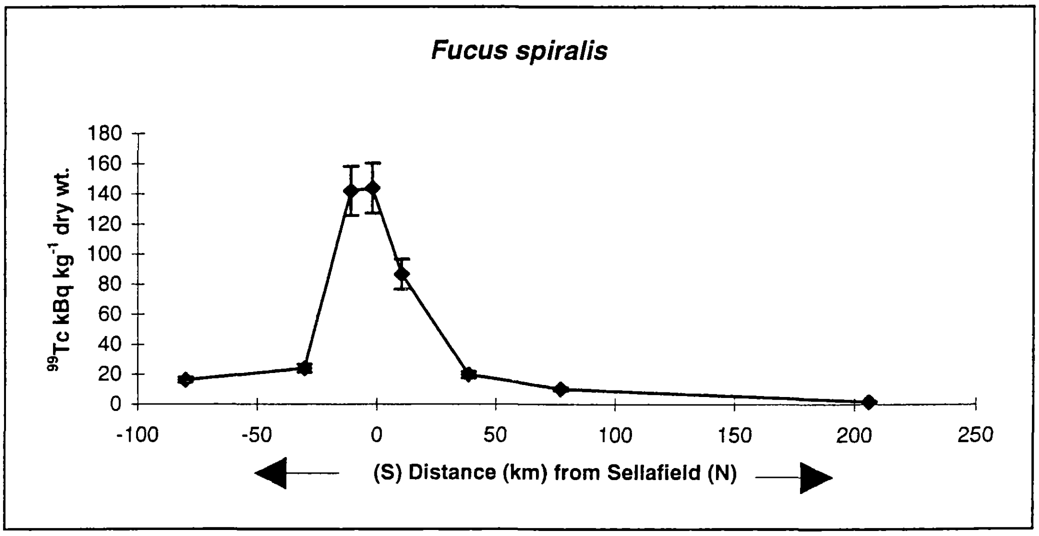


Figure 3. 34 ^{99}Tc activity in *Fucus spiralis* - spatial variation.

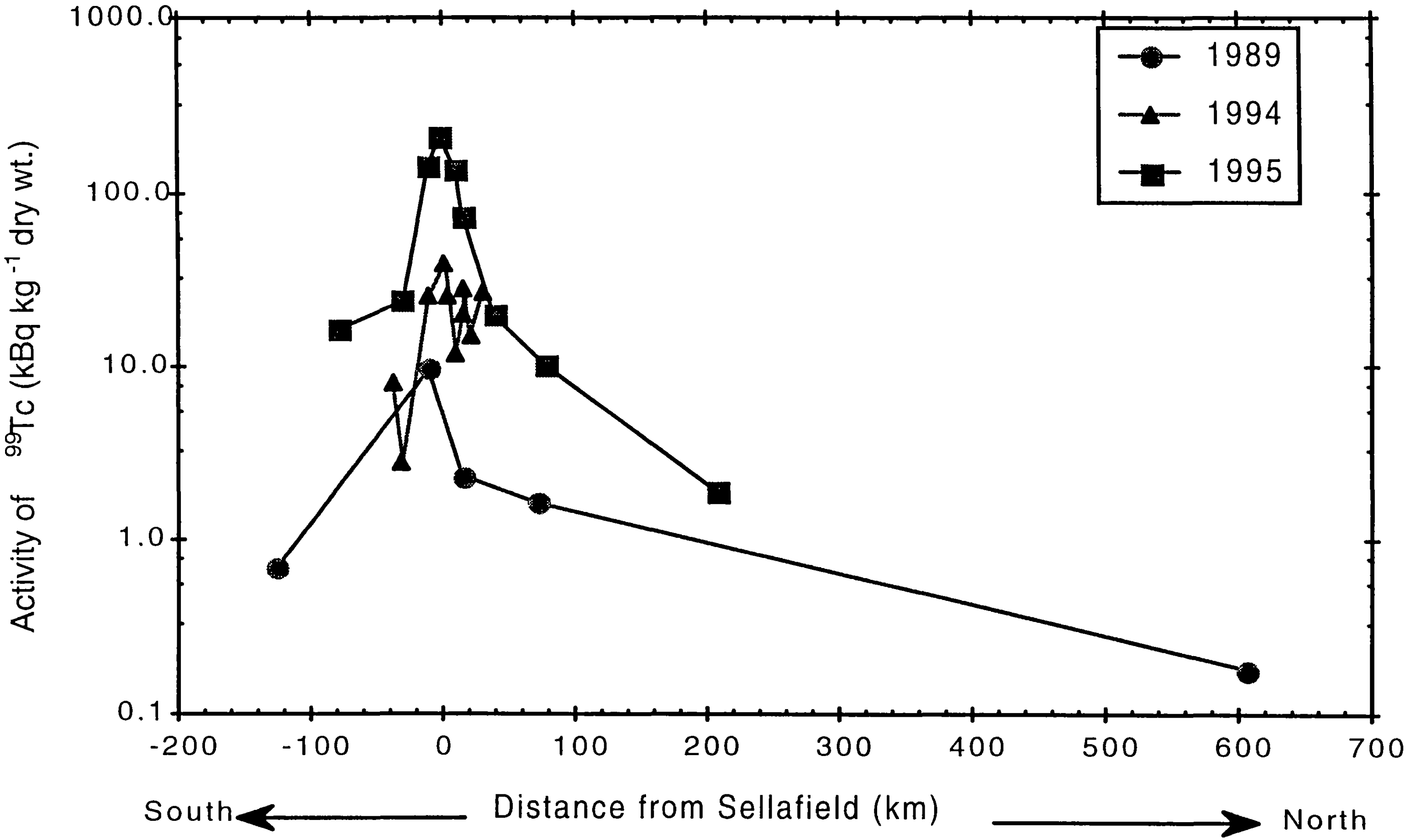


Figure 3. 35 Spatial distribution of ^{99}Tc during 1989, 1994 and 1995.

The results for all three years are shown in Figure 3.35. The low levels of technetium observed in 1989 shows the pre-EARP situation. The concentration of technetium-99 in seaweed before EARP, was very low (<2.00 kBq kg^{-1}) for sites away from the Sellafield outfall, however, for Ravenglass it was around 10 kBq kg^{-1}. The low level of ^{99}Tc at sites farther away can be attributed to the greater dilution of the technetium discharges from Sellafield with distance. Recently, the EARP discharges greatly enhanced the level of technetium-99 in the surface water throughout the sampling area. For example, maximum concentrations of ^{99}Tc around Sellafield increased from 9.6 kBq kg^{-1} (dry wt.) in 1989 to 40 and 213.7 kBq kg^{-1} (dry wt.) in 1994 and 1995 respectively. The EARP pulses were found to enhance ^{99}Tc concentrations in seaweeds up to 77 km north and 80 km south of Sellafield.

Although the aim of this study was not to calculate transit times the results indicate that a) ^{99}Tc is behaving conservatively in seawater, b) *Fucus* species respond rapidly to environmental levels and could be used for this purpose. This is also suggested from the observed temporal variation of ^{99}Tc distribution in seaweeds (Figures 3.18 - 3.23).

3.2.4 Sediment Core Analysis.

Sediment radionuclide concentration profiles are often used as a tool for studying Sellafield discharges to the Irish Sea. It has been demonstrated that sediment profiles can preserve a temporal record of Sellafield discharges. Kershaw et al. (1990) estimated discharge rates for ^{238}Pu based on sediment cores taken from Maryport Harbour, where such releases were not measured. As discussed in Chapter 1, ^{99}Tc discharge data from Sellafield are not available prior to 1978 and so, by measuring the ^{99}Tc activity profile of a suitable sediment core, it was hoped to get an indication of environmental levels of ^{99}Tc prior to '78.

A core (1-m depth) had been collected from Southwick water (Solway Coast), south-west Scotland (Figure 3.36) during 1986 and dated using sediment radionuclide profiles (MacKenzie et al., 1994). The same core has been used for the present study and analysed for ^{99}Tc. This sediment core was sectioned mostly at 5 cm length.

Detailed descriptions of the study area have been presented elsewhere (MacKenzie et al., 1989; Hooker, 1990; Scott et al., 1991). Importantly, the erosion of vertical river banks leads to very rapid sediment accumulation. This sediment accumulation rate can be seen visually on a scale of centimetres per year. The present core was collected from a location which is in the accretion stage of this cycle. Details of sections made from the core and their analyses for different radionuclides were detailed in earlier work (MacKenzie et al., 1994). This study area has been found to experience rapid accumulation of sediment with little post-depositional mixing (MacKenzie et al., 1994) and is thus suitable for studying temporal variations in sediment radionuclide deposition transported from Sellafield.

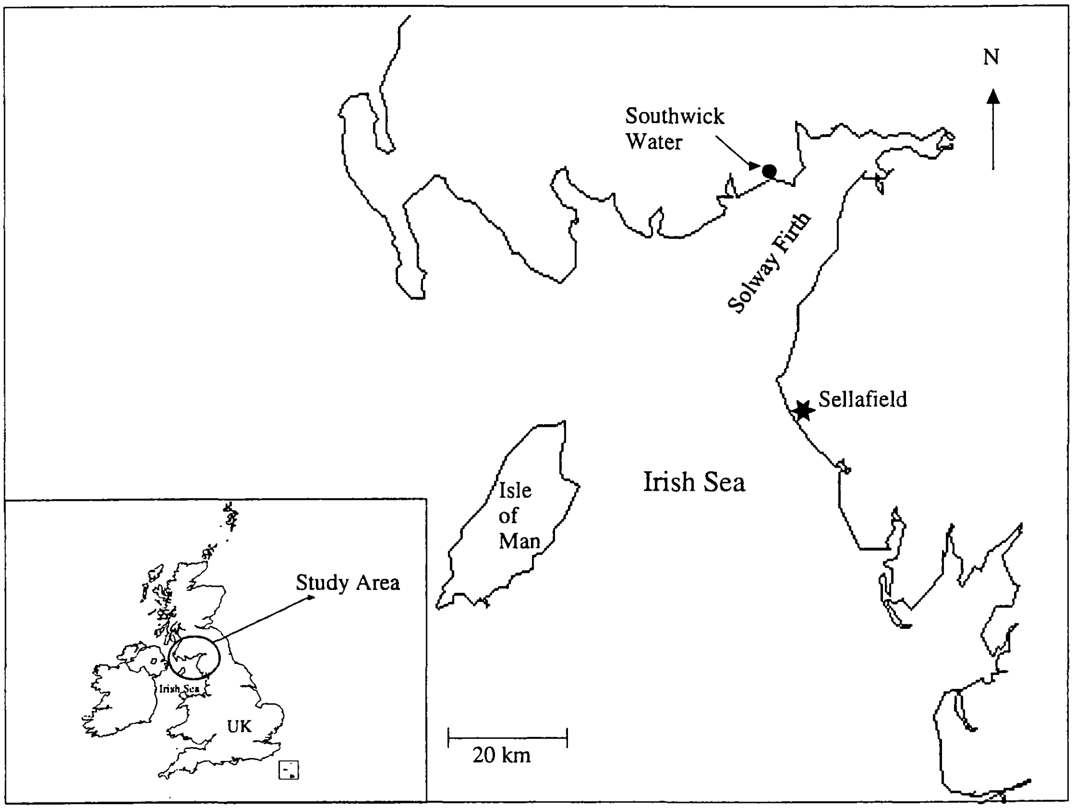


Figure 3. 36 Map showing sediment core sampling site (Solway Firth, South-west of Scotland).

The data already available for this core, ^{137}Cs, ^{241}Am and ^{239,240}Pu concentration profiles, are shown in Figure 3.37. The supply of Sellafield waste radionuclides to the study site can be considered to involve one of two transport mechanisms (or a combination), namely solution transport or particulate transport.

Although the data bear a qualitative resemblance to the Sellafield discharge pattern, MacKenzie et al. (1994) did not find any significant linearity between ^{137}Cs, ^{241}Am and ^{239,240}Pu activities and annual discharge rates from Sellafield.

MacKenzie et al. (1994) have further implied that the isotope activity ratios at any given depth in sediment (decay corrected to the time of deposition) should be equal to those of the Sellafield discharge of the appropriate year if a simple mechanism involving solution transport was operating. Examination of the core data, confirmed that the activity ratios between ^{137}Cs, ^{241}Am and ^{239,240}Pu are completely incompatible with solution transport. MacKenzie et al. (1987) have identified the movement of contaminated silt as the dominant mechanism of supply of Sellafield waste radionuclides to the Solway Coast.

In particulate transport, the radionuclides are assumed to be partitioned between aqueous and solid phases upon discharge. Thus the particle-reactive radionuclides (e.g., most actinides) are rapidly taken up by surface sediment close to the discharge point relative to the soluble species (e.g. ^{137}Cs, ^{99}Tc). The deposited nuclides can be subsequently transported by sediment reworking and dispersal processes. The sediment which is transported will have been mixed vertically before its transport. Thus the radionuclide concentrations and activity ratios in the sediment can be related to those of the time-integrated discharge (allowing for radioactive decay and growth), rather than annual discharges. MacKenzie et al. (1994) found excellent correlation between nuclide activities and activity ratios with the time-integrated discharges.

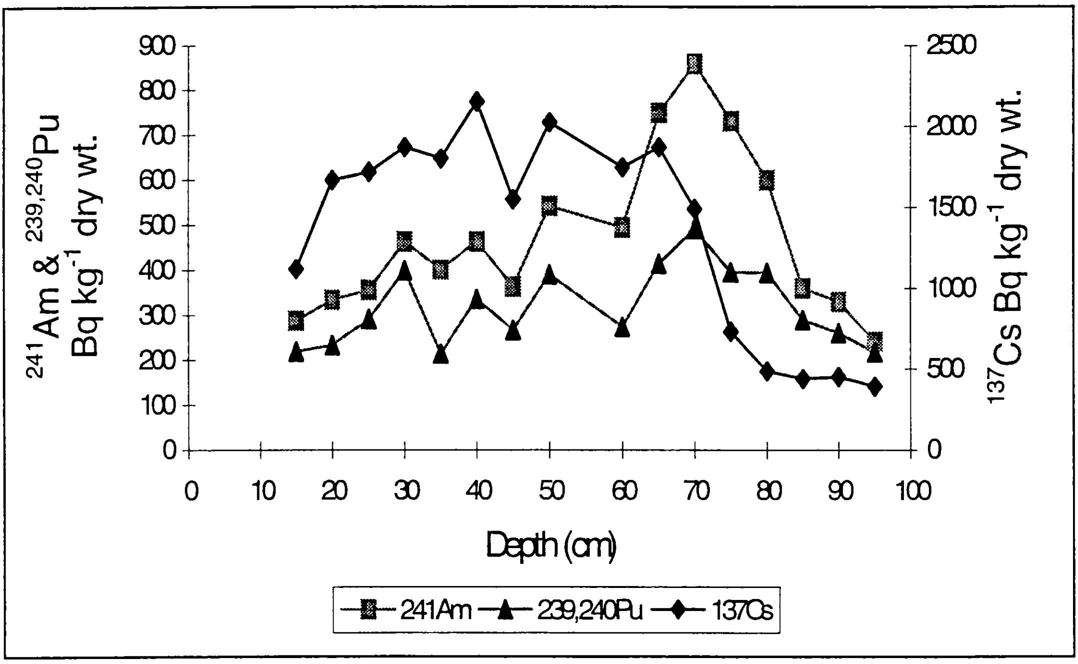


Figure 3. 37 Sediment ^{137}Cs, ^{241}Am and ^{239,240}Pu activity profiles versus depth (cm) (MacKenzie et al., 1994).

The ^{99}Tc concentration profile obtained in the present study is shown in Table 3.13 & Figure 2.38.

Depth (cm)	^{99}Tc* (Bq kg^{-1})	^{137}Cs (Bq kg^{-1})	^{241}Am (Bq kg^{-1})	^{239,240}Pu (Bq kg^{-1})
2-4	8.7±1.0	572±19	185±20	146±3
4-6	1.6±0.2	655±21	183±20	99±4
8-10	6.7±0.7	1084±33	279±29	232±12
10-15	8.6±0.9	1118±34	288±30	219±9
15-20	9.7±1.1	1667±49	334±34	234±13
20-25	9.9±1.1	1716±50	356±36	291±11
25-30	12.9±1.5	1871±55	464±46	400±18
30-35	19.3±2.2	1801±53	402±40	215±9
35-40	5.9±0.7	2152±63	464±46	336±10
40-45	3.8±0.4	1549±45	364±37	267±13
45-50	7.3±0.8	2023±59	543±53	390±12
55-60	4±0.5	1747±51	496±48	274±11
60-65	5.9±0.7	1871±55	750±71	415±19
65-70	8±0.9	1491±44	859±80	493±23
70-75	15.5±1.8	734±24	732±69	396±11
75-80	11±1.3	489±17	601±57	395±12
80-85	9.2±1.0	441±15	361±36	290±11
85-90	6.5±0.8	453±16	330±33	261±10
90-95	1.7±0.2	393±13	242±26	218±9

Table 3. 13 Levels of ^{99}Tc, ^{137}Cs, ^{241}Am and ^{239,240}Pu in Sediment core (Bq kg^{-1} dry wt.) (*50g sediment sample sizes were used for ^{99}Tc extraction).

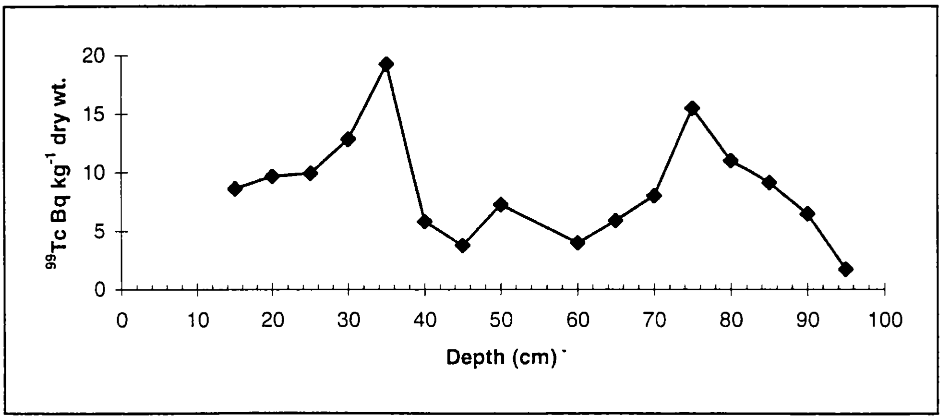


Figure 3. 38 Sediment ^{99}Tc activity profile of the core versus depth (cm).

^{99}Tc levels varied between 1.7 and 19.3 Bq kg^{-1} dry wt. throughout the core. Two major peaks were observed, one at 30-35 cm and the other at a depth of 70-75cm.

Based on the dating system used in the earlier study (4.9 cm yr^{-1}, MacKenzie et al., 1994), the ^{99}Tc profile is plotted against time along with ^{99}Tc discharge data (Figure 3.39).

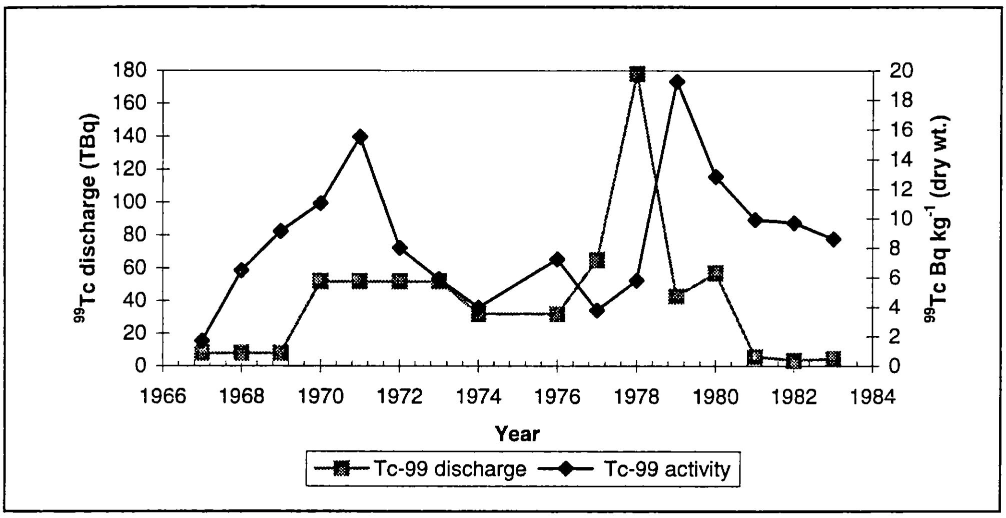


Figure 3. 39 Comparison of temporal variation in ^{99}Tc annual discharge rates (TBq) with observed ^{99}Tc profile in the sediment core (Bq kg^{-1} dry wt.)

^{99}Tc discharge data before 1978 were estimated from ^{99}Tc levels in seaweeds collected from Greenland waters (Aarkrog et al., 1987). The predicted annual discharge rates were 8 TBq (1952-1969), 52 TBq (1970-1973), 32 TBq (1974-1976) and 65 TBq (1977).

A peak observed in the ^{99}Tc sediment profile at 30-35 cm resembles the peak ^{99}Tc discharge rate reported for 1978. After 1978, the ^{99}Tc levels in the sediment followed the decrease in the ^{99}Tc discharge rate. The observed decrease in sediment ^{99}Tc concentration is, however, far less than the decrease in discharge rates, which, in turn, supports the arguments that the supply of ^{99}Tc to the study site is controlled by the "integrated discharges" in off-shore sediment. Prior to 1978 there is a very little agreement between the ^{99}Tc levels measured in the core and the predicted discharges. It is interesting to note that previous data (Figure 1.9) have also indicated that environmental levels of ^{99}Tc prior to 1978 have been similar to those observed after the 'peak' discharges of 1978. Thus, it may be that the high levels of ^{99}Tc now present in the environment after EARP are no higher than levels present in the late 60s and early 70s.

The present data set can be compared with earlier off-shore sediment cores measured by Nicholson et al. (1992). In the first core (54°21 'N 3°38 'W), the maximum technetium-99 concentration observed (23 Bq kg^{-1}) was in the 10-20 cm section, followed by 0-5 cm (18 Bq kg^{-1}) and then 5-10 cm (16 Bq kg^{-1}). In the second core (54°30 'N 3°44 'W), a higher concentration (15 Bq kg^{-1} dry wt.) was found in the surface (0-5 cm) and decreased with increasing depth. In both cores, lower values were observed in the 20-30 cm section. The technetium-99 levels observed are comparable with the present data. The two seabed cores have a contrasting distribution of ^{99}Tc even though both were taken close together. It was suggested that the variations observed in between the first and second core were due to bioturbation processes (the mixing of seabed sediments by marine organisms (Nicholson and MacKenzie, 1989). Nevertheless, the absolute levels of ^{99}Tc in the surface sediments are of a similar magnitude to the levels observed in the saltmarsh core and thus could be the source material.

Although discharge data on technetium-99 from Sellafield are incomplete, attempts were made to normalise the sediment ^{99}Tc activity to integrated discharge rates with other radionuclides. This approach was used by MacKenzie et al. (1994) to support their 'particulate transport' hypothesis. The obtained ratios are presented in Figure 3.40 (Tc/Cs ratios) and Figure 3.41 (Tc/Pu ratios) normalised to their annual and integrated Sellafield discharges.

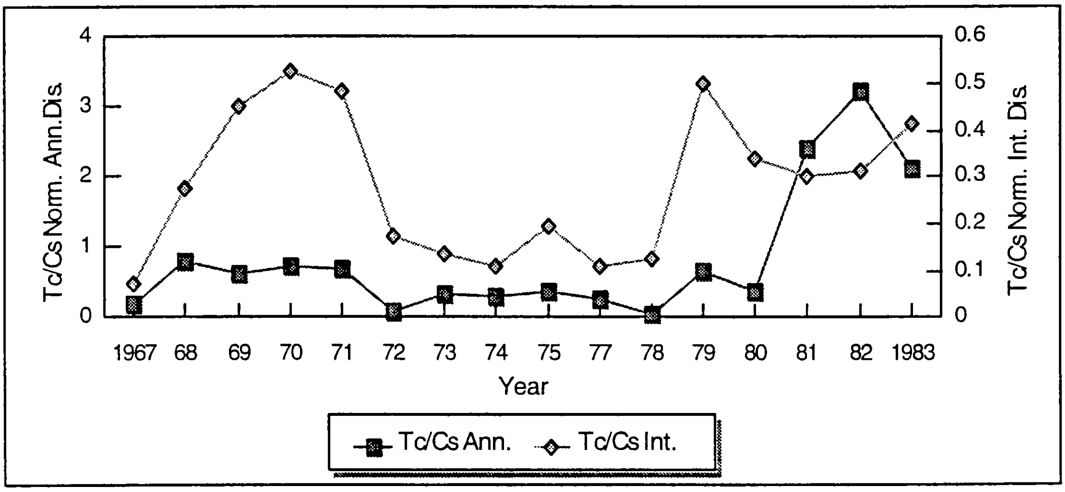


Figure 3. 40 ^{99}Tc/^{137}Cs activity ratios normalised to their corresponding ratios in annual and integrated discharge rates.

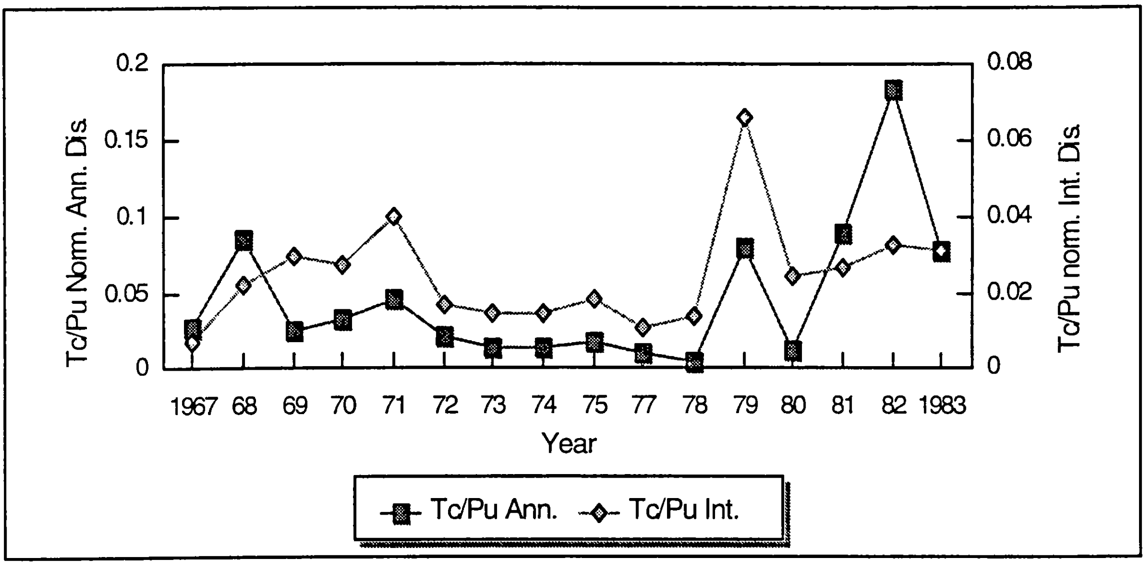


Figure 3. 41 $^{99}Tc/^{239,240}Pu$ activity ratios normalised to their corresponding ratios in annual and time integrated discharge rates.

The observed Tc/Cs ratios are far higher (10 times) than Tc/Pu ratios due to the higher Kd shown by plutonium (Hetherington, 1975). No meaningful difference between the activity ratios normalised to either the annual or integrated discharges could be derived. Given the huge uncertainty in historic discharges of ^{99}Tc from Sellafield, however, this is perhaps not surprising.

3.2.5 ^{99}Tc in Saltmarshes.

Saltmarshes are important ecological areas, where transfer of radionuclides from the marine environment to the terrestrial foodchain is possible. Samples of soil, grass and plants were taken from the saltmarsh near Newbiggin in the Ravenglass estuary during July 1995.

Three plant samples were collected from the top, middle and bottom regions of the bank. Soil samples were also collected from these three regions. A grass sample was also collected from the top region. Technetium-99 levels in soil and plant samples are presented in Table 3.14. The grass sample had the highest technetium-99 level (1.18±0.05 kBq kg^{-1} dry wt.) while soil taken near the grass was below the detection limit. The grass occurs at the very top region of the mud bank, and their fibrous roots are capable of more absorption than the tap root system of woody plants (higher plants). The soil collected near the surface of the grass was however rather sandy. The plant samples taken at three different regions show in order of ^{99}Tc accumulation, bottom region > middle region > top region while for the soil the pattern is top region > bottom region > middle region.

The variations observed in soil are perhaps due to the heterogeneous nature of the soil. The difference in ^{99}Tc levels between the plants can be explained by water inundation. The top and mid region plants can be compared with earlier data available for grass samples taken at above high water mark (HWM) (12 to 18 Bq kg^{-1}) and at HWM (11-34 Bq kg^{-1} dry wt.) in 1990 (Nicholson et al., 1992). The observed order of magnitude increase in ^{99}Tc activity in plants was comparable to the order of magnitude increase in ^{99}Tc discharges from Sellafield.

SAMPLES	^{99}Tc (Bq kg^{-1} dry wt.)
Grass (top region)	1179±54
Soil (under grass)	BDL
Bottom region plant	770±26
Middle region plant	606±29
Top region plant	518±116
Top region soil	177±6
Middle region soil	93±12
Bottom region soil	123±9

Table 3. 14 ^{99}Tc activity in saltmarshes (BDL = Below Detection Limit).

3.2.6 $^{137}Cs/^{99}Tc$ ratio.

3.2.6.1 Introduction.

Technetium-99 is believed to behave conservatively, similar to ^{137}Cs, in the aquatic environment. Sellafield derived radiocaesium has been widely used as an oceanographic tracer in the marine environment in the past. In order to compare and contrast the ^{99}Tc and ^{137}Cs behaviour, ^{137}Cs was also measured in all seaweeds collected during this study and the Cs/Tc ratios calculated. The $^{99}Tc/^{137}Cs$ activity ratio has been used as an effective method of monitoring the behaviour of ^{99}Tc in the environment (Attrep et al., 1971; Holm, 1988; Garcia-leon et al., 1993).

3.2.6.2 Samples & Methods

Seaweed samples used for technetium analysis were measured for ^{137}Cs. About 20 g of dried seaweed powder was placed in a plastic container, tightly closed and counted. The efficiency of the detector was measured using a known activity of ^{137}Cs spike mixed with seaweed powder.

The detector used to measure ^{137}Cs was a germanium lithium drifted (Ge(Li)) detector having 21% relative efficiency to a 3"x3" Na(I) crystal co-axial detector. It had a resolution better than 2 keV for the ^{60}Co peak at 1332 keV. The detector was protected against external γ -radiation by lead shielding. Thus, the overall background at the photopeak of 661.6 keV, corresponding to the γ -emission of ^{137}Cs, is reduced. The geometry size was kept constant by using the same cut plastic containers. All samples were counted for a minimum of 160,000 seconds.

The detector efficiency was determined by counting algal material in the standard geometry, homogeneously spiked with a known ^{137}Cs activity. ^{137}Cs spike was obtained from Amersham International plc. ^{137}Cs liquid spike (63.98 Bq) was carefully added to 20g of seaweed (dried) powder, and dried under an infra red lamp. After initial evaporation, the spiked powder was thoroughly mixed and left for complete drying. The dry spiked seaweed powder was transferred to a plastic container made specially to hold 20g of seaweed powder, and gamma counted. Events produced in the detector are amplified and stored using a Canberra Series 85 MCA and analysed with SpectranAT software run on IBM PC-AT. An efficiency of 2.29% was calculated for ^{137}Cs at 661.6 keV with 1.02% error.

The calibration was periodically counter-checked using IAEA Reference materials (Sample Nos.156, 307, 308 and AG-B-1), and the results obtained are presented in Table 3.15.

Sample Code	Original activity	Activity corrected	Activity observed
IAEA AG-B-1	16.7	13	13.1±10%
IAEA 307	4.9	4	5.2±18%
IAEA 308	5.6	5	6.1±13%
IAEA 156	264	216	215.8±2%

Table 3. 15 IAEA Reference samples measurement for ^{137}Cs (Bq kg^{-1} dry wt. ±1 sigma error).

3.2.6.3 Results & Discussion.

The observed inter seaweed species variation in ^{137}Cs & ^{137}Cs/^{99}Tc activities ratios are given in Table 3.16. Large variations in the ^{137}Cs/^{99}Tc activity ratios are not only observed between sites but also within different seaweed species collected from the same site. For example, the ^{137}Cs/^{99}Tc activity ratios in *Chondrus crispus* and *Fucus spiralis*, collected from Ravenglass in 1995 were 6.7×10^{-2} and 9.8×10^{-4} respectively. In order to explain this variation it is worth considering the inter-species variation in ^{137}Cs concentrations.

Green seaweeds accumulated ^{137}Cs equally well as brown seaweeds. Among the seaweeds analysed from St. Bees Head and Whitehaven harbour the green seaweed (*Enteromorpha linza*) had the highest ^{137}Cs activity, followed by brown seaweeds (e.g., *Fucus vesiculosus*). In contrast to this, brown seaweeds registered higher levels of caesium-137 than green seaweeds at Ravenglass. In general, green seaweeds are efficient in bio-accumulating caesium-137 from the environment (Pentreath, 1978). The red alga, *chondrus crispus*, collected from Ravenglass site, also accumulated caesium comparably to green alga.

Site/Sample	Species	^{137}Cs (Bq kg^{-1} dry wt.)	^{137}Cs/^{99}Tc
St. Bees			
Green alga	*Enteromorpha linza*	83.4±4.9	5.8×10^{-2}
Brown alga	*Ascophyllum nodosum*	36.1±4.2	3.0×10^{-4}
Brown alga	*Fucus spiralis*	39±4.7	4.50×10^{-4}
Brown alga	*Fucus vesiculosus*	67.5±2.8	4.95×10^{-4}
Seascale			
Brown alga	*Dictyopteris membranacea*	50.3±4.7	4.36×10^{-4}
Brown alga	*Fucus serratus*	72.3±5.6	4.55×10^{-4}
Brown alga	*Fucus spiralis*	56.7±5.3	3.93×10^{-4}
Brown alga	*Fucus vesiculosus*	35±2.4	1.64×10^{-4}
Ravenglass			
Green alga	*Enteromorpha linza*	54.5±6.7	4.41×10^{-2}
Brown alga	*Dictyopteris membranacea*	141.2±5.5	6.57×10^{-4}
Brown alga	*Fucus spiralis*	139.1±5.2	9.78×10^{-4}
Red alga	*Chondrus crispus*	60.4±5.2	6.70×10^{-2}
Whitehaven			
Green alga	*Enteromorpha linza*	136.7±5.2	4.47×10^{-1}
Brown alga	*Ascophyllum nodosum*	32±4.2	7.44×10^{-4}
Brown alga	*Fucus vesiculosus*	58.5±4.4	7.73×10^{-4}
Haverigg			
Brown alga	*Fucus spiralis*	93.4±6.8	3.90×10^{-3}
Maryport			
Brown alga	*Ascophyllum nodosum*	52.5±8.2	1.77×10^{-3}
Brown alga	*Fucus spiralis*	94±7.3	4.78×10^{-3}
Prestwick			
Brown alga	*Fucus spiralis*	54.6±6.8	2.85×10^{-2}
Rockcliffe			
Brown alga	*Pelvetia canaliculata*	49.1±4.7	3.41×10^{-3}
Brown alga	*Fucus spiralis*	58.8±4.8	5.76×10^{-3}
St. Lytham			
Brown alga	*Fucus spiralis*	82.3±5.8	5.07×10^{-3}

Table 3. 16 ^{137}Cs & ^{137}Cs/^{99}Tc activity ratios in different seaweeds - 1995.

Seaweed / Sites	St. Bees	Seascale	Ravenglass	Maryport	Rockcliffe	*Whitehaven	Average
A. nodosum	0.93				0.56	0.54	0.68
F. vesiculosus	1.73	0.62					1.18
D. membranacea		0.88	1.02				0.95
P. canaliculata						0.84	0.84
C. crispus			0.43				0.43
E. linza	2.14		0.39			2.33	1.62

Table 3. 17 ^{137}Cs activity in seaweeds relative to *Fucus spiralis* (*relative to *Fucus vesiculosus*).

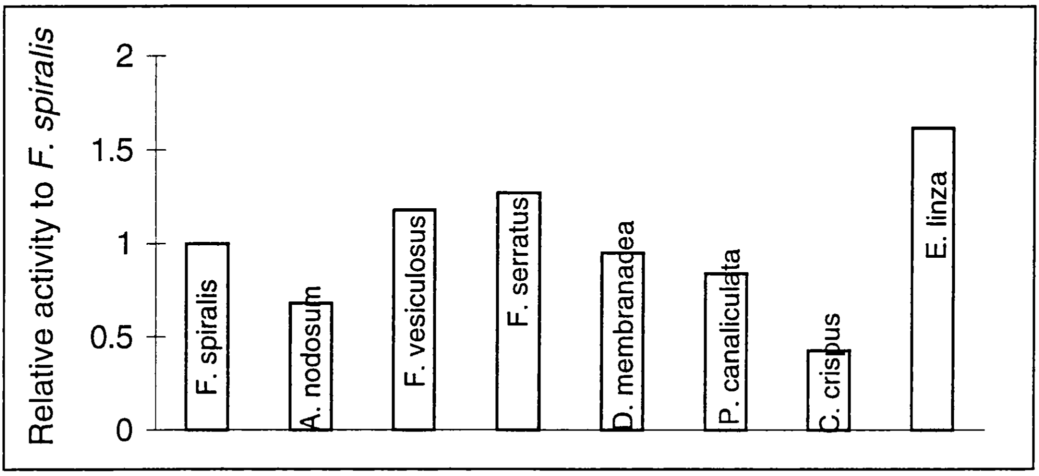


Figure 3. 42 Composite diagram showing ^{137}Cs activities in seaweeds.

The activity of ^{137}Cs in a variety of seaweeds relative to *Fucus spiralis*, a common seaweed found in most of the present study sites, was calculated and is given in Table 3.17. The site averaged relative activity of ^{137}Cs for various seaweed species is presented in Figure 3.42. In contrast to ^{99}Tc, large variations in ^{137}Cs levels between red, green and brown seaweeds are not seen. The large variations observed in ^{137}Cs/^{99}Tc activity ratios between species are due to the fact that ^{137}Cs is readily taken up by all species whereas ^{99}Tc uptake varies dramatically.

The ^{137}Cs/^{99}Tc ratios have also varied temporally in seaweeds. Temporal variations in Cs/Tc ratios were calculated from samples collected at Whitehaven harbour (Table 3.18) and Ravenglass (Table 3.19). The results are also presented diagrammatically in Figures 3.43 and 3.44. Large decreases in ^{137}Cs/^{99}Tc activity ratios are observed at both sites following the commissioning of EARP in March '94.

Month/Year	^{137}Cs/^{99}Tc ratio
November 1992	0.0109
March 1993	0.0102
August 1993	0.0196
February 1994	0.0101
July 1994	0.0015
December 1994	0.0019
July 1995	0.0007

Table 3. 18 Temporal variations in ^{137}Cs/^{99}Tc activity ratios - Whitehaven.

Month/Year	^{137}Cs/^{99}Tc ratio
November 1992	0.0305
August 1993	0.0454
February 1994	0.0199
July 1994	0.0026
December 1994	0.0006
July 1995	0.0009

Table 3. 19 Temporal variations in ^{137}Cs/^{99}Tc activity ratios - Ravenglass.

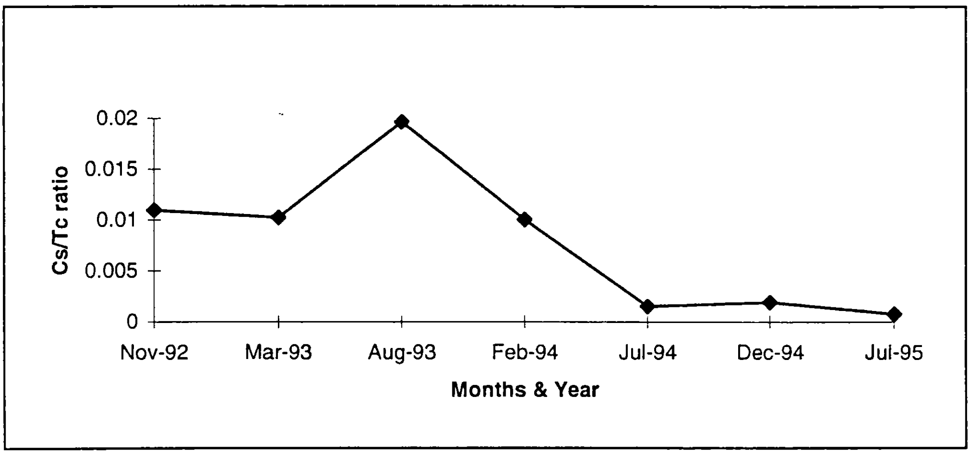


Figure 3. 43 Temporal variations in ^{137}Cs/^{99}Tc activity ratios (Whitehaven).

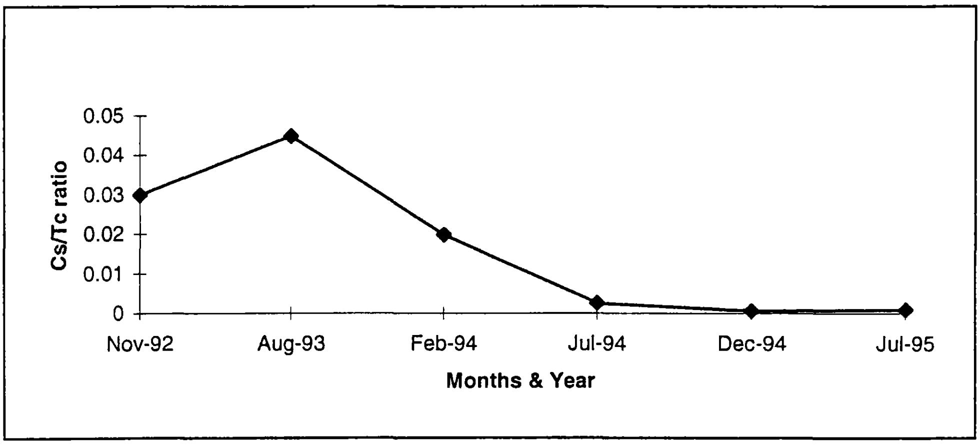


Figure 3. 44 Temporal variations in $^{137}Cs/^{99}Tc$ activity ratios (Ravenglass).

For reference the annual discharge rates of ^{137}Cs and ^{99}Tc from Sellafield for 1989-1995 are given in Table 3.20 and the $^{137}Cs/^{99}Tc$ activity ratios are presented in Figure 3.45. The $^{137}Cs/^{99}Tc$ discharge ratio for 1989-93 is fairly constant. However, the $^{137}Cs/^{99}Tc$ ratio decreased dramatically in 1994 due to EARP discharges in agreement with the pattern observed in the seaweed data.

YEAR	^{137}Cs (TBq)	^{99}Tc (TBq)	Cs/Tc
1989	29	6.1	4.8
1990	24	3.8	6.3
1991	16	3.9	4.1
1992	15	3.2	4.7
1993	22	6.1	3.6
1994	14	72	0.19
1995	12	190	0.06

Table 3. 20 Annual discharge (TBq) levels of ^{137}Cs, ^{99}Tc and $^{137}Cs/^{99}Tc$ discharge ratio from Sellafield (1989-1995).

In addition to annual discharges of caesium, re-dissolution of caesium from sediment (McCartney et al., 1994) could also influence the $^{137}Cs/^{99}Tc$ ratios observed in seaweeds. It is found, however, that $^{137}Cs/^{99}Tc$ ratios in seaweeds are far lower than in discharges - due, presumably, to the high accumulation of ^{99}Tc in the brown seaweeds used for this study.

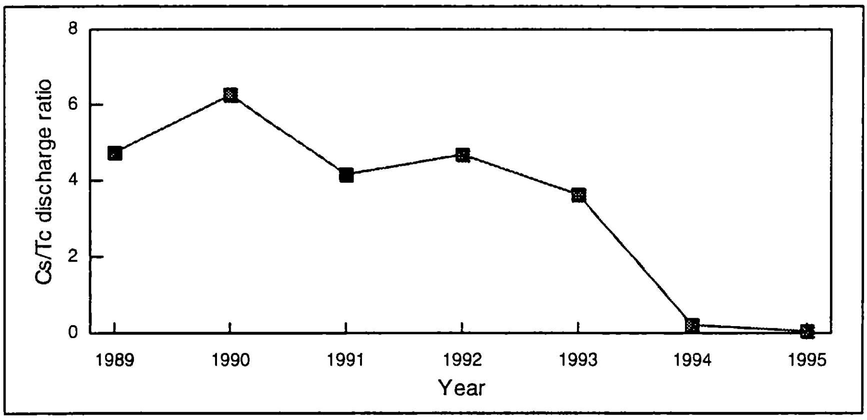


Figure 3. 45 ^{137}Cs/^{99}Tc activity ratios in annual discharge rates from Sellafield (1989-1995).

Spatial variations in the ^{137}Cs/^{99}Tc activity ratios in the years 1989, 1994 and 1995 have also been considered. The data obtained are presented in Tables 3.21, 3.22 and 3.16 respectively.

Sites/1989	Distance (km)	^{137}Cs	^{99}Tc	Cs/Tc ratio
Colwyn Bay	125 (S)	50±2	700±80	0.071
Ravenglass	11 (S)	274±3	9600±1104	0.029
Whitehaven	15 (N)	131±2	2330±267	0.056
Sandyhills	70 (N)	133±2	1630±187	0.082
Poolewe	606 (N)	4.2±1	180±20	0.023

Table 3. 21 ^{137}Cs & ^{137}Cs/^{99}Tc activity ratios in seaweeds (Bq kg^{-1} dry wt.) - 1989.

Sites/1994	Distance (km)	^{137}Cs	^{99}Tc	Cs/Tc ratio
Walney	38 (S)	67±1.6	8200±943	0.008
Haverigg	30 (S)	96±2.3	2800±322	0.034
Ravenglass	11 (S)	39±1.7	25700±2900	0.002
Seascale	2 (S)	38±2.0	38900±4400	0.001
Nethertown	5 (N)	97±2.3	25500±2900	0.004
St. Bees	10 (N)	45±1.7	11800±1300	0.004
Whitehaven	15 (N)	51±1.6	19400±2200	0.003
Parton	16 (N)	75±2.3	28100±3200	0.003
Harrington	20 (N)	55±1.9	14800±1700	0.004
Workington	30 (N)	58±1.6	26400±3000	0.002

Table 3. 22 ^{137}Cs & ^{137}Cs/^{99}Tc activity ratios in seaweeds (Bq kg^{-1} dry wt.) - 1994.

Figure 3.46 shows the ^{137}Cs levels in seaweeds collected during 1989 while Figure 3.47 and 3.48 show 1994 and 1995 respectively. Similar to technetium, the sites nearer to

Sellafield had higher caesium levels in seaweeds. In fact a large gradient in ^{137}Cs levels can be seen in 1989 but not in 1994/1995 - probably due to the fact that discharges from Sellafield have been low in recent years and the major source is probably de-sorption from the seabed.

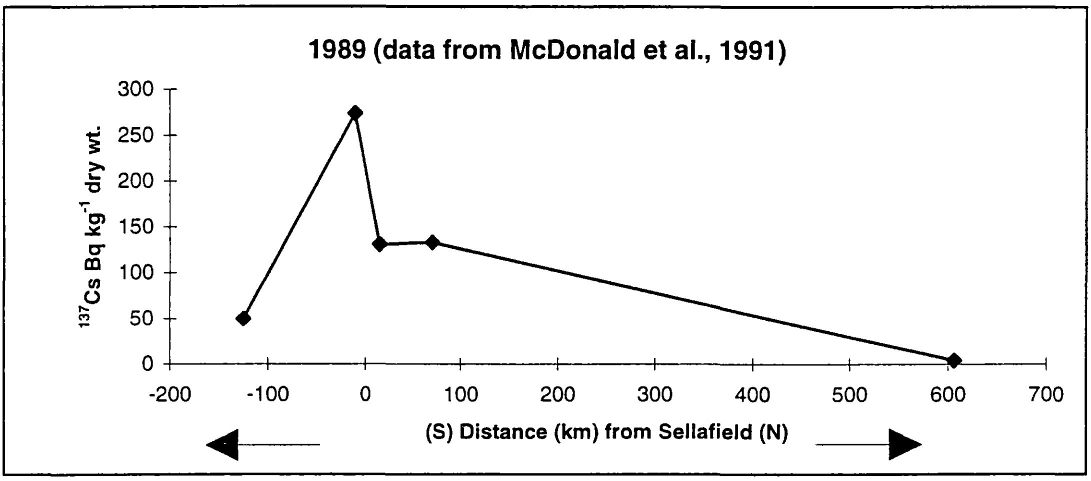


Figure 3. 46 Spatial variations in ^{137}Cs activities during 1989.

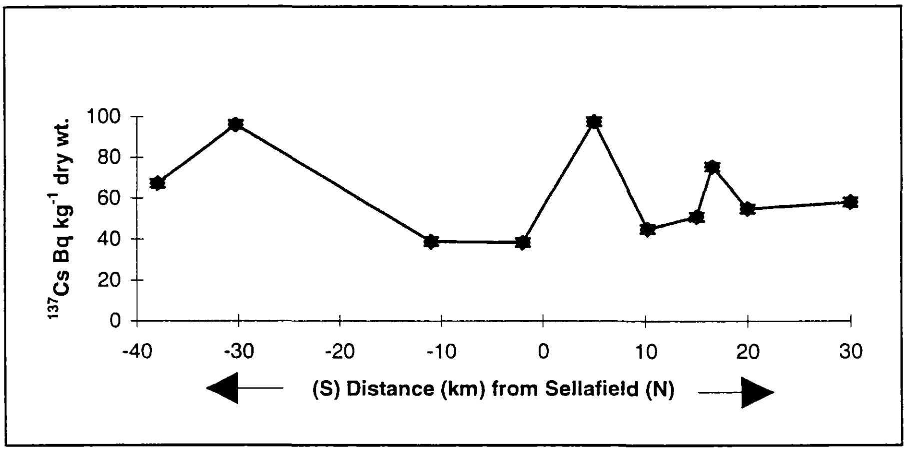


Figure 3. 47 Spatial variations in ^{137}Cs activities during July 1994.

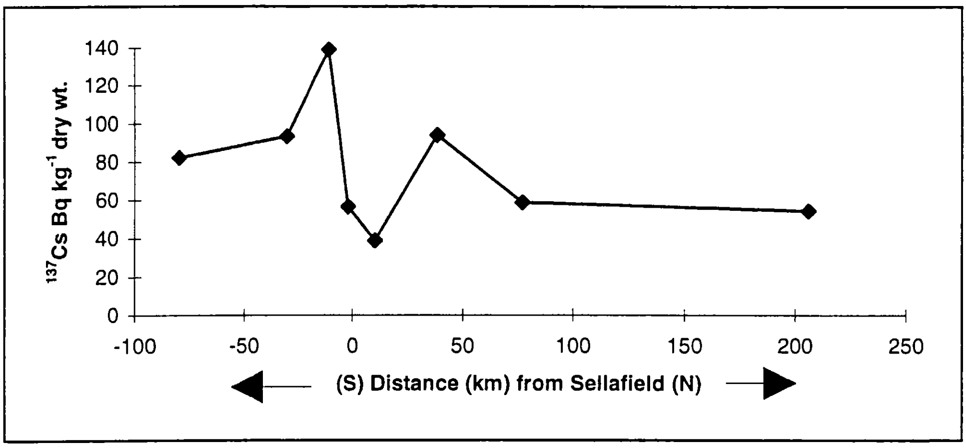


Figure 3. 48 Spatial variations in ^{137}Cs activities during July 1995.

Spatial variations in the ^{137}Cs/^{99}Tc activity ratio are shown in Figure 3.49 for 1989, the pre-EARP situation. Figures 3.50 and 3.51 shows the post- EARP situation (1994 and 1995 respectively).

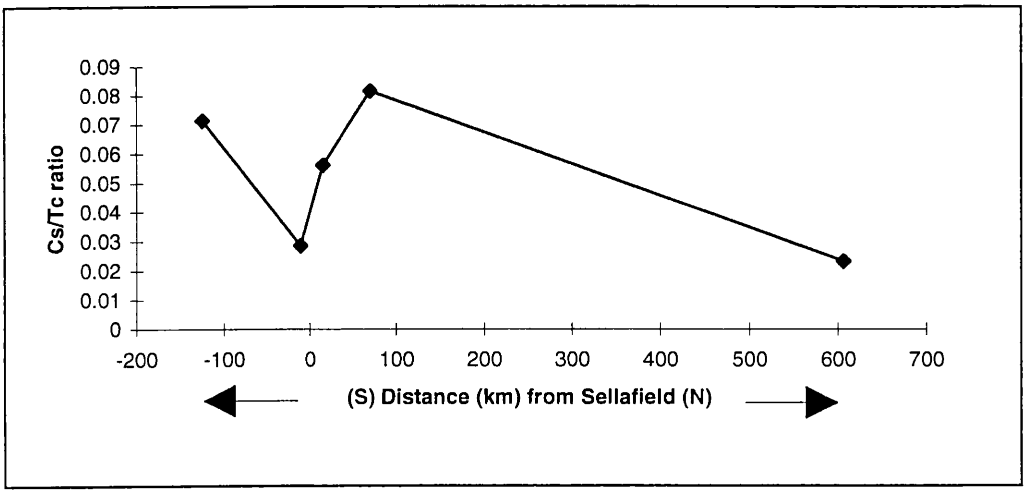


Figure 3. 49 Spatial variations in ^{137}Cs/^{99}Tc ratios during 1989.

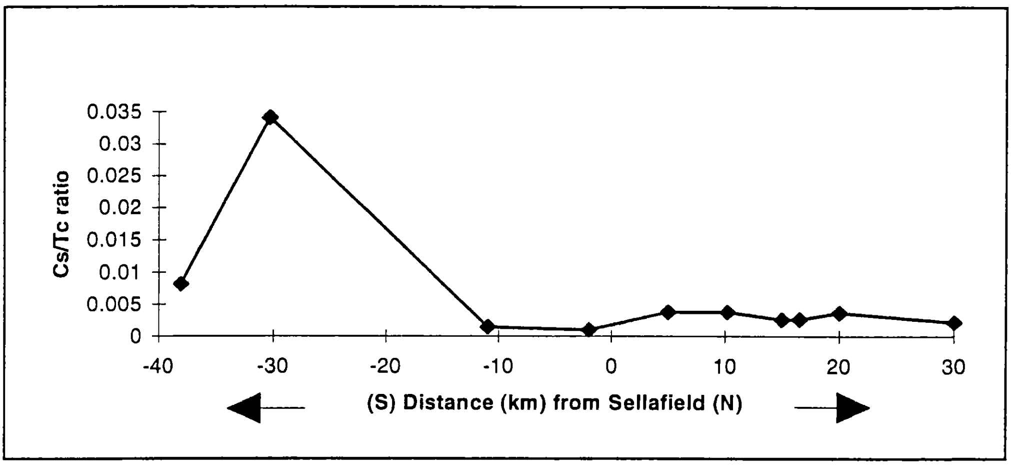


Figure 3. 50 Spatial variations in $^{137}Cs/^{99}Tc$ ratios during 1994.

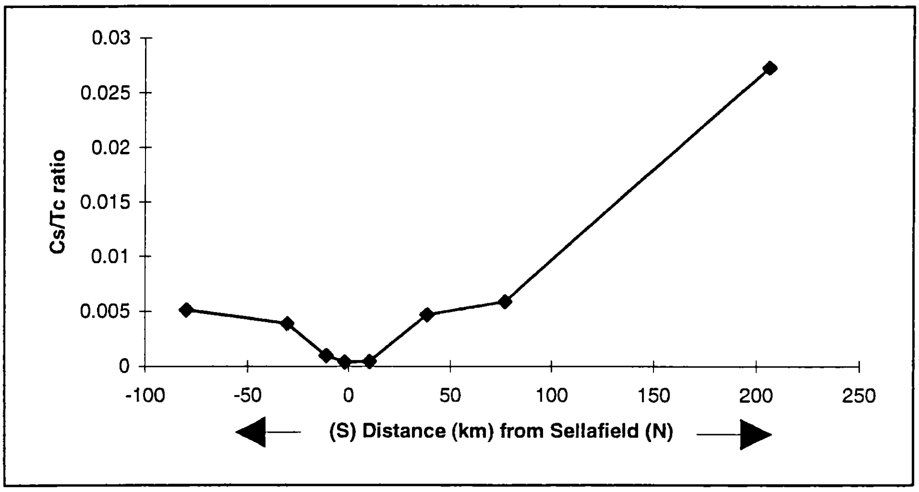


Figure 3. 51 Spatial variations in $^{137}Cs/^{99}Tc$ ratios during 1995.

The year to year variation in the $^{137}Cs/^{99}Tc$ distribution is best illustrated in Figure 3.52, in which data for all 3 years are plotted.

Increases in ^{99}Tc discharges in 1994 and 1995 caused a decrease in the $^{137}Cs/^{99}Tc$ ratios. The discharges of ^{99}Tc from Sellafield are still on an upward slope and so the $^{137}Cs/^{99}Tc$ ratio observed in the Irish Sea in 1995 represent younger discharges (with a lower $^{137}Cs/^{99}Tc$ ratio) than the ratios observed further afield. This increase in the $^{137}Cs/^{99}Tc$ ratio with distance thus indirectly represents the time taken to enhance ^{99}Tc levels in coastal waters of Scotland due to EARP technetium-99.

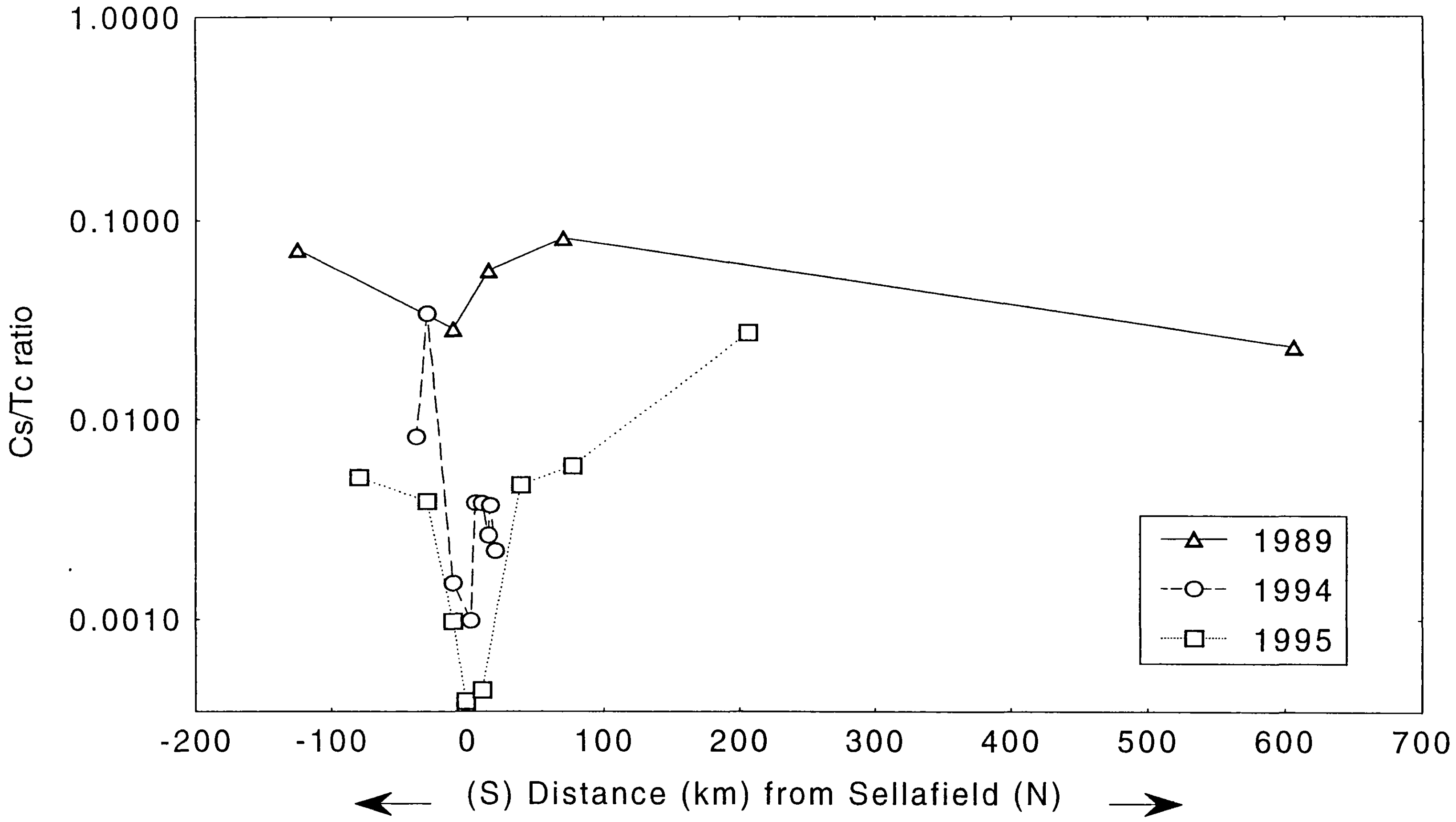


Figure 3. 52 Spatial variation in Cs/Tc activity ratios (1989, 1994 and 1995).

3.2.7 Springfields, Lancashire.

BNFL at Springfields have an operational facility for fuel fabrication and fuel handling. As discussed in Chapter 1, some technetium-99 follows the uranium stream during reprocessing of irradiated fuel. This can escape into the environment through wastes produced during fuel fabrication. In the present study, sediment samples were analysed from the River Ribble which receives effluents from Springfields works. For example, 0.03 TBq of ^{99}Tc were discharged in 1995. Discharge rates over the period 1991-1995 are shown in Table 1.7 (about 296 GBq of technetium-99 were discharged until 1995 into River Ribble). The observed technetium-99 levels in sediments are plotted at their respective sites in Figure 3. 53 and are given in Table 3.23.

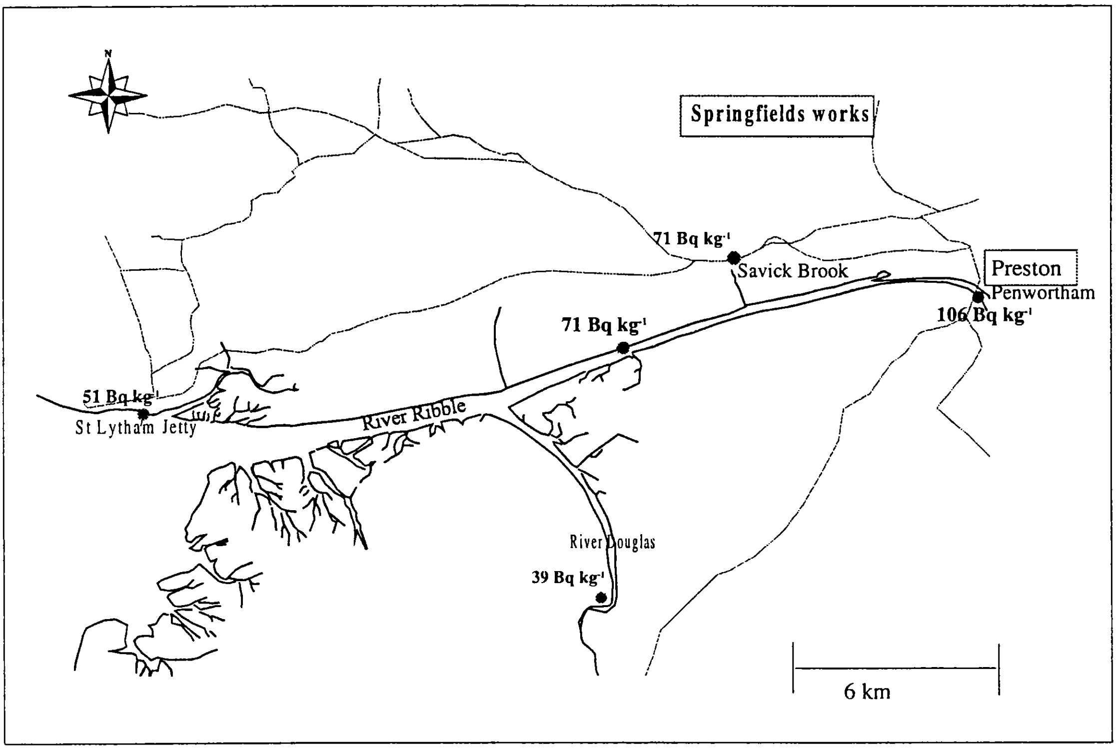


Figure 3. 53 Map showing sampling sites and ^{99}Tc activity in sediment from River Ribble.

Sampling sites	^{99}Tc (Bq kg^{-1} dry wt.)
Penwortham Bridge	106±12.2
Savick Brook	71±8.2
Near sewerage work	71.2±8.2
River Douglas	39.1±4.5
St. Lytham Jetty	50.6±5.8

Table 3. 23 ^{99}Tc activity from the River Ribble sediment.

The technetium-99 concentrations ranged from 39 to 106 Bq kg^{-1} dry wt. These technetium-99 levels are similar to levels in Irish Sea coastal sediment (Seascale sediment was 62 Bq kg^{-1} dry wt.). The upstream site (Penwortham Bridge) had the highest ^{99}Tc activity (106.04 Bq kg^{-1} dry wt.). Regular monitoring of the Ribble estuary for technetium-99 has been undertaken by MAFF (MAFF, 1995) and has found ^{99}Tc in shrimps (0.52 Bq kg $^{-1}$ wet wt.), however, no mud sample was analysed. The recent increase in ^{99}Tc discharges from Sellafield may have increased ^{99}Tc levels, and thus, it was measurable in the present study. The level of technetium-99 in River Ribble mud is not higher than the levels recently observed in Irish Sea sediments; thus there is no evidence of a significant Springfields contribution to the total technetium-99 inventory of the Irish Sea.

3.2.8 Capenhurst, Cheshire.

As mentioned in Chapter 1, Capenhurst (also a BNFL establishment) has an operational facility for fuel enrichment, and fuel handling. A significant amount of technetium-99 has been routinely discharged from the Capenhurst works into a small Brook called Rivacre. For example, 0.00530 TBq of ^{99}Tc were discharged in 1995 (discharge rates over the period 1989 - 1995 are shown in Table 1.8). Regular monitoring work has found that technetium-99 is accumulated in green algae (which is found in the Brook) and silt (MAFF, 1994). To investigate the technetium-99 distribution in Rivacre Brook and to trace the movement of technetium from Capenhurst to the River Mersey green algae, along with sediment samples, were collected and analysed.

Green algae samples were identified as *Cladophora rupestris*. A seaweed, *Fucus vesiculosus* was collected from the River Mersey. The technetium-99 concentrations found in algae and sediment are given in Table 3.24. Figure 3.54 shows the sampling sites and the technetium-99 levels measured in *Cladophora rupestris* and *Fucus vesiculosus*.

Site/Sample	**^{99}Tc (Bq kg^{-1} dry wt.)**
Rivacre Brook III - *Cladophora rupestris*	30000±3500
Rivacre Brook IV - *Cladophora rupestris*	9000±1000
River Mersey - *Fucus vesiculosus*	4000±500
Rivacre Brook I - Sediment	6±0.7
Rivacre Brook II - Sediment	359±41.3
Rivacre Brook III - Sediment	1445±166.2
Rivacre Brook IV - Sediment	13±1.5
River Mersey - Sediment	7±0.8

Table 3. 24 ^{99}Tc activities in algae and sediments from Capenhurst environment (50g sediment sample size used).

In general, technetium-99 levels decreased with distance from discharge point. Higher level of technetium-99 (30 kBq kg^{-1} dry wt.) were found in the upstream site (Rivacre Brook III), and lower levels (4 kBq kg^{-1} dry wt.) were found downstream (River Mersey) irrespective of algal types. Regular monitoring work during 1994 (MAFF, 1995) has found that the alga *Cladophora* sps., accumulated 0.27 kBq kg^{-1} (wet wt.) from Rivacre Brook which is significantly lower than the present study values.

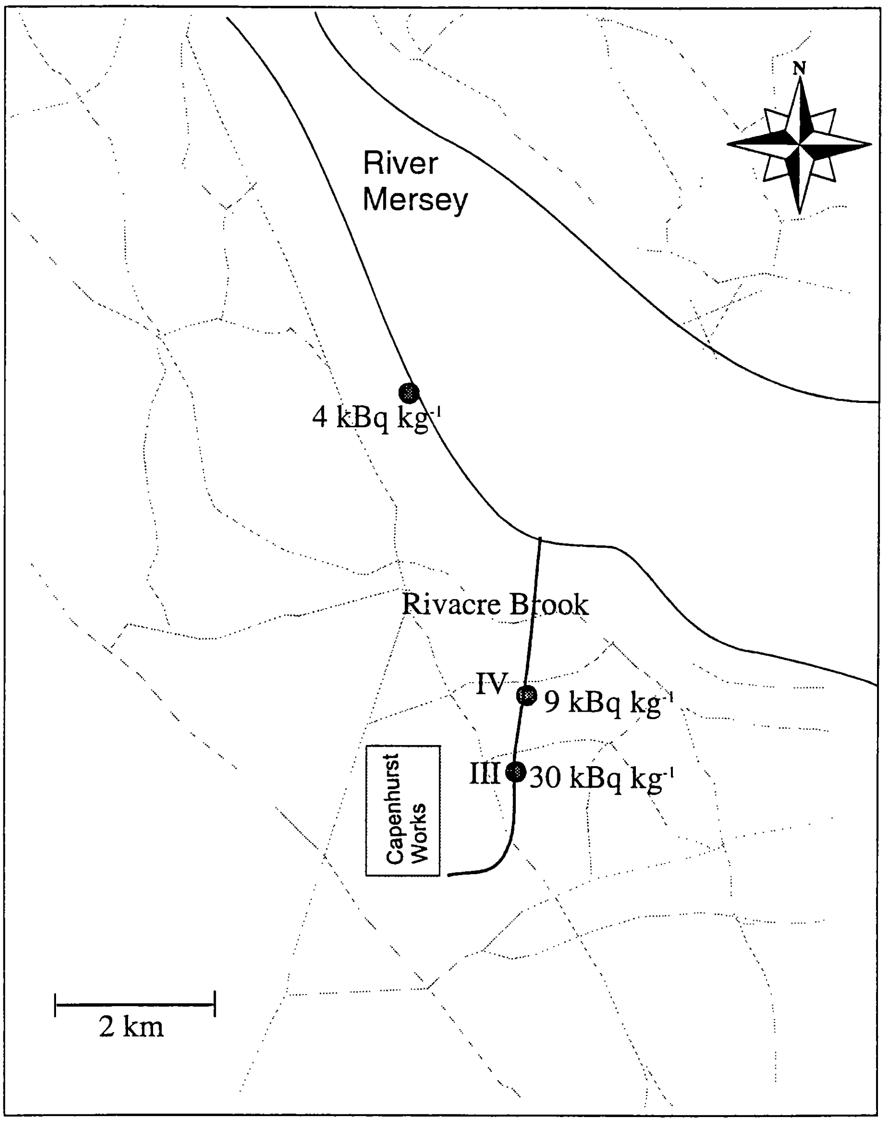


Figure 3. 54 Map showing sites and ^{99}Tc activity in algae samples from Capenhurst area.

Figure 3.55 shows the sediment sample sites and the corresponding technetium-99 levels in Rivacre Brook and River Mersey. In the case of sediment, the downstream sediment from River Mersey shows a lower value than the upstream sites (Rivacre Brook). However, the level of technetium-99 is two orders of magnitude higher in one of the Rivacre Brook sites (1.45 kBq kg^{-1} dry wt.) which also shows high technetium-99 levels in the alga *Cladophora rupestris* collected from there. .

Recently, MAFF (1995) published a ^{99}Tc concentration of 1.10 kBq kg^{-1} (wet weight) for mud samples taken from Rivacre Brook which is comparable to the present study.

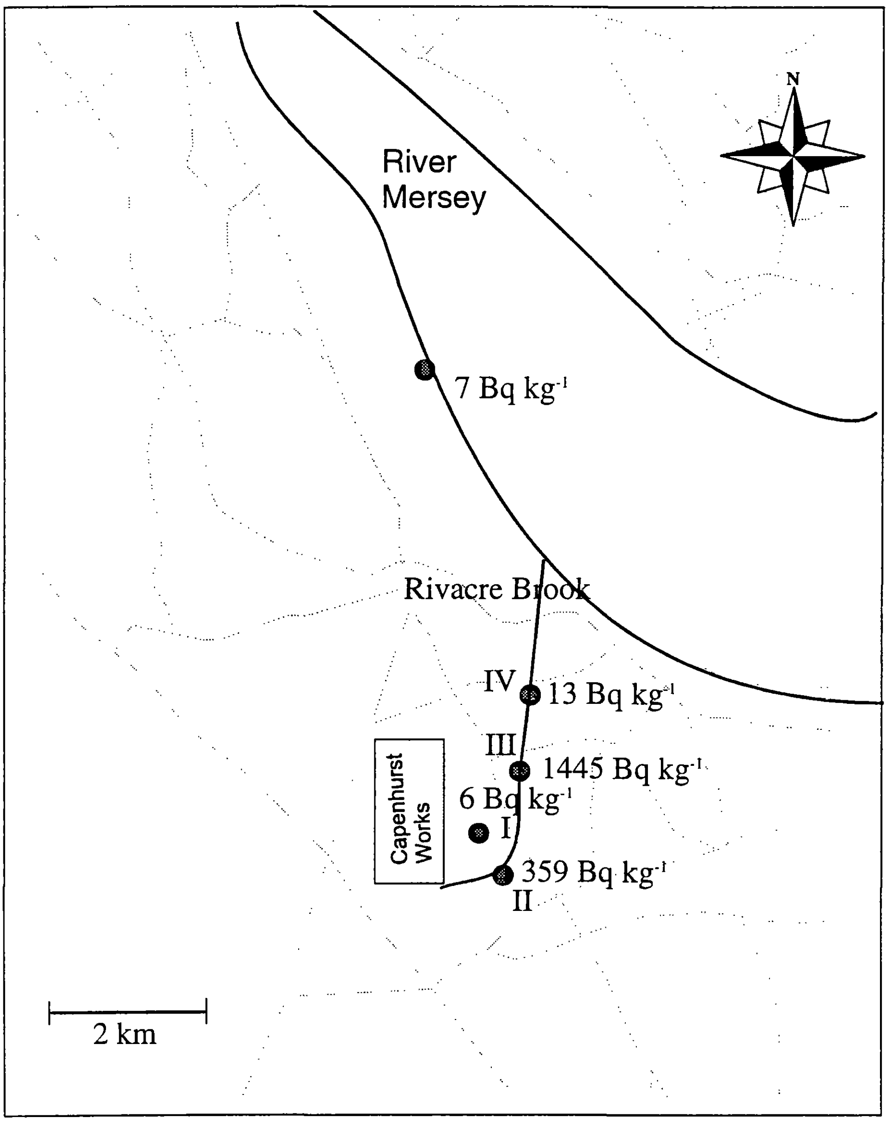


Figure 3. 55 Map showing sampling sites and ^{99}Tc activity in sediments from Capenhurst area.

The observed variations among the sampling sites are not explained due to data non availability on sediment type. Overall, concentrations are significant within Rivacre Brook but dilution by River Mersey makes the source to the Irish Sea insignificant.

3.3 THE BEHAVIOUR OF ^{99}Tc IN THE IRISH SEA

Technetium-99 discharged into the Irish Sea, is believed to be present in the anionic pertechnetate form, TcO_4^-. Marine organisms, in particular, seaweeds living in the inter-tidal areas are known to bio-accumulate the pertechnetate form of technetium-99.

Technetium-99 has been analysed in seaweeds, mussels, winkles and sediments samples taken from several coastal sites within the Irish Sea over the last few years. Coastal sediments showed lower technetium-99 concentrations (84 Bq kg^{-1} dry wt.) than, winkles (136 Bq kg^{-1} dry wt.), mussels (464 Bq kg^{-1} dry wt.) and seaweeds (75.58 kBq kg^{-1} dry wt.) taken from Whitehaven harbour (July 1995). ^{99}Tc accumulation in biota varies between species and also within seaweed species. Among seaweeds, the highest ^{99}Tc concentrations were found in the brown seaweeds while the lowest concentrations were found in green and red seaweeds.

Temporal variations in ^{99}Tc levels in the seaweeds, mussels and winkles collected at Ravenglass and Whitehaven over the period (1989-1995) clearly showed a trend of increasing ^{99}Tc in recent years (1994-1995) due to increased discharges from Sellafield. ^{99}Tc levels in all the species were consistently higher at Ravenglass than Whitehaven, in agreement with the general dispersion trend. The dramatic increase in environmental levels of ^{99}Tc is best represented by the seaweed data, due to greater frequency of sampling. For example, ^{99}Tc levels in *Fucus spiralis* collected from Ravenglass increased from 3.8 to 142 kBq kg^{-1} (dry wt.) over the period Feb-1994 - July 1995. The increase in seaweed is, however, mirrored in the rise in ^{99}Tc activities in both mussels and winkles. Although these brown seaweeds are not eaten by humans, their use as fertiliser could make the seaweed pathway important in technetium transfer to humans. Increases in ^{99}Tc levels in saltmarsh plants, which may represent another important pathway back to man, were also observed.

Spatial variations in the ^{99}Tc distribution in seaweed (e.g. *Fucus spiralis*) were also studied. The highest activity in 1995 was observed at the site closest to Sellafield (144 kBq kg^{-1} dry wt. at Seascale) and the lowest at the furthest sampling point (1.91 kBq kg^{-1} dry wt. at Prestwick). Samples from 1994 and 1995 clearly shows the impact of EARP discharges in seaweed farther afield from Sellafield. A general increase in ^{137}Cs/^{99}Tc activity ratios with distance from Sellafield in 1995 indicates that these sites, further afield from Sellafield, are yet to be exposed to the highest ^{99}Tc discharge levels. As the present study sampling was done basically on a yearly basis (July 1994 and July 1995), the exact time taken for the appearance of EARP pulses at particular places can not be calculated. Although the aim of this study was not to calculate transit times, the results indicated that technetium is behaving conservatively in seawater and *Fucus* responds rapidly to environmental levels and could be used for this purpose.

Analysis of a sediment core collected from the Solway Firth showed significant temporal variations in environmental levels of ^{99}Tc over the time period 1967-1983. No correlation was found between sediment levels and estimated discharges prior to 1978. Decreases in sediment technetium concentrations from 1978 to 1986 were far less than the decrease in discharges over this time period. This could be explained by either: a) uncertainty in discharge rates reported for technetium-99, or b) supply of ^{99}Tc to the Solway coast is controlled by the "integrated discharges" in off-shore sediment.

Technetium levels observed in mud samples from the River Ribble (Springfield area) show comparable levels to Irish Sea coastal samples. The observed ^{99}Tc levels in the sediment can not be said to be Springfields derived without further investigation. The technetium-99 discharged from Sellafield may have influenced the River Ribble sediment concentrations by means of sediment transport.

^{99}Tc levels in Rivacre Brook, into which effluents from Capenhurst are released, do show a clear enhancement over ambient levels. The highest algae sample had a ^{99}Tc concentration of 30 kBq kg^{-1} (dry wt.) where the maximum sediment concentration was 1.44 kBq kg^{-1} (dry wt.). Although these levels may represent an important local source, their effect on ^{99}Tc levels in the Irish Sea is minimal due to the large scale dilution of ^{99}Tc activity by the River Mersey.

CHAPTER 4: CONCLUSIONS.

The main source of technetium-99 in the environment is the nuclear fuel cycle and to a lesser extent past atmospheric nuclear weapons tests. Use of technetium isotopes in nuclear medicine and in research laboratories adds comparatively trivial amounts of ^{99}Tc to the environment. ^{99}Tc has been routinely discharged into the Irish Sea from the Sellafield reprocessing plant for many years. Over the period 1981-1993 discharges of ^{99}Tc were approximately 3 - 6 TBq yr^{-1}, but in 1994, following the commissioning of EARP, increased to 72 TBq. In 1995, it was further increased to 190 TBq (95% of its new authorised limit) with EARP operating at its full capacity. Furthermore, it is expected that the discharge rates are going to remain at this level for several years. It has been recognised that ^{99}Tc may be the single largest contributor to future doses, to populations living in the vicinity of Sellafield.

Since ^{99}Tc emits only soft beta particles (Emax=292 keV), its detection in the environment has historically been a difficult task. Direct beta detection requires long counting times and complex chemistry to remove other beta emitters from technetium-99. The absence of a more suitable method for its analysis has led to a lack of understanding of its behaviour in the aquatic environment. However, the increased ^{99}Tc levels expected in the Irish Sea, coupled with recent advances in analytical methodologies, should now make the detailed study of the behaviour of ^{99}Tc in the marine environment possible. The use of mass spectrometry combined with an inductively coupled plasma source (ICP) has been found to provide adequate detection limits and have a relatively high sample throughput. However, an efficient chemical procedure is required to remove isobaric interferences. The most significant interference is from ruthenium-99, which has a natural abundance of 12.7%.

An anion-exchange method (using Dowex 1X8, 50-100 mesh) has been developed for the preconcentration of ^{99}Tc present in the seawater. By this method, more than 90% of the technetium was recovered from 50 l seawater samples. Experimental results showed that only 50% of the added ruthenium was retained during the anion-exchange process. A gross clean-up of the column was carried out with 0.1 M nitric acid before technetium was eluted for further purification.

Ashing and leaching processes were used to recover technetium from seaweeds, mussels, winkles and sediment samples. Samples were treated with ammonia prior to ashing at 700°C to reduce volatilization of technetium. 8M HNO_3 was subsequently used for the leaching of technetium.

The technetium recovered from both the anion-exchange and the leaching methods were subjected to an iron-hydroxide precipitation step which removes up to 75% of the remaining ruthenium. However, a loss of up to 15% of technetium was observed during this precipitation process.

To remove the final traces of Ru from the sample, 2 methods were investigated. First, solvent extraction using cyclohexanone and carbon tetrachloride was found to offer >99% technetium recovery with >99% ruthenium decontamination. However, this method was replaced with a new extraction chromatography method (TEVA Spec extraction method) which offered a similar level of decontamination from ruthenium but produced clearer samples which were more suitable for ICP-MS analysis. The analytical method developed was found to give a 45-70% chemical yield with a decontamination factor for Ru of up to 10^5-10^6 for a variety of sample matrices. The chemical yield was monitored by the gamma counting of the final solution for the added tracer (^{95m}Tc or ^{99m}Tc). In ICP-MS, the analytical method developed was found to give a detection limit of 13 Bq kg^{-1}, although it can be varied depending on the sample volume.

This analytical method was also optimised for the use of liquid scintillation counting. Two ml of sample (2% HNO_3 base) were added to a glass counting vial along with 5 ml scintillation cocktail (Ultima Gold LLT, supplied from Packard Co., USA). Samples were counted in low level counting mode (450 nsec as delay before burst) at an optimum window (10-87 keV) for 100 minutes. A counting efficiency of 69% was obtained. The impact of quenching (chemical) was investigated for a range of tSIE (quench indicator) and was found to be minimal under the present counting conditions. Tritium interference was also found to be insignificant.

Use of a single instrument (only LSC) for measuring both yield tracer and technetium-99 was also investigated. It was found that both the yield tracer (^{99m}Tc) and ^{99}Tc could be measured in LSC. Enough ^{99m}Tc was added such that in a short initial count, the contribution from ^{99}Tc is minimised. The sample is then left for several days to allow decay of the short-lived tracer (^{99m}Tc half-life, 6 hours) and recounted. The detection limit achieved in LSC is 6 Bq kg^{-1} for 100 minutes counts, and can be improved by increasing counting time if necessary.

Using the analytical method developed an initial study of ^{99}Tc in the Irish Sea environment was undertaken.

A number of seaweed species (brown, green and red seaweeds) were collected from the Irish Sea coast. Of the seaweeds analysed, brown seaweeds (mainly Fucales) were found to show the highest affinity towards ^{99}Tc. The general order of ^{99}Tc accumulation was: Brown algae > Green algae > Red algae. Among the brown algae, it was: *Fucus vesiculosus* > *Ascophyllum nodosum* > *Pelvetia canaliculata* >> *Dictyopteris membranacea* > *Fucus serratus* > *Fucus spiralis.*

The observed inter-seaweed variations can be attributed to the difference in their morphology and physiology. The brown algae, having thick body (e.g., *Fucus vesiculosus*, Plate 5b) with more meristems (growing regions) accumulate more technetium than green alga (e.g., *Enteromorpha linza*, Plate 8) having tubular (long narrow) bodies with single apical meristem. Besides their morphological difference, differences in their metabolism may also have played a role in ^{99}Tc accumulation. Brown seaweeds tend to survive longer than green or red seaweeds, therefore have more time to accumulate ^{99}Tc. For example, *Ascophyllum nodosum*, can live up to 15 years while both green and red algae were annually cleared by grazing pressure exerted by many inter-tidal animals (e.g., *Littorina sp.*). To investigate the influence of various biological parameters, a future study could include studies on biomass turn-over in relation to technetium-99 concentration variations over different seasons. The growth of seaweeds is also influenced by the chemistry of the seawater. So, a future study could also include the determination of both physical and chemical parameters (e.g., temperature, salinity, pH and essential nutrients).

Among the various marine species (seaweed, mussel, winkles) collected for ^{99}Tc analysis, seaweeds accumulated the highest activities. Mussel and winkles accumulated ^{99}Tc ~2 orders of magnitude less than seaweeds. For example, the CF (based on fresh wt.) observed for seaweed (*Fucus spiralis*), mussel and winkles collected at Ravenglass (Jul-1995) were 24000, 500 and 100 respectively.

^{99}Tc concentrations in seaweeds, mussels and winkles from the Irish Sea were found to vary temporally and spatially. For example, at Whitehaven harbour, samples collected pre-EARP contained less ^{99}Tc than seaweeds collected post-EARP. ^{99}Tc concentration ranged from 2.33±0.3 (Oct-1989) to 75.6±8.7 (Jul-1995) kBq kg^{-1} dry wt., in seaweeds; from 0.03±0.01 (Feb-1994) and 0.46±0.06 (Jul-1995) kBq kg^{-1} dry wt., in mussels; and from BDL (Feb-1994) to 0.14±0.02 (Jul-1995) kBq kg^{-1} dry wt., in winkles. The same order of increase in ^{99}Tc was observed in saltmarsh samples relative to literature values. In general, an order of magnitude increase was observed between pre and post EARP samples. This increase in ^{99}Tc activities in all sorts of samples agrees with the reported increase in ^{99}Tc discharges from Sellafield.

Increases in the levels of ^{99}Tc in seaweeds, following the commissioning of EARP, have also been observed outwith the Irish Sea. However, it is evident from consideration of ^{137}Cs/^{99}Tc activity ratios, that the maximum discharge levels encountered in 1995 are yet to reach these further removed sites. The ^{137}Cs/^{99}Tc activity ratio at sites near Sellafield are lower (reflecting recent discharges with a lower ^{137}Cs/^{99}Tc ratio) than that observed at sites further removed.

Past levels of ^{99}Tc in the Irish Sea environment were reconstructed using a previously dated core collected from a saltmarsh on the Solway coast. The high ^{99}Tc level (19.3 Bq kg^{-1} dry wt.) observed in the core for 1979 can be attributed to the high ^{99}Tc discharge during 1978. High environmental levels were also observed in the early 70s in general and in 1971 in particular (15.5 Bq kg^{-1} dry wt.) for which time period discharge data are not available. These unknown higher discharge rates are also evident from the high technetium-99 accumulation in *Fucus vesiculosus* prior to 1978 (Figure 1.9). Thus, it may be that the high levels of ^{99}Tc now present in the environment after EARP are no higher than levels present in the late 60s and early 70s.

^{99}Tc levels found in sediments from the River Ribble (in to which the Springfield works discharges ^{99}Tc) varied from 39.1±4.5 to 106±12.2 Bq kg^{-1} (dry wt.). These levels are comparable to those measured in Irish Sea sediment (e.g., Seascale sediment, 62 Bq kg^{-1} dry wt.). Sediments and plants analysed from Rivăcre Brook (where Capenhurst works discharges ^{99}Tc), however, showed a significantly higher level of ^{99}Tc. A very high ^{99}Tc concentration (30 kBq kg^{-1} dry wt.) was found in *Cladophora rupestris* (green alga); and also in sediments (1.45 kBq kg^{-1} dry wt.). Although, significant ^{99}Tc levels were observed in Rivacre Brook, their effect on ^{99}Tc levels in the Irish Sea is minimal due to the large scale dilution of the signal by the River Mersey.

Thus, to summarise, an analytical method has been developed for the determination of ^{99}Tc in a wide variety of marine sample types. This method has been successfully applied to a preliminary study of the response of the Irish Sea environment to the large increase in ^{99}Tc discharges following the commissioning of EARP in 1994. Concomitant increases in ^{99}Tc levels have been observed in many different sample types, although it is unlikely that equilibrium conditions have yet been stabilised. The relatively high levels of ^{99}Tc recently observed in the Irish Sea and surrounding regions would now support a more detailed study of radiologically or environmentally significant processes (e.g. the uptake mechanism in brown seaweeds, sea-to-land transfer, behaviour of ^{99}Tc in sub-oxic waters).

APPENDIX.

I. Seawater

1) FILTRATION

- 50 litres of seawater are filtered through a 0.45 μm membrane filter.
- The pH is adjusted to 9 using ammonia solution, and yield tracer added.

2) ANION-EXCHANGE

- 32 ml of Dowex 1X8 (50-100 mesh) Cl^- resin is packed into a 21cm column and the sample passed through at a flow rate of 25 - 30 ml min^{-1}.
- Rinse column with 500 ml de-ionised water.
- Wash column with 500 ml 0.1 M HNO_3.
- Elute Tc with 250 ml of 12 M HNO_3 (flow rate ~1 ml min^{-1}).

3) PRECIPITATION

- The elute evaporated to small volume (5 - 10 ml) under 80°C.
- Add 2-3 ml $Fe(III)Cl_3$ to the sample and add 10 M NaOH until precipitation.
- Centrifuge at 2500_{RPM} for 6 min. and discard the precipitate.

4) EXTRACTION CHROMATOGRAPHY

- The pH of the sample is adjusted to 3 using 8 M HNO_3 and 2-3 ml 30% v/v H_2O_2 is added.
- Heat the sample for 30-45 min. at 70°C and cool.
- Add 0.3 g of TEVA Spec resin into sample and stir for 3 hours using magnetic stirrer.
- Collect the resin after stirring and pack into a glass column (8 cm x 10 mm dia.).

- Wash column with 25 - 30 ml 1 M HNO_3.

- Elute Tc with 30 ml 4 M HNO_3.

- Evaporate the elute to near dryness and dissolve in 10 ml 2% HNO_3.

- Measure tracer yield at this stage before analysis.

5) ICP-MS/LSC ANALYSIS

- Add ^{115}In (10 ppb) as internal tracer in sample for ICP-MS analysis. For LSC, 2 ml of sample is mixed with 5 ml Ultima Gold™LLT cocktail.

II. Seaweeds

1) PRE-TREATMENT

- 10-20 g of dried seaweed powder is added with yield tracer.
- 20-30 ml of Ammonia added to the spiked sample.
- Ash the sample in muffle furnace (pre-heated to 250°C) at 700°C for 6 hours (Temperature is raised from 250°C to 700°C at a increment of 50°C every hour).
- Cool and reflux the sample to leach Tc with 25-50 ml of 8 M HNO_3 over a hot plate for 2-3 hours. Add 5 ml H_2O_2 (30% v/v) during leaching process.
- Filter off residue and take the filtrate into clean beaker.

2) PRECIPITATION

- Add 10 M NaOH until get precipitate.
- Centrifuge at 2500_{RPM} for 6 min. and discard the precipitate.

3) EXTRACTION CHROMATOGRAPHY

- Follow the same procedures described for seawater analysis.

4) ICP-MS/LSC ANALYSIS

- Follow the same procedures described for seawater analysis.

III. Sediments

1) PRE-TREATMENT

- 50 g of dried sediment is spiked with yield tracer.
- Wet the sediment completely with ammonia.
- Ash the sediment in muffle furnace (pre-heated to 250°C) at 700°C for 6 hours (Temperature is raised from 250°C to 700°C at a increment of 50°C every hour).
- Add 100-150 ml of 8 M HNO_3 and reflux under warm condition for 48 hours while stirring with magnetic stirrer. Add 10-30 ml H_2O_2 (30% v/v) during stirring process.
- Filter off and discard residue. Take the filtrate in a clean (250 ml capacity) beaker.
- Evaporate the filtrate to near dryness and dissolve the residue with 25 ml 1 M HNO_3.

2) PRECIPITAION

- Follow the same procedure described for seaweed analysis.

3) EXTRACTION CHROMATOGRAPHY

- Follow the same procedure described for seawater analysis.

4) ICP-MS/LSC ANALYSIS

- Follow the same procedure described for seawater analysis.

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