CHLORPROPHAM DISTRIBUTION IN POTATO STORES AND EVALUATION OF ENVIRONMENTAL ISSUES RELATING TO ITS USE.

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Bsc (Hons) University of Glasgow 1999

Thesis submitted for the degree of Doctor of Philosophy

January 2004

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Abstract

Work described in this thesis was designed to address a number of environmental issues relating to the use of chlorpropham (CIPC) as a sprout suppressant in potato stores. Studies considered the behaviour of CIPC during the application process and storage and also the potential for it to be released into the environment. All commercial studies were carried out in box stores, rather than bulk stores.

A survey of potato growers was carried out to provide up-to-date industry information on store management practice and to determine the extent of chlorpropham use in the UK. Results confirmed that the vast majority of crop held in the UK for both pre-packing and processing is treated with chlorpropham. In most cases, several applications are necessary to maintain sprout control throughout the season, which highlights the inefficiency of the application process.

Thermal fog application (the industry standard) is known to be inefficient, and to result in uneven distribution of chlorpropham around the store. This can lead to unacceptably high chemical residues in crop at certain locations, and poor sprout control in places that do not receive the correct dose. The imminent introduction of a Maximum Residue Level (MRL) for chlorpropham means that store managers must be able to predict with confidence the amount of chemical reaching each tuber. Analysis of crop from commercial stores found chemical levels ranging from 0-50 mg kg^{-1} following conventional application. Washing significantly reduced these very high levels in most cases. Improvements in chemical distribution (and a lowering of the highest chemical levels) were seen when the movement of air and fog around the store were manipulated using fans or by restricting air flow using polythene sheeting.

A method for the collection and analysis of air samples was developed and used to quantify CIPC in samples of air from treated stores. Vapour concentrations were found to be of the order of $\mu g\ l^{-1}$ (parts per billion), and to increase linearly with air temperature. 3-chloroaniline (a metabolite of CIPC) was also identified in the air samples, suggesting significant breakdown of the CIPC molecule may occur during chemical application or storage. The mechanism of breakdown was not identified. Contaminated fabrics within the store are believed to provide a reservoir of chemical that can readily volatilise and be found in the vapour phase. The presence of chlorpropham in the air has implications for crop contamination and the extent of chemical loss from the store.

Samples of effluent from potato washing plants were collected and analysed on several occasions. The CIPC concentration in liquid effluent (after removal of all suspended material) was found to range from several mg/l (parts per million) in untreated samples to <0.01 mg l^{-1} following filtration and digestion. Although sophisticated methods for cleaning up effluent are available, they are costly to implement and as such are generally only found at larger establishments. With increasing amounts of crop washed on-farm or prior to delivery to large processing plants, washing effluent is often disposed of with little or no treatment. The Environmental Quality Standard (EQS) for CIPC in surface water is $10\mu g\ l^{-1}$, so untreated effluent would require significant dilution to meet requirements. Environmental pollution by agrochemicals is becoming more and more of a problem, so a simple method for reducing the chemical load in washing effluent would be a significant advantage to the industry.

Simple methods for removing residues of chemical from water were developed and evaluated in the laboratory. The addition of a small volume of 30% hydrogen peroxide was shown to be effective at degrading CIPC (at concentrations ~2ppm) in distilled water. The presence of suspended or dissolved material in the solution interfered with the process by consuming the oxidant and reducing the rate of chemical breakdown. Modifications to this method (e.g. the addition of UV light) would be required to make it commercially viable.

Sorption onto waste materials such as soil and potato peel was also considered as a method for removing CIPC from water. Laboratory studies showed significant uptake of chemical from solutions with concentrations similar to, and in excess of, those found in samples of washing water to date. Contact time and solution concentration governed the extent of uptake onto soils in addition to soil properties. However, the studies also showed that CIPC held on soils may be released back into solution under certain conditions e.g. if fresh water is added.

The possibility of untreated crop picking up detectable chemical residues during storage or washing with CIPC treated crop is an issue of real concern to the industry. Studies carried out at a commercial washing facility showed that the chemical concentration in water in the washer barrel did reduce after untreated crop had passed through. Whether this chemical was taken up onto crop or the associated soil was unclear, but GC analysis suggested a very small amount (too small to quantify) was present on the peel of the potatoes.

The fate of a large proportion of the chemical applied to a store is unknown at present, with only a relatively small amount accounted for by crop residues. A simple model was used to estimate the amount of chemical lost from the store during the application process, and as a result of routine venting throughout the season. Leakage during application was the most significant process, with up to 30% of the chemical estimated to be lost in this way. Losses through venting are much less. This model did not take into account the potential loss through chlorpropham degradation to 3-chloroaniline and other products.

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Acknowledgements

Thanks first and foremost to my supervisor Dr Harry Duncan, whose boundless enthusiasm and knowledge of the potato industry, of science in general, football, politics and the world at large has been a constant source of inspiration. Although he has finally seen the back of his last two PhD students, it's hard to imagine him ever retiring from the potato world...

The funding of this work by the British Potato Council is gratefully acknowledged, along with the input and hard work of staff at its Sutton Bridge Experimental Unit. The contributions of our various commercial collaborators, in terms of their time and resources, have also been much appreciated.

Thanks to all staff and students of the Environmental, Agricultural and Analytical Chemistry Section for their company, comments and occasional jokes at our expense! In particular to Michael Beglan (the all-knowing) for his patience and good humour in the laboratory, and to my colleague (and fellow spud-girl) Geraldine Dowd for valuable discussion and support throughout our studies.

Thanks to my parents and family, without whose constant encouragement I wouldn't have got this far. In particular to Dad, for proof-reading and criticism of this text and to Mum for listening to me and helping me keep a sense of perspective.

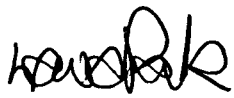
Finally to my partner Geoff: it can't have been easy playing second fiddle to the humble potato for so long, so thanks for your patience! We've been through some difficult times together in the past three years, so here's to a happy, settled 2004.....

Author's declaration

Except where specific reference is made to other sources, the work presented here is the original work of the author. It has not been submitted, in part or in whole, for any other degree.

Certain elements have already been published elsewhere, in contract reports to the BPC. Copies of these reports can be obtained through the BPC's Publications Office, and are also available on their website: www.potato.org.uk

A summary of the work reported in Chapter 8 was presented as a paper at the 15th Triennial Conference of the European Association of Potato Research in Hamburg, Germany (14-19th July 2002).



January 2004

Definitions and Abbreviations

***Chemical names*:**

Chlorpropham (CIPC)	=	isopropyl N-(3-chlorophenyl)carbamate
3CA	=	3-chloroaniline
Tecnazene (TCNB)	=	1,2,4,5-tetrachloro-3-nitro-benzene
DMN	=	1,4-dimethylnaphthalene
Maleic hydrazide (MH)	=	3,6-pyridazinedione

Units:

ppm	=	parts per million
$mg\ l^{-1}$	=	milligrams per litre
$mg\ kg^{-1}$	=	milligrams per kilogram
$\mu g\ l^{-1}$	=	micrograms per litre

Legislative terms:

MRL	=	Maximum Residue Level
EQS	=	Environmental Quality Standard
ADI	=	Acceptable Daily Intake
NOEL	=	No Observable Effects Level
CAS number	=	Unique identification number assigned by the Chemical Abstracts Service
RDA	=	Recommended Daily Intake

Chapter 1

INTRODUCTION

1.1 Introduction to the potato industry and the use of sprout suppressants

1.1.1 The potato industry

The annual UK market for potato based snacks, frozen, chilled and dehydrated products has an estimated retail value of £3.7 billion [Harris, personal communication], so a guaranteed supply of quality crop throughout the year is of utmost importance. Over the past 25 years, the market has increased significantly: for example, the tonnage processed into chips and crisps rose by 35% in total in the years from 1990 to 2000. The pre-pack, or ware, sector has also shown similar increases.

In the UK, potatoes straight from the field can supply the market for about four months [Khan, 1999] but the continuing demand throughout the season can only be met either by stored British crop, or by importing from other climatic regions (e.g. Spain) later in the year. From both an economic and an environmental viewpoint, successful storage of the local crop is preferable.

In the UK, much of the potato crop harvested in autumn is put into storage in order to provide a steady supply throughout the year. The aim of storage is to maintain the quality of the crop: while good storage cannot improve the quality of the starting material (i.e. the crop as it comes out of the ground), storage under the wrong conditions can have a detrimental effect on the condition, and hence the value, of the crop. Crop 'quality' can be defined as a combination of colour, texture, taste and appearance.

Key factors in maintaining crop quality during storage include the prevention of i) crop dehydration ii) crop disease and decay iii) sprouting iv) accumulation of sugars. In order to achieve these aims, store design must include i) adequate ventilation ii) adequate insulation iii) the ability to control climate (e.g. maintain stable humidity and temperature) iv) protection from light.

Dehydration and sprouting of the crop will result in decrease in weight and thus value of the stored crop. The accumulation of reducing sugars (which can largely be controlled by storing at the correct temperature) causes a dark fry colour, resulting in an undesirable product for the crisping and processing industry. Sugar content is less of a concern for the ware and pre-pack markets, where tubers are only washed or brushed prior to reaching the consumer: appearance is the most important factor for this market e.g. tubers should be free of blemishes and wounds, with a shiny skin finish. Exposure to light can cause greening of the surface of the tubers, as a result of chlorophyll production. The glykoalkaloids associated with this greening can impart a bitter, undesirable flavour to the crop.

Historically, the low sugar requirement in processing crop has driven the demand for sprout suppressant chemicals. The accumulation of reducing sugars (e.g. glucose and fructose) occurs at low temperatures as a result of conversion of starch to sugars. (There is also the phenomenon of senescent sweetening, which is related more to physiological age and length of storage than directly to storage conditions). To achieve the correct sugar balance in processing potatoes, they must be held at relatively high temperatures (e.g. $\geq 8°C$), at which they are likely to sprout (although optimum storage temperature depends on a number of factors including cultivar and anticipated storage period). As a result, sprout suppressant chemicals may be necessary to maintain sprout control throughout the season.

Treatment with chlorpropham (CIPC) and other sprout suppressants is becoming increasingly common in low-temperature pre-pack stores, as a result of increasing demand for long-term storage; the tendency to hold a variety of cultivars in one store; and the desire for increased shelf-life once taken out of store.

Although the reliance on sprout suppressant chemicals has become widespread in recent years, retailers and consumers increasingly demand food produced in an 'environmentally friendly' way and free of pesticide residues. Pesticide chemicals, regardless of their nature, are becoming increasingly unacceptable to the UK government and consumer. The recent phenomenon of media "naming and shaming" on the basis of chemical residues in food means that many larger retailers now insist that their suppliers produce their crop without the use of chemicals. They are, however, not prepared to compromise on quality, which leaves the industry in something of a predicament: responsible use of chemicals is necessary to maintain the necessary quality standards, but retailers will not buy poorer quality produce or produce containing detectable chemical residues.

The idea that natural products are less harmful to the environment than synthetic chemicals is a common one. However, Kerstholt *et al* (1997) compared environmental profiles for two sprout suppressant chemicals: chlorpropham and carvone, a naturally occurring compound derived from caraway seed. Nine environmental effect scores were evaluated for each compound, based on energy use and emissions during the 'life-cycle' of the compound (i.e. all the processes involved in its use, from extraction of raw materials during production to the emission of waste products). Surprisingly, perhaps, carvone scored worse than chlorpropham in seven of the nine areas, only performing better in terms of human toxicity and ozone depletion. This case illustrates the problems with placing all 'pesticides' under the same umbrella in terms of public perception and legislation.

1.1.2 Potato storage

These days, the majority of commercial potato stores have the capacity to hold many thousands of tonnes of potatoes in either boxes or a bulk pile. In the past, smaller scale storages (e.g. clamps, dickie pies) were often located on farms, but larger-scale facilities have become more common over the years because of their economic benefits.

In box stores, potatoes are held in one-tonne boxes that are stacked in formation in the store. Columns are often up to eight boxes high, with spaces left around and between the stacks for ease of access, and to allow air to circulate. In bulk stores, potatoes are held in a pile that may be up to 20 feet in height. In some stores, nets may be used to separate different consignments. In bulk stores, the walls must be reinforced to bear the weight of the entire pile of potatoes.

There are several advantages to box storage over bulk, including better traceability of the crop; easier visual assessment of the crop condition; prevention of disease spread and less risk of pressure bruise and tuber damage. However, there are also drawbacks to this method of storage e.g. contamination of boxes with chemical residues, difficulties with air and chemical circulation and the financial outlay for the boxes. In the UK, box storage is currently more popular than bulk, although this has not always been the case.

Modern commercial stores have sophisticated store control systems, enabling accurate control and monitoring of ventilation, air circulation, temperature and humidity data. The ability to control the store environment remotely is particularly useful in the period following a chemical application in which personnel cannot re-enter the store. The sooner store conditions can be returned to normal, the less crop damage is likely to occur.

1.1.3 Sprout suppressant strategies

CIPC is the most commonly used sprout suppressant worldwide, and is currently the only chemical available in the UK for use post-harvest. However, a number of chemicals have been identified over the years as having sprout suppressant activity. Most of these (e.g. jasmonates, higher alcohols, some volatile monoterpenes, ozone) have not been used commercially. The paragraphs below detail those treatments that are, or have been, available for control of sprouting in commercial crops. The chemical structures of the compounds are shown in Table 1.

- **Chlorpropham (CIPC):** A carbamate first introduced in the 1950s by Marth and Schultz of Pittsburgh Plate and Glass Co of the USA. Currently the only chemical available for post-harvet sprout suppression in the UK. Available in a variety of formats including dust, granules and thermal fog, which is the only method of application currently approved in the UK

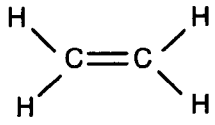
- **Propham (IPC):** The non-chlorinated analogue of CIPC, IPC was commonly used in the past as a sprout suppressant in continental Europe, either on its own or in combination with CIPC. However, its use is now banned in the EU.

- **Tecnazene**: An organochlorine now banned in the EU. Previously, it was applied as a dust at store loading. However, it was relatively expensive and unable to control sprouting past the break of dormancy. Had the advantage of being suitable for use during the wound-healing period, when CIPC is not.

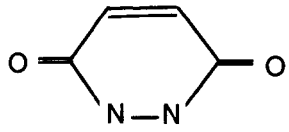
- **Maleic hydrazide**: Applied to growing crop in the field. Translocated in the growing plant from the aerial parts to the tuber. Effectiveness can be variable, and dependent on climatic conditions at the time of application: application too early can limit tuber size and crop yield, too late and efficacy may be affected. Generally used in combination with post-harvest CIPC treatment. Has the advantage of controlling volunteers in the field during the following season.

- **Ethylene**: Used extensively as a ripening agent in the fruit industry, it has recently been generating interest as a sprout suppressant for stored potatoes. In commercial practice, sugar accumulation in the crop would make it unsuitable for use on processing crop. Ethylene itself has been implicated in the deterioration of crop quality following application of CIPC as a thermal fog (it is produced as a by-

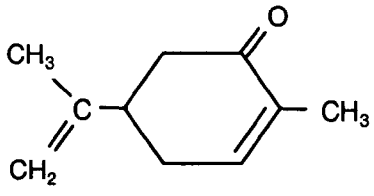
Table 1 Chemical structures of sprout suppressant chemicals



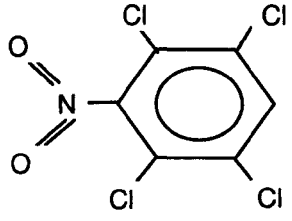
Ethylene



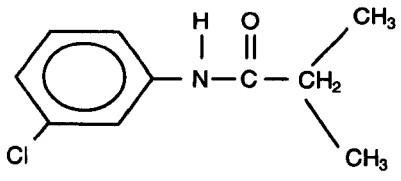
Maleic hydrazide



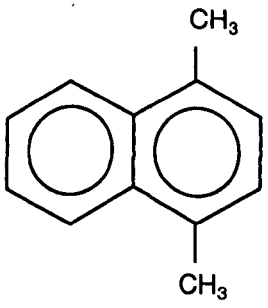
Carvone



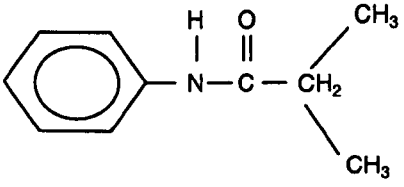
Tecnazene



Chlorpropham



1,4-dimethylnaphthalene



Propham

Hydrogen peroxide

product of combustion of petrol by the fogging machinery). Ethylene at high levels will control sprouting, but at low levels can stimulate crop activity; therefore dose rates will be critical in achieving success as a sprout suppressant.

- **DMN (1,4 dimethylnaphthalene)**: An aromatic hydrocarbon occurring naturally at low levels in the potato [Meigh *et al* (1973)], its potential as a sprout suppressant was first identified in the 1980s at Glasgow. Has recently been developed in the US and is used extensively, both alone and in combination with CIPC. The chemical is currently undergoing the registration process in the EU, and is expected to be available for commercial use in 2005.

- **Carvone**: A monoterpene found in high concentration in caraway seed oil, this compound has received some attention in Europe (e.g. Luxan's Talent™ formulation). However, it is relatively expensive to produce, and has a characteristic unpleasant odour. Cost is likely to be prohibitive to widespread use.

- **Hydrogen peroxide**: Has been used with some degree of success in Israel for a number of years [Afek *et al* (2000)]. However, the problem of achieving an even distribution of chemical throughout the box stores common in the UK means that it is unlikely to be successful on a commercial scale. It has the advantage of being residue-free (decomposing to H_2O and O_2) but the disadvantage of introducing moisture to the store, which is unpopular in Britain's wetter, colder climate.

In addition to sprout suppressant chemicals, modification of the storage environment or the crop itself has also received some attention to date:

- **GM technology:** could have potential, in particular for producing cultivars that maintain low sugar levels when stored at low temperature, negating the use of sprout suppressants [Sowokinos and Glynn (2002)]. This is potentially good science, but very much unacceptable to the public.

- **Irradiation:** Can control sprouting effectively, but can adversely affect crop quality by increasing sugar levels and susceptibility to damage. Also unacceptable to the consumer.

- **Controlled atmosphere storage:** Modification of the carbon dioxide and oxygen levels in the store atmosphere can be used to control sprouting

[Khanbari and Thompson (1996); Coleman (1998)]. However this method has implications for crop quality (e.g. high CO_2 can result in the physiological defect 'blackheart') and can also expensive to implement.

1.1.4 Chlorpropham

This section summarises data on various features of the CIPC molecule and its use and fate. Many of these issues are expanded upon in the experimental chapters that follow, and as such are not presented in any detail.

Uses: Chlorpropham [isopropyl-N-(3-chlorophenyl)carbamate], also known as CIPC, is a member of the phenylcarbamate class of herbicides and has historically had a number of uses: it is a highly selective pre-emergence herbicide; it is effective at controlling weeds in various crops e.g. alfalfa, blueberries, seed grass, sugar beet. It can be used for the control of suckers in tobacco and post-harvest for the prevention of sprouting in potatoes.

Synthesis: Chlorpropham is relatively easy to synthesise, from the reaction of i) 3-chloroaniline with isopropyl chloroformate or ii) 3-chlorophenyl isocyanate with propan-2-ol, which presents the opportunity of producing chlorpropham radio-labelled either on the ring or the side chain of the molecule. Radio-labelling can be very useful in the study of the fate, transport and metabolism of the chemical. Chlorpropham is also resistant to both acid and alkaline hydrolysis under mild conditions, and shows only slight degradation by UV light.

Mode of action: Chlorpropham is a mitotic inhibitor, and interferes with spindle formation during cell division. It has also been shown to interfere with several other metabolic processes such as respiration and carbohydrate metabolism [e.g. Blenkinsopp *et al* (2002)], but the ability to inhibit cell division is widely accepted as responsible for its sprout suppressant action. In a study of the effect of chlorpropham on root tip cells of wheat [Eleftheriou and Bekiari, 2000], the authors noted that no microtubules were present in either dividing or differentiating cells treated with CIPC at 50μM concentration. Cells also became binucleate, or polyploid, and often exhibited incomplete cell walls as a result of the inhibition of cytokinesis.

CIPC is known to control sprouting when present in the vapour phase [van Vliet and Sparenberg (1970)] and has been shown to affect growth in wild plant species treated with its vapour [Franzaring *et al* (2001)].

Physical properties: The main physical properties of chlorpropham are summarised in Table 2 below.

Table 2 Physical properties of chlorpropham (CIPC)

CAS number:	101-21-3
Molecular formula	$C_{10}H_{12}ClNO_2$
Molecular weight	213.7
Appearance	Light brown crystalline solid
Melting point	41°C
Boiling point	247°C (decomposes)
Water solubility	89 mg/litre at 25°C
Vapour pressure:	1.33 mPa at 25°C

Environmental fate:

In the environment, breakdown of chlorpropham can occur via a number of biotic and abiotic processes. Various aspects of the physical interactions of herbicides in the environment (e.g, degradation, binding, volatilisation, leaching etc) have been described by other workers [Cleve and Goring (1972); Hartley and Graham-Bryce (1980); Hance (1980); Fletcher and Kirkwood (1982)]. Where chlorpropham is discussed in such work, the authors have tended to focus on the chemical as soil-applied (e.g. for control of weeds in commodity crops) rather than on its behaviour when used post-harvest as a sprout suppressant.

Microbial breakdown: Biological breakdown of chlorpropham in soils has been well characterised. Chlorpropham is moderately persistent in soil, but will be degraded by soil microbes. Soil half-life has been shown to range from 30 to 65 days, depending on climatic conditions and soil properties [Anon, http (1996)]. Hydrolysis of the chlorpropham molecule, at either the ester or amide bond of the carbamate linkage, yields 3-chloroaniline, propan-2-ol and carbon dioxide. These products have been identified in studies carried out in soil, pure microbial cultures and isolated enzyme systems [Kaufman and Kearney (1965); Kaufman (1967); Clark and Wright (1970)]. Wright and Maule

(1982) demonstrated the transformation of IPC and CIPC to the corresponding anilines by micro-algae, while the soil fungus *Fusarium oxysporum* Schlecht was shown to be capable of degrading CIPC to hydroxylated (phenolic) products by Fletcher and Kaufman (1979). Immobilisation of chlorpropham in soil can also occur as a result of adsorption and absorption onto ectomycorrhizal fungi, which are also capable of degrading the chemical to 3-chloroaniline [Rouillon *et al* (1989)].

The leaching potential of chlorpropham is low, because of its tendency to be adsorbed to soil organics. Photodegradation, volatilisation and hydrolysis do not readily occur in the soil [Anon, http 1996].

Breakdown in water: Hydrolysis half-life in water has been estimated at >1000 days for pH values in the range 5-9 [Wolfe *et al* (1978)]. The estimated minimum half-life for the direct sunlight photolysis of CIPC in clear surface waters is 121 days. Although pesticide molecules in water can be broken down by sunlight, direct photolysis in the environment is expected to be of only minor importance because sunlight penetrating to the Earth's surface contains only a very small amount of the short-wavelength light found in their UV-absorption bands [Burrows *et al* (2002)]. Therefore, indirect photolysis (where energy from sunlight is absorbed by other species which then interact with the pesticide molecule) is an important process in removing non-sunlight absorbing xenobiotics from water. Compounds present in natural waters play an important role in this process: for example, sunlight irradiation of organic matter present in surface waters has been shown to produce reactants such as singlet oxygen, peroxide and hydroxyl radicals amongst others [Galadi and Julliard (1996)].

Metabolism in plants and animals: Carbamates are generally classed as having low mammalian toxicity because they are readily absorbed and excreted by the body. Chlorpropham is degradable and is metabolised to water-soluble products in higher plants as a result of hydroxylation of either the aromatic ring or the alkyl side chain. Boyd (1988) provided a comprehensive summary of the available literature on the mechanisms of chlorpropham metabolism in plants and animals.

In the potato crop, addition of a methoxy group to the ring structure to form isopropyl N-(3-chloro-4-methoxyphenyl)carbamate was observed by Heikes (1985). 3-chloroaniline, formed as a result of hydrolysis of the amide bond, was identified in samples of potato peel by Worobey and Sun (1987) along with small amounts of 3,3 dichloroazobenzene. The

authors concluded its presence could be a result of either metabolism of CIPC by the crop or contamination of the CIPC formulation.

1.2 Analysis methods for chlorpropham (CIPC)

A number of methods of analysis have been used for determination of CIPC over the years: the following section offers a review of the published methods, but is not intended to be exhaustive. Sherma (1999) published a comprehensive review of modern analysis methods for pesticides in general, and numerous multi-residue methods can be found in the literature: the discussion in this section will therefore be limited to methods specific for CIPC.

1.2.1 Extraction methods

CIPC can be extracted from a number of matrices using a variety of methods. For routine extraction from tubers and other plant material, extraction with a suitable solvent is suitable.

Traditionally, liquid-liquid extraction was employed for the extraction of CIPC from water, but this method has now been superseded by solid phase extraction onto cartridges, which offers several benefits including better recovery, sample concentration prior to analysis and the ability to sample in the field.

In recent years, a number of sophisticated methods have been developed for extracting CIPC from both solids and liquids: ultrasonic extraction [Babić *et al* (1998)], solid phase microextraction (SPME) [Volante *et al* (1998)], supercritical fluid extraction (SFE) and microwave-assisted solvent extraction (MAE) [Sun and Lee (2002)] to name but a few.

In studies reported in this thesis, simple solvent extraction of CIPC from plant material and soils; solid-phase extraction from liquids and collection of residues in air on adsorbent resin were utilised, based on methods developed by previous workers in this laboratory [Khan (1999); Tirmazi (1998); Boyd (1986)].

1.2.2 Spectroscopic analysis

Colorimetric analysis: In the 1950s and 1960s, a number of colorimetric methods for CIPC determination were published. These methods all involved the acid hydrolysis of

chlorpropham in a sample (or more commonly an extract) to yield 3-chloroaniline, which was then steam distilled and reacted with phenol-hypochlorite to form a blue complex and determined colorimetrically [Gard and Rudd (1953); Gard *et al* (1954); Gard and Reynolds (1957); Gard (1959)]. However, this method was quite complicated and prone to interferences, both from the sample matrix and nitrogen containing compounds similar to aniline.

In 1959, Montgomery and Freed (1959) published a simplified method, utilising alkaline hydrolysis and colorimetric determination after coupling with the dye N-1-naphthylethylenediamine dihydrochloride. In this method the solvent extraction stage was eliminated by hydrolysis of the whole sample, and the colour development stage was more reliable. Gard and Ferguson (1963) adapted this procedure for the analysis of trace CIPC in urine and milk from dairy cows, and the same authors also used it to determine CIPC in a range of food crops [Ferguson and Gard (1969)].

Infrared (IR) absorption: Ferguson *et al* (1963) used infrared spectroscopy to determine the concentration of CIPC in potatoes, following maceration and extraction with dichloromethane. They found the method to be more specific for CIPC in the presence of similar compounds (e.g. monuron and diuron) than the various colorimetric techniques. However, IR methods are less sensitive than the colorimetric methods, and can only be utilised in situations where >0.1mg of CIPC is present in the extract [Ercegovich and Witkonton (1972)].

1.2.3 Chromatographic analysis

A number of chromatographic techniques, including thin layer chromatography (TLC) [Babić *et al* (1998)], high performance liquid chromatography (HPLC) and gas chromatography (GC) have also been employed over the years for CIPC determination following extraction from various media e.g. soils, water samples and plant material.

For the determination of chlorpropham, HPLC and GC are often considered complementary to one another, with neither technique offering a significant advantage over the other. However, HPLC is sometimes considered more suitable for the thermally labile carbamates because it can be carried out at lower temperatures. It also has the advantage of requiring, in general, less sample clean-up than GC: relatively dirty extracts can be injected directly into reversed-phase systems as long as the extracting solvent is miscible in water.

HPLC: A number of methods for determining CIPC were published in the 1980s and 1990s. Detection is generally by UV detector at wavelength 235-250nm, although several other detectors have been used for CIPC e.g. diode-array [de Bertrand *et al* (1991)] and fluorescence [Miles and Moye (1988)].

Wilson *et al* (1981) described a method of determining CIPC residues in fruit and vegetables, following extraction with methanol and clean-up on acid alumina, with a limit of detection of 0.12ppm in potatoes. A slightly modified version of this method was also used by Camire *et al* (1995) to determine the fate of CIPC and TBZ residues in industrially extruded potato peels. Peña-Heras and Sánchez-Rasero (1982) reported two reversed-phase HPLC methods for the determination of pure and formulated CIPC. Corti *et al* (1991) carried out a comparative study of HPLC versus HPTLC (High Performance Thin Layer Chromatography) for determining thiabendazole, IPC and CIPC residues in potatoes, and concluded that HPTLC was a simple and precise alternative to HPLC. However, the HPLC was much more sensitive: limits of quantification were 0.08 and 0.007ppm for HTPLC and HPLC respectively.

More recently, HPLC analysis has been coupled with modern extraction techniques for the determination of CIPC in various matrices e.g. solid phase extraction (SPE) from water [DiCorcia and Marchetti (1991); Junker-Buchheit and Witzenbacher (1996)]; on-line trace enrichment methods for analysis of water [Hidalgo *et al* (1998)]; on-line solid-phase microextraction (SPME) from water [Gou *et al* (2000)]; microwave-assisted extraction from soils [Sun and Lee (2002)].

Gas chromatography: Prior to the development of all-glass flow paths for GC, metal inlet liners and/or columns were common. Direct GC analysis of CIPC was not possible because significant pyrolysis of the CIPC molecule would occur on contact with metal surfaces at temperatures in excess of 200°C [Romagnoli and Bailey (1966)]. Where untreated glass was present in the system, sorption and degradation of the molecule could also occur. As a result, derivitisation of CIPC was often necessary to stabilise the molecule prior to analysis e.g. by bromination [Gutenmann and Lisk (1964)] or acetylation [Lawrence and Laver (1975); Hajslova and Davidek (1986)]. However, this process is time consuming, and contributes to error and inaccuracy in the determination of the parent compound.

In recent times, the use of silanised glass columns and injection liners has overcome this problem, and GC now has significant advantages over other methods of analysis for pesticides: it is quick, cheap, and straightforward; very sensitive; often does not require

sample clean-up prior to analysis and can be used in combination with other techniques for confirmation of identity. Direct GC analysis of CIPC is possible using a range of columns (both packed and capillary) and detectors (e.g. FID, ECD). The following paragraphs detail some methods from the recent literature, but this list is by no means exhaustive.

Routine CIPC analysis in stored potatoes is generally carried out by means of extraction in a solvent (e.g. acetone, *n*-hexane), followed by clean-up and determination of the residue by gas chromatography. Capillary columns are most often used nowadays [Tsumura-Hasegawa *et al* (1992); Conte and Imbroglini (1995); Lentza-Rizos and Balokas (2001)] although packed columns are sufficient and sometimes easier to maintain [Khan (1999)]

Where identification of CIPC and its metabolites is required, residues are commonly determined using gas chromatography in conjunction with other analytical techniques e.g. GC-MS [Heikes (1985); Worobey and Sun (1987); Nagayama and Kikugawa (1992); Volante *et al* (1998)].

In studies reported in this thesis, routine CIPC analysis was carried out on either i) a Pye Unicam PU4500 packed column GC equipped with flame ionisation detector (3% OV-17 packing material) or ii) a Hewlett-Packard HP5890 capillary/megabore GC equipped with flame ionisation detector and 15m DB-1 column.

1.3 The application process

CIPC can be applied to crop in a number of forms including dust, granules, emulsifiable concentrate, thermal fog and vapour. At present, thermal fog application is the only approved method in the UK: at-loading formulations (e.g. dusts, granules and dips) are not available, although used in other countries, because the wound healing process can be inhibited by CIPC, leading to disease during crop storage.

Over the years, the method of thermal fog application has changed considerably. In the past, hand-held fogging equipment (e.g. Swingfog applicator) was used on-farm, or slightly larger commercial foggers were located in-store, or were used to apply chemical through a number of application ports in the store wall. In the last 20 years or so, the trend has been towards bigger fogging machines capable of applying the chemical faster, and with greater force. It is standard practice to carry out applications, and any subsequent applications through the same port. Using current equipment and application techniques, CIPC treatment of a 2,000 tonne store takes approximately 1 hour.

1.3.1 How the fog is produced

Fogging machines are essentially petrol driven engines, into whose exhaust stream CIPC (dissolved in a solvent) is added. On leaving the fogger, both the exhaust gas and the chemical are ducted into the store. High temperature and the addition of large volumes of air are required to produce a good quality fog. There are several key components to the fogger, as illustrated in Figure 1 below.

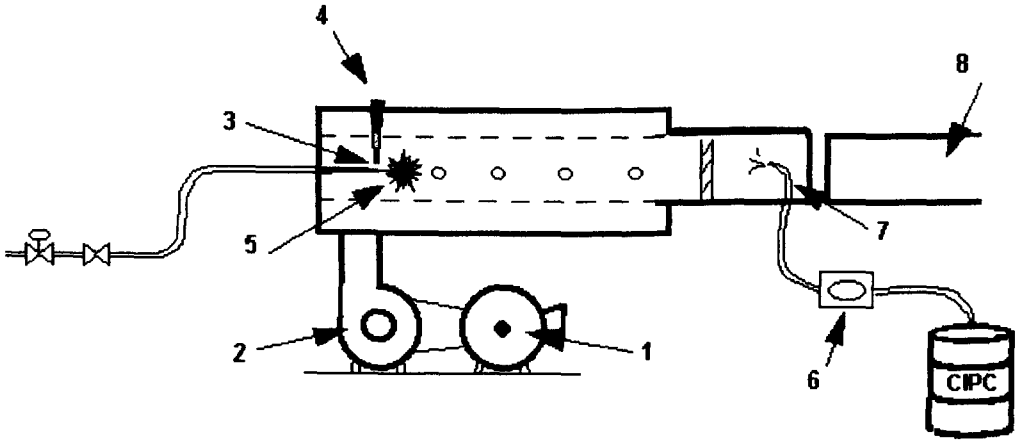


Figure 1 Schematic diagram of a fogging machine [after M. D. Lewis, M. K. Thornton, and G. E. Kleinkopf (http://www.kimberly.uidaho.edu/potatoes/cipc.htm)]

The motor (1) drives the blower (2) which pulls in large volumes of ambient air, and delivers it to the combustion chamber (3) at a controlled rate. Fuel is introduced to the air stream, and ignited via a spark plug (4) to produce a high temperature (500°C) air stream that passes through the fogger. Rate of fuel delivery is used to adjust the burner temperature. The CIPC formulation, consisting of a solution of up to 50% CIPC in a solvent, is pumped (6) into the air stream via a nozzle (7) near the outlet, then blown into store through metal ducting pipe (8) which can be up to 7m in length. The outlet of this pipe is positioned in the store for optimum fog delivery.

Figure 2 shows a commercial fogger during application (photograph courtesy of Stored Crop Conservation).

Figure 2 A commercial fogger, showing formulation supply line (front left) and metal ducting pipe to rear

The volume of air introduced to a store during the thermal fogging process has been calculated (as described elsewhere in this thesis) at between 750 and 1000m^3 per hour. This value does not take into account the volume of combustion gases.

Thermal fog application is known to be inefficient, with only a small proportion of the applied chemical reaching the crop. The fate of the rest is uncertain, but it is assumed to be lost to the atmosphere (either in vapour or particulate form) or sorbed onto the fabric of the store, or lost with the associated sediment during the washing process. Each of these processes have environmental implications of their own, and will be discussed in detail in the following chapters.

1.3.2 CIPC formulations

In the UK, the thermal fogging process is carried out using a formulation of CIPC, rather than with the active ingredient alone. In the USA, and elsewhere in the world, fogging equipment has been developed for the application of CIPC as a solid, which is melted and added to the exhaust stream of the fogger. However, at the time of writing the application of solid CIPC was not available in the UK. In environmental and regulatory terms, use of the solid is more desirable since one of the chemical components associated with the process, but not vital for its success (i.e. the solvent), has been removed. Flammable solvents used in the fogging process have also been implicated in several explosions in potato stores in the UK, although there is significant evidence to the contrary [Duncan (1999)]. Under normal working conditions, solvent will not accumulate to levels at which explosion is possible (6-36% methanol in air). Indeed, the production of very fine particles

of CIPC in a 'dry' fog may be responsible for initiating a process similar to that of explosions in flourmills: CIPC dust has been shown to explode with spectacular results under experimental conditions in the absence of any other flammable materials (see Figure 16 in Chapter 3).

A CIPC formulation, as used in the UK, will consist of a high concentration solution of CIPC (up to and in excess of 50% w/v) in one of four solvents: methanol, isopropanol, dichloromethane and methyl pyrollidone.

Methanol formulations (e.g. MSS CIPC 50M) are popular in processing type stores, in spite of concerns regarding the low flash point of methanol. Isopropanol formulations (e.g. MSS BL500) are often (wrongly) marketed as a low-flam alternative to methanol, although its flash point is very similar to that of methanol: ~13°C as compared to 11°C for methanol.

Dichloromethane formulations (e.g. Luxan's Gro-Stop range of products) are marketed on the basis of their non-flammable solvent. This is an advantage because it allows fans and store machinery to remain on during application without the risk of sparks, which may help improve the distribution of chemical around the store. However, as a chlorinated solvent, dichloromethane itself is unpopular in public health and environmental terms, and some countries (e.g. Germany) oppose its use in the food industry.

Methyl pyrollidone is the least volatile of the four solvents, but such formulations (e.g MSS Warefog) are popular, particularly in cold store situations.

1.3.3 Problems associated with the application process

In addition to the perceived explosion risk, there are a number of other problems associated with the application process: many are relevant to the reported work and will be more fully described in later sections:

1. Thermal fog application results in uneven chemical distribution around the store. In particular, residue levels can be very high at the surface of boxes at the top of a stack, or at the top of a bulk pile. This phenomenon is attributed to the accumulation of high temperature fog at the top of the store, followed by settling out of particles under gravity. Higher chemical levels are also found at the far end of the store from the application port and may be related to the large volume of air, and amount of force, employed to blow fog into the store.

2. The uneven distribution of chemical can result in unacceptably high residues in some parts of the store (e.g. top surfaces), and corresponding low values in the more difficult-to-reach parts (e.g. the middle of a bulk pile or stack of boxes). High chemical residues can lead to problems meeting Maximum Residue Level (MRL) requirements: at present, there is no established MRL in the UK, although much of continental Europe has a statutory MRL of 5mg kg^{-1} (ppm). CIPC is currently undergoing an EU review, and a Europe-wide MRL is expected in late 2003. At the opposite end of the spectrum, efficacy of the treatment may be affected where residue levels are too low: this can lead to sprouting in-store and result in a further application, which will exacerbate the problem of high residues in vulnerable areas while not improving efficacy in the problem areas in the store.

3. Although stores are sealed and all store controls switched off during application, they are not completely airtight: if they were, the store would pressurise during application. As a result, some of the applied chemical must escape through vents and louvres as fog is blown in and the store air is replaced. In addition to the significant loss experienced during the application process, chemical will continue to be lost through routine venting throughout the season. However, only vapour will be lost at this stage, and as such the magnitude of the loss will be far less than during application when both particles and vapour are present in the escaping fog.

4. In addition to problems relating directly to CIPC, the application method itself has been implicated in an observed decline in crop quality following treatment. Combustion products from the fogger, including CO_2 and C_2H_2 are ducted into the store along with the CIPC fog. Ethylene in particular has been correlated with a darkening in fry colour following application, and its effect can be lessened by venting the store earlier than the label-recommended 24 hours post-application [Dowd (2002)]. Recent BPC advice [Briddon, personal communication] has suggested that stores should be vented "when fog has cleared" which they estimate to be approximately 8 hours after application. However, investigation of factors influencing processing quality of stored crop was outwith the scope of this study: the reader is referred to the BPC-funded work of Dowd for more detail on this issue.

1.3.4 Crop residues and distribution

1.3.4.1 Distribution of chemical around the store

Many workers have found that, following commercial application of CIPC as a thermal fog (or aerosol), the distribution of chemical around a store is very uneven. Although the patterns of variation differ, this effect is common to both box and bulk pile storages.

Boyd (1988) observed variability in crop residues in a commercial store that were related to the position of the sample within the store. This effect was also associated with differences in the degree of sprouting around the store.

Khan (1999) studied the distribution of chemical in boxes in three commercial cold stores. Deposit levels varied with sampling site in each of the stores, but there were patterns common to all. In general, the highest chemical levels were found at the top of the store, decreasing toward the floor. An interesting effect noted was the very different amounts of chemical reaching the top and bottom halves of tubers located at the surface of top boxes: chemical levels on bottom halves were fairly consistent and similar to those determined in lower boxes; while top halves were significantly higher and more variable than at any other location. An improvement in the distribution of chemical was noted when internal circulation was used during and after application.

Conte and Imbroglini (1995) noted that, following aerosol application, chemical levels in both boxes and bulk piles varied significantly as a function of the sampling point within the store.

In 1996, Burfoot *et al* published a paper describing a mathematical model designed to predict the distribution of CIPC around a box store following thermal fogging. The model included factors such as fog particle size, the temperature difference around and within boxes and the rate of chemical application and examined their effects on the uniformity of chemical deposition. However, one limitation of the model was that it considered air movement only in the vertical direction. Xu and Burfoot (2000) later developed a 3-dimensional model based on mass, momentum and energy equations. Both studies concluded that uneven distribution of chemical is a consequence of the way in which the application is carried out.

In bulk piles, the highest chemical levels are often found at or near the bottom of the store, since application is commonly carried out through ducts in the floor [Corsini *et al* (1979)].

Kleinkopf *et al* (1997) also reported this pattern of distribution in a bulk pile, but suggested that it may be reversed by introducing half of the chemical from the bottom of the store, and half from the top by reversing the direction of the circulating fans. The authors also showed that chemical dispersal throughout the pile could be improved by running the store fans during aerosol application at 15-20% of their normal rate. Because the fog is denser than air, some circulation of air is required to promote the movement of CIPC around the store. However, if fans are run on full speed, the pattern of distribution was found to be even more variable.

1.3.4.2 Distribution of residues in the tuber

CIPC is known to remain mostly on the skin of the tuber, and not penetrate to any significant degree [van Vliet and Sparenberg (1970)]. Corsini *et al* (1979) estimated the concentration of CIPC necessary for complete sprout inhibition to be 20ppm in the skin (or 2ppm on a whole tuber basis).

Hajšlová and Davidek (1986) studied the penetration of IPC and CIPC into the flesh of treated tubers, and concluded that CIPC penetrates more than IPC, perhaps because of its higher polarity and better water solubility. They found ~4% of the total CIPC content of the tuber in the flesh 2 days after application, compared with only 1.3% of the total IPC. Although their figures appeared to show an increase in the amount of CIPC penetrating the tuber with time, this effect is misleading. Figures were calculated as a percentage of the total found on the tuber at any one time, and as chemical evaporated from the surface layer, so the amount in the flesh became a relatively larger proportion of the total. In practice, the actual amount of CIPC in the flesh remained fairly constant or even reduced slightly with time.

Coxon and Filmer (1985) showed that very little chemical penetrated the flesh of the tuber following 34 weeks of storage. The use of a methanol formulation was expected to facilitate the penetration into soils and crop, but no increase in crop residue was seen. The authors did, however, conclude that there was evidence of bound non-extractable residues within the potato.

Khan (1999) investigated the presence of bound residues in the potato, and found that conventional extraction with hexane did not result in recovery of all CIPC present. Extraction of the starch fraction of the tuber with methanol resulted in the recovery of additional chlorpropham, that amounted to an increase of ~10% in the residue level based on the fresh weight of the whole tuber. The author did not exclude the possibility of

chlorpropham being bound to other potato components. The presence of bound (or non-extractable) residues in the food crop has obvious implications in terms of food safety.

1.3.4.3 Factors influencing changes in residue level

Storage losses: The rate of volatilisation can be influenced by storage temperature and the amount of ventilation in the store. For example, Corsini *et al* (1979) noted the biggest reduction in residue levels at the top of the bulk pile between the months of March and May, when ventilation was increased to maintain the desired temperature in store. More loss would be expected in a processing store than in a pre-pack because of the increased volatility of the chemical at higher temperatures.

Hajšlová and Davidek (1986) attributed decreasing residue levels of both IPC and CIPC during storage to evaporation of chemical from the surface of treated tubers.

Tsumura-Hasegawa *et al* (1992) followed the dissipation of dichlorvos, chlorpropham and pyrethrins following post-harvest treatment of potatoes, and found in each case a two-stage dissipation of chemical. An initial, rapid reduction in chemical residues was attributed to pesticide loss from the surface of the crop with the second, slower rate of dissipation attributed to a more continuous process, such as biological or enzymatic breakdown. Residue levels declined more slowly at 5°C than under ambient conditions.

However, Coxon and Filmer (1985) suggested that losses through volatilisation might be less than expected. They measured the vapour pressure of CIPC absorbed onto filter paper to be $1*10^{-5}$ mm Hg, but when held on skin the value was 15 times less.

Microbial decomposition: suggested by Kleinkopf *et al* (1997), although the amount of microbial activity in stores is generally believed to be small because of the environmental conditions i.e. small amount of soil, fairly dry etc.

Metabolism by the crop: Heikes (1985) identified a metabolite of chlorpropham in tubers 21 days after CIPC application: this metabolite was isopropyl N-(3-chloro 4-methoxyphenyl) carbamate, formed by the attachment of a methoxy group onto the substituted phenyl ring. This compound was identified in baked potatoes, potato chips (crisps) and French fries at levels of 0.004ppm, 0.008ppm and 0.063ppm respectively. At the time, this was the only metabolite of chlorpropham to have been identified in potatoes.

However, Worobey and Sun (1997) identified both 3-chloroaniline and 3,3'dichloroazobenzene in potato peels from market potatoes, both in the low ppb ($\mu g\ kg^{-1}$) range. Coxon and Filmer (1985) also carried out studies into the fate of chlorpropham in potato peel using radiolabelled (^{14}C or ^{36}Cl) chlorpropham. None of the three metabolites described previously (isopropyl N-(3-chloro 4-methoxyphenyl) carbamate; 3-chloroaniline and 3,3'dichloroazobenzene) were identified in this study, but it is likely that the TLC radioscanning method was not sensitive enough to pick them up. The authors concluded that no metabolism involving cleavage of the side chain of the molecule had occurred on the basis that the $^{36}Cl/^{14}C$ ratio of chlorpropham present in extracts was identical to that of the original molecule.

Washing: Can remove significant, but variable, amounts of the chemical present on the tuber. The effectiveness of washing will be dependent on the degree of attachment of the chemical to the skin, which may in turn be influenced by the position of the crop in the store. For example, washing has been shown to remove 88% of CIPC [Tsumura-Hasegawa *et al* (2002)] and 33-47% [Lentza-Rizos and Balokas (2001)].

Peeling: Peeling has been shown to be the most effective means of reducing residues of surface-applied, non-systemic pesticides [Lewis *et al* (1996)]. Lentza-Rizos and Balokas (2001) reported a 91-98% reduction in chemical residues following peeling. Conte and Imbroglini (1995) found that peeling removed significantly more chemical than washing: perhaps unsurprising since most chemical is known to remain on the skin and not penetrate the flesh. Since the majority of potatoes are processed and consumed after the removal of the peel (with the exception of jacket potatoes, potato skins and jacket potato crisps), the amount of chemical ingested by the consumer is likely to be significantly lower than estimated based on whole tuber residue. This brings an added element of safety to the MRL guideline value.

Cooking: Frying and baking have been shown to reduce the CIPC content of frozen potatoes by ~20%. The loss of CIPC may be due to thermal degradation and subsequent loss of the 3-chloroaniline produced [Nagayama and Kikugawa (1992)]. Residues in peeled, fresh potatoes were shown to be reduced by up ~50% during boiling and microwave cooking by Khan (1999).

Various methods of wet and dry cooking were employed by Mondy and co-workers [1992a, 1992b and 1993]; all of which resulted in a decrease in CIPC content of potatoes. Moist heat (e.g. boiling, pressure cooking, steaming) reduced levels more than dry heat

(e.g. microwaving, baking with and without tinfoil). Transfer of residues to cooking water was noted in the wet cooking methods.

Lewis *et al* (1996) examined the carry through of pesticide residues during the production of potato crisps and jacket potato crisps. In general, residues of thiabendazole (TBZ), tecnazene (TCNB) and chlorpropham (CIPC) were shown to reduce at each stage in the manufacturing process e.g. slicing, blanching and cooking. The residues found in crisps represented only 2% of the theoretical carry-over for potato crisps, and less than 10% of the theoretical carry-over for jacket potatoes. These low values were attributed to the fact that the experiment was carried out during the summer months, when untreated field potatoes were being processed in the factory. During times when treated material is being processed, transfer of residues from potatoes to cooking oil, and subsequently back onto the potato crisps as oil is absorbed, is expected [Ritchie *et al* (1983)].

Packaging material: CIPC is known to affect the ascorbic acid and phenolic content of treated potatoes [Ponnamopalam and Mondy (1986)]: the increased phenolic level is thought to be due to a cellular stress response to CIPC. Mondy *et al* (1993) stored CIPC treated tubers for 4 months in i) mesh bags and ii) polythene bags. At the end of the storage period, both sets were tested for CIPC residue, enzymatic discolouration, phenolic and ascorbic acid content. CIPC residues were significantly higher on tubers held in polythene bags than mesh bags, presumably because of differences in loss through volatilisation. This difference in CIPC retention by the crop may be responsible for some of the differences in quality between the two sets of tubers. Tubers stored in polythene also exhibited significantly higher discolouration and phenolic content and lower ascorbic acid (Vitamin C) content. Although not directly related to tuber quality, maintaining the ascorbic acid content of potatoes is important since a significant proportion of the Recommended Daily Amount (RDA) in the diet comes from the potato.

1.4 Thesis objectives

Work presented in this thesis was part of a 3-year British Potato Council (BPC) funded research project entitled "Optimisation of the application of CIPC and evaluation of environmental issues relating to its use in the UK". As such, its aims are applied in nature, and all have obvious commercial benefits.

CHAPTER 2: This section includes a compilation and discussion of data collected during a survey on CIPC use and store management practice. Recent and incoming EU legislation is likely to change the way in which post-harvest chemicals are used, and in order for the industry to move forward, it is important to have a clear understanding of current practice. This part of the described work aimed to meet this need.

CHAPTER 3: Uneven distribution of chemical following thermal fog application can lead to problems in terms of efficacy and unpredictable chemical residues on crop. The imminent introduction of an MRL means industry must be able to predict with confidence the amount of chemical reaching each tuber. Achieving uniform distribution of chemical around the store will allow the number of applications and the dose rates to be tailored to achieve maximum sprout control with minimal chemical residues. This chapter discusses modifications made to the layout of the store and to the way in which the application process is carried out and the effect of such alterations on the way chemical is distributed around the store. Resulting deposit (unwashed) and residue (washed) levels of CIPC on commercial crop were determined and discussed in the context of an MRL.

CHAPTER 4: Describes studies carried out in experimental stores at Sutton Bridge Experimental Unit to determine the concentration of CIPC in air in treated stores. Various factors influencing the concentration in air (e.g. temperature, equilibration time) were addressed. The amount of CIPC present as a vapour in treated stores will have an effect on the amount of chemical lost from the store and also the likelihood of crop picking up residues from the air, which can be a particular problem for organic crop held in CIPC treated stores. Thus, it is important to know the quantity of CIPC present in air because of its commercial and environmental implications.

CHAPTER 5: Small-scale headspace studies were conducted in the laboratory using more volatile analogues of CIPC. The aim of this series of experiments was to investigate the behaviour of chemicals in sealed systems in the presence of various materials likely to be found in potato stores (e.g. soils, water, polyurethane foam). Such information can then be used to predict the movement of CIPC in the environment, and the most likely sinks for the chemical, which will in turn allow adequate removal techniques to be developed.

CHAPTER 6: The presence of CIPC in water effluent was investigated, with particular reference to crop washing operations (as opposed to crop processing facilities which present a whole different range of problems). Samples of effluent from commercial washing facilities were collected and analysed in order to determine the chemical load in

such effluent. The form of the chemical (e.g. dissolved in the aqueous phase or sorbed onto solids) will also provide detail on the likely fate and behaviour of the chemical load present in the environment. Commercial sampling was followed by laboratory studies which aimed to provide more detail on the partitioning behaviour of CIPC in a washing situation i.e. does it remain in solution, or is it taken up onto solid surfaces such as soils and potato peel? Adsorption onto cheap waste materials was to be considered as part of this project as an alternative to the comparatively expensive options of charcoal or UV light treatment, so these studies also provided detail on the feasibility of such an approach.

CHAPTER 7: These days, crop washing is often carried out by growers prior to delivery to processors or retailers and as a result the sophisticated methods of residue removal often employed at large-scale washing plant may not be available. Feasible methods for reducing chemical residues in contaminated water were an important part of this study, with particular reference to methods that are low-cost and/or easy to implement on site. This chapter describes the removal of CIPC residues from solution using small amounts of hydrogen peroxide. The influence of pesticide concentration, oxidant concentration and the presence of soil and/or dissolved organic material on the rate of chemical removal were investigated.

CHAPTER 8: Data from experimental work were used to create a simple model to estimate the amount of CIPC lost from a store throughout the season. The amount of chemical recovered on the crop represents only a small fraction of the total applied, and the fate of the rest is at present unknown, or unquantified. To enable the industry to answer questions credibly and present a caring and responsible attitude towards chemical use, more detail on the processes governing the loss of CIPC from stores is required. This chapter aims to address this need.

CHAPTER 9: Presents a summary of the thesis findings and discusses the applications of the reported work in a particularly commercial, or applied, context. Developments regarding the use of CIPC in the potato industry that have occurred since the work was completed are also presented and discussed. The potential for continuation of the work is clear, and suggestions and recommendations for future work are offered.

Chapter 2

COLLECTION OF SURVEY DATA ON CHLORPROPHAM USE AND STORE MANAGEMENT PRACTICE IN THE UK

2.1 Introduction

2.1.1 Background to the study

CIPC is the most commonly used sprout suppressant worldwide, and is currently the only post-harvest chemical available for use in the UK, following the banning of tecnazene after the 2001 storage season.

The aim of the reported work was to obtain detailed up-to-date information about the way in which chlorpropham is used on stored potatoes in the UK. Store management practice (pre- and post-application) was investigated along with the application method, because both can have significant effects on the efficacy of the treatment, and consequently the need for repeat applications.

Although traditionally associated with processing crop (held at high temperature to prevent low-temperature sweetening of the crop), in recent years the use of CIPC has become more widespread on pre-pack and general ware crop. The low holding temperature in pre-packing stores ($\leq 5°C$) means that crop respiration and sprouting pressure is generally fairly low. In the past, this has meant that CIPC use has not been required to maintain crop quality during storage. However, consumer demand for year-round supply of high quality crop has driven the trend towards longer storage times and larger industrial-scale storage facilities holding thousands of tonnes of crop. Maintaining sprout control, while made easier by the sophisticated environmental controls in modern buildings, can be complicated by the huge tonnage, in particular where different cultivars are held in the same store.

Guidelines on sprout suppressant application state that they should be used only to deal with active signs of sprouting and not as "insurance treatments" [Pringle and Cunnington, (2002)]. However, applications are often made on a calendar basis, irrespective of crop condition.

At the time this study was carried out, the most recent industry data on chlorpropham use dated from 1994, and was fairly limited as it came from a section in a study not specifically targeted at CIPC users [Storey *et al* (1994)]. During the course of the reported work, a more recent review of pesticide use was published by the Ministry of Agriculture, Fisheries and Food and the Scottish Executive Rural Affairs Department [Fox *et al* (2000)]. This survey detailed the use of a number of pesticides, including chlorpropham, on both ware and seed crop during 1998. This report has since been superseded by an updated survey carried out in 2000 [Dennison *et al* (2003)].

2.1.2 Structure of the study

The survey consisted of two separate questionnaire forms, which were completed by recipients and returned by post.

In autumn 2000, a short (2-page) questionnaire was formulated at Glasgow, in consultation with staff at BPC's Sutton Bridge Experimental Unit. This questionnaire was distributed to 500 of the country's top growers via a contacts list supplied by the BPC, which was taken from an existing database of registered CIPC users. 199 of the 500 questionnaires were completed and returned.

After the initial questionnaires were returned, a more detailed form was sent out to a smaller number of growers (mostly those who had indicated a willingness to provide further detail on their completed short questionnaire) – 117 of these more detailed surveys were completed and returned.

Since a detailed discussion of the findings from the first questionnaire has already been published elsewhere [Park (2001)], only a short summary of the most important points will be presented here. This chapter will also include a detailed discussion of the findings from the more detailed questionnaire, as well as a summary of the most important findings from the survey as a whole.

2.1.2.1 Short questionnaire

A blank copy of the short questionnaire can be found in Appendix 2.

The paper was split into three sections, and was limited to basic information and yes/no answers wherever possible to encourage a good response.

Section A: Business information and contact details. In accordance with the Data Protection Act (1998) no personal details, company contact information or other identifying data were held electronically. Each completed record was assigned a unique reference number that was entered onto the Microsoft Access database along with the responses to survey questions. Where further contact was to be made with individuals or companies, details were taken from the paper copies of the questionnaire, which were kept on file in the lab.

Section B: General information on the type of stores used by the company, the end use of the crop and what chemical treatments, if any, would be used in an average season.

Section C: Details specific to the season 1999/2000. Respondents were asked to provide store management and application information on **one** particular store onsite – the one in which crop was held for the longest period of time during the 1999-2000 storage season.

2.1.2.2 Long questionnaire

A blank copy of the long questionnaire can be found in Appendix 2.

Again, the questionnaire was divided into three sections. The sections covered similar subject areas to those described in the initial questionnaire, although each section contained more questions, and required more detailed responses.

2.1.2.3 Recipient list

The 500 recipients of the short questionnaire were selected by the British Potato Council, and mainly came from their database of registered CIPC users. As a result, the sample population is biased in some respects, as discussed in later sections. In particular, figures on the proportion of growers using CIPC and the percentage of crop treated will be affected.

However, the aim of the survey was to gather information on industry practice where CIPC is being used, so it was necessary to restrict the scope of the questionnaire to those using CIPC on a regular basis in their stores.

In addition, a large number of the questionnaires were sent out to suppliers of a major potato processing company, and as such, bias was introduced to some data e.g. figures relating to crop end-uses and store conditions.

Although there may appear to be limitations to the study as a result of who was selected to fill in the questionnaire, its findings are still valid and did provide much useful information on the way CIPC is used in the UK. However, caution must be exercised when extrapolating the findings to the industry in general (as opposed to our small sample population) and when comparing the results with published statistics taken from more wide-ranging studies.

2.1.3 Handling of data

Data from the questionnaires was entered into an electronic database, to facilitate easy sorting and searching of the data, and to make retrieval of specific details quick and simple. When constructing or working with a database, the user must become familiar with a number of terms and concepts.

2.1.3.1 Construction of database in Microsoft Access 97/2000

In Access, a **record** is the set of details or information relating to one person, company or item. In this instance, a record refers to the set of answers from a single completed questionnaire. **Fields** are each individual piece of information i.e. the response to one particular question.

When setting up a database in Microsoft Access, it is important to have a clear idea of the types of manipulation required of the data, as the ability to successfully query the database can be dependent on how it is constructed. A flat-file database has a very simple design, whereas a relational database holds a number of cross-referenced files that are linked together by a common field or fields. Relational databases, while very useful in certain contexts, can be difficult to work with unless the user is proficient in the use of databases. In this case, a flat-file database was constructed, and all information was entered into one data table. This design was adequate for the purposes of the study since only straightforward analysis of the data was expected (e.g. summing and averaging of data). Data was to be shared between Glasgow University and staff at the British Potato Council so a simple table was considered the most appropriate way to present it.

2.1.3.2 Extraction of information and presentation of results

Querying the database

Information was extracted from the database using the 'Query' function in Microsoft Access. The types of queries that could be performed were defined by the way in which both the questionnaire and database had been formulated (as discussed in later sections).

Presentation of findings

Data are presented in both tabular and graphic form. In tables, the number of responses and the total tonnage held by those answering that particular question are presented as base values, to allow percentages and proportions to be calculated for each option. 'Null responses' (where the question is unanswered) can make identifying trends in the data difficult in some instances, and were particularly common for questions with yes/no tick boxes. Calculating proportions relative to the base value (rather than relative to the total described tonnage or total number of responses to the questionnaire) was considered the best way to deal with them. In any study of this kind, they are bound to be a problem, in particular where questionnaires are filled in and returned by post. MAFF's PUSG surveys are completed by trained personnel during visits to each surveyed site – omissions and mistakes are less likely to occur in a system like this, than in ours where respondents completed the questionnaire and returned it by post with no guidance on how to complete it.

2.2 Results from the initial questionnaire

A copy of the two-page short questionnaire sent out in the autumn of 2000 can be found in Appendix 2.

Of the 500 questionnaires sent out, 200 were returned. This unexpectedly high return rate (40%) reinforces the importance of CIPC to the potato industry, particularly in today's climate where the chemical is undergoing an EU review and has an uncertain future. While the industry appreciates the importance of showing responsible use of agrochemicals, it is also aware of its reliance on CIPC, which is currently the only sprout suppressant chemical available for post-harvest use in this country. This questionnaire was sent out early in a 3-year study examining ways of using the chemical more effectively, and assessing potential environmental or food contamination problems. This was explained to the recipients of the questionnaire in the accompanying cover letter from the BPC, and the degree of

importance placed on these issues may have precipitated the good response to the survey. (The prize draw might have been an added incentive!)

The following sections give a brief overview of the most interesting points to arise from responses to the initial questionnaire.

2.2.1 General storage information

2.2.1.1 Store types and total tonnage

Of the total tonnage described, 52% was held in box stores and 48% in bulk. The total tonnage declared by the respondents was 623,012 tonnes, although two respondents did not give any detail of their tonnage. This represents approximately 9% of the total UK production during 1999-2000.

In the analysis of most of the data, 623,012 tonnes was taken as the base tonnage, from which percentages and proportions were calculated.

2.2.1.2. End use of crop

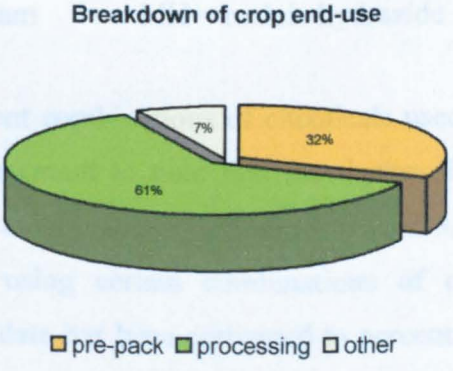


Figure 3 Proportion of total crop stored for different end uses

On the questionnaire form, only three end-use options were provided. The "Other" category could include options such as seed and general ware, and other uses, depending on the respondents interpretation of the question. The 'pre-pack' and 'processing/chipping' options could also have been further broken down to provide a more detailed picture.

This is one of the questions where the list of recipients may have introduced bias into the results. Since CIPC has traditionally been associated more with the processing industry, it is likely that most registered users of the product are processors. However, it may also be

that sprout suppression is more often necessary in processing stores at higher temperature than in cold stores where crop activity is reduced. Caution should be exercised if extrapolating this particular data to the industry as a whole, as this figure does not necessarily reflect the true market share of the two types of crop.

2.2.1.3 Extent of sprout suppressant use

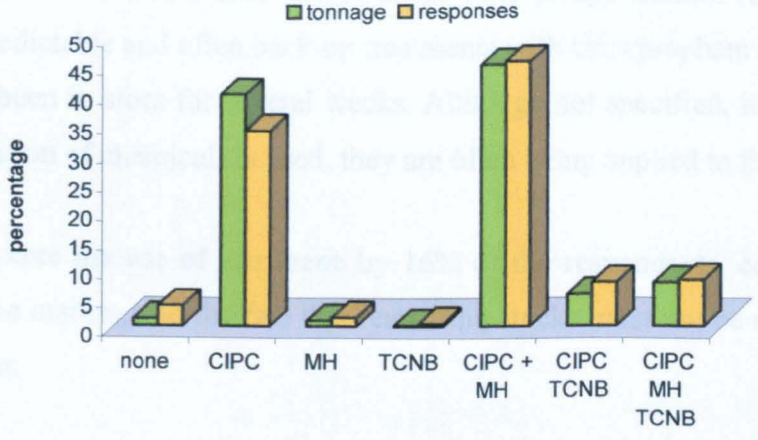


Figure 4 Percentage of responses indicating use of a range of sprout suppressants, and associated proportions of the total tonnage

Key: CIPC = chlorpropham MH = maleic hydrazide TCNB = tecnazene

Figure 4 shows the different combinations of chemicals used by growers who completed the questionnaire. It is important to note that the figures do **not** represent the tonnage actually treated with each combination of chemicals in 1999/2000. What they do show is the number of growers using certain combinations of chemicals, and the tonnage associated with each. The data has been converted to percentages of the total in each case (612,013 tonnes and 199 responses) to allow the data to be presented on the same graph.

For example, 45% of the total tonnage described is held by those who use (or have used) both CIPC and maleic hydrazide on their crop. However, it may be that some crop is treated pre-harvest with maleic hydrazide and not treated again during storage. Other crop may be left untreated in the field, but receive a chlorpropham treatment in-store. This question was designed to provide a general picture of the extent of use of each chemical, not to provide detail on the actual treatments received by particular crop. Such detail was to follow in the later section of the questionnaire, relating to specific conditions in the 1999-2000 storage season.

Chlorpropham was by far the most widely used sprout suppressant, used by 95% of respondents, either alone or in combination with other chemicals. Chlorpropham/maleic hydrazide was the most common combination of treatments. While maleic hydrazide can be very useful, particularly for controlling volunteers in the field, its efficacy in terms of sprout control is dependent on getting good coverage and an even amount into each tuber. This can often be difficult to achieve with the crop still in the ground, and will largely depend on climatic and environmental factors at the time of application. As a result, its results can be unpredictable and often back-up treatments with chlorpropham are necessary once the crop has been in store for several weeks. Although not specified, it is likely that where this combination of chemicals is used, they are often being applied to the same crop.

It is interesting to note the use of tecnazene by 16% of the respondents, considering its withdrawal from the market, and the fact that remaining stocks must not be used after the 2001 storage season.

2.2.2. Specific details for season 1999/2000

In this section, each respondent was asked to describe storage conditions in the individual store in which they held crop for the longest time during 1999/2000. As a result, the base tonnage for the following sections reduced to 175,065 tonnes since most commercial storage facilities will have more than one store.

2.2.2.1. Store type and store management

55% of the described tonnage was held in boxes, with 45% in bulk.

The majority of the crop (68%) was cured for between 10 and 14 days.

Store temperature ranged from 2°C to 13°C, reflecting the use of the crop for both pre-pack and processing. Low temperature storage of crop leads to an increase in reducing sugar content, and an associated darkening of fry colour, while high temperature storage increases crop respiration and can shorten dormancy. As a result, the end use of the crop can generally be deduced from the holding temperature of the store.

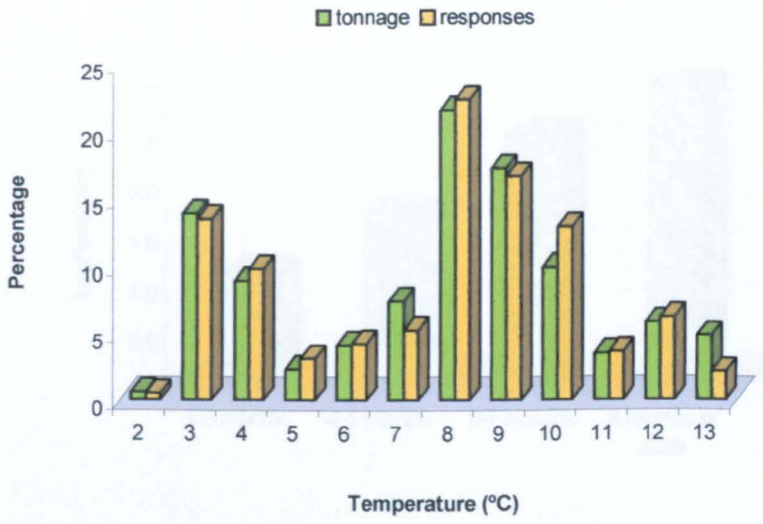


Figure 5 Holding temperature and associated tonnages and responses

Store temperature data fits well with the earlier information on end use. In this instance, 26% of the crop was held at ≤ 6°C and 74% at >6°C. Earlier data suggested that 32% of the total crop (612,013 tonnes) was held for the pre-pack market (generally at ≤5°C to maintain crop quality), 60% for processing (≥8°C to prevent low-temperature sweetening) and 7% for other (non-defined) purposes, that may include seed and general ware among others.

The major movement of crop out of store occurred after 6-7 months of storage (45%). Only 8% was held for 3 months or less, with 29% in store for between 4 and 5 months, and 18% for 8 months or longer.

Mean store temperature decreased with increasing storage time, from 9°C at 1-3 months to 7.3°C at 8 months or more. This trend reflects the need for storage at more moderate temperatures to maintain quality for longer periods of time. The percentage of the stored crop held at≥12°C fell off rapidly after 3 months, while the relative amounts at low and moderate temperatures increased throughout the season.

2.2.2.2 CIPC applications

90% of respondents indicated use of CIPC on some or all of their crop during 1999/2000. In total, 164,705 tonnes (90% of base tonnage) were treated.

Over a storage period of more than 8 months, the minimum number of treatments was 0 and the maximum was six. Figure 6 shows how the mean number of applications increased with storage time.

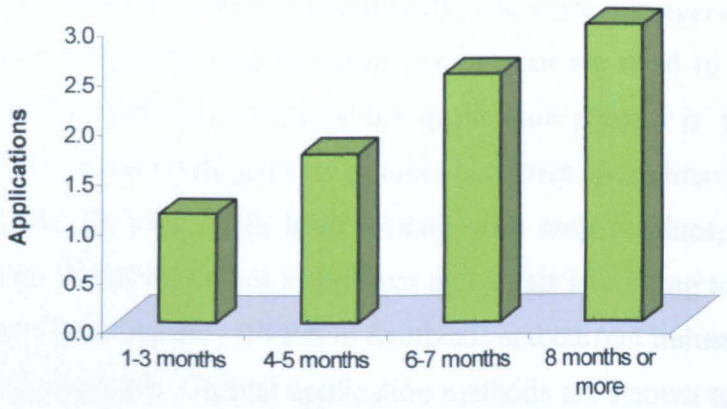


Figure 6 Mean number of CIPC applications for various storage times

The range of applications also increased with storage time, from 0-2 at 1-3 months, to 0-5 at 4-5 months and 0-6 from 6 months on.

The number of applications being carried out suggests that more than one formulation may have been used in the same store. Label instructions state a maximum weight of active ingredient that can be applied in one season, and describe dose rates that generally allow for 3 applications during the season. No dose rate information was requested on the questionnaire form, so it is possible that where crop is treated up to 6 times, it is receiving a larger number of applications at a reduced rate.

However, it is known that a significant amount of 'dual-labelling' occurs in industry, and that many store managers feel that adequate sprout control cannot be achieved throughout the whole season by three applications of CIPC. Indeed, many believe that they are acting within GAP guidelines in terms of protecting crop quality when carrying out multiple applications. However, there are a number of problems associated with the use of so much chemical.

Although there are several formulations of CIPC with different names, they are essentially all the same in terms of the active ingredient, and often concentration (e.g. MSS CIPC 50M and BL 500). What differs is the solvent in which the chemical is applied. It is stated clearly on each label that it is an offence to apply more active ingredient in one season than the stated total dose. There is, however, nothing on the label that precludes the use of other formulations, and so dual labelling (although not in itself against the law) can be considered by some to be a useful way of getting around the label restrictions.

What needs to be addressed is the issue of why so many applications are deemed necessary. CIPC is a relatively expensive commodity, and store managers are unlikely to commission any more treatments than the crop requires, so we need to ask what is so different about store management practice or the application process in the UK that we need to use so much chemical while growers in other countries (Scandinavia and the USA in particular) can make do with much less? Along with crop residues, the amount of chemical released into the environment in effluent and in air is coming under increasing scrutiny by the Environment Agency (SEPA in Scotland) and current industry practice will not meet the required standards. Current application methods are known to be inefficient, with only a small proportion of the chemical introduced to the store actually reaching the crop.

There is also a tendency to over-treat crop by applying at regular intervals, rather than as required by the crop. In industry, visual assessment of crop condition can be tricky, particularly in the middle of a stack of boxes, or in the middle of a bulk pile, so CIPC is often used as an 'insurance' treatment to prevent any movement, even though this goes against BPC and product label advice [Pringle and Cunnington (2001)].

In cold stores in particular, the reason for CIPC use is not entirely clear. At low temperature, crop respiration and activity will be low, and it would seem that during a few months of storage, sprouting should not be an issue. It has been suggested that the primary purpose of CIPC when applied in such cases may be to provide an extension of shelf life once the crop is removed from store. However, crop in cold stores has been observed to sprout even when crystals of chlorpropham are present on the surface of tubers.

Store managers or their own staff carried out 7% of chlorpropham applications, while the remaining 93% were carried out by specialist contractors.

2.2.2.3 Post-application

38% of respondents indicated that some air circulation was carried out during the chemical application, although no details were given on how this was achieved e.g. fans running continuously during application or short pulses of fans for clearing fog out of ducts. This is another question where the individual's interpretation of the question may have affected the result.

Since formulation labels (with the exception of Luxan Gro-Stop Fog and Gro-Stop HN) do not recommend the use of fans during application because of the perceived combustion

risk, it is likely that at least some of these responses relate to the clearing out of ducts immediately post-application.

The majority of stores (76%) were switched back on within 24 hours of application. Traditionally, formulation labels have recommended that stores remain off for 24 hours following application, and this was the most common response (52%). However, recent work has shown that the useful portion of the fog has fully settled within 8 hours of application [Briddon and Jina (2000)], and that fry colour can be damaged the longer the store remains closed [Dowd (2001)]. These developments have led to the BPC issuing the advice that stores should be vented 'when the fog has cleared' which they suggest is around 8 hours post-application. However, this advice must be qualified by stating that any such action will be done at the grower's own risk if not compatible with label instructions because of potential insurance claims in the event of any problem with the application. However, recent alterations to several labels (e.g. MSS CIPC 50M) have incorporated this advice, and a common recommendation now is that normal ventilation can be resumed 12 hours after the application.

19% of store managers indicated that stores were left for 48 hours or longer post-application before fans were switched back on. If these stores are not vented for in excess of 48 hours, the CIPC application process will most likely have damaged the crop. However, damage to fry colours as a result of the accumulation of ethylene in the store atmosphere (as a product of the combustion of petrol) has been shown to be reversible, at least in part, if the store is correctly managed throughout the season.

It is possible that the original question could have been misinterpreted in this case. The distinction between the switching back on of store controls and personnel re-entering the stores was not made clear, which may have led to some confusion. It is possible that store control was activated remotely, but that personnel did not re-enter the store for 48 hours or that stores were left sealed and switched off for 48 hours. These responses could be a product of the way the survey was carried out (returns by post rather than questionnaires completed during site visits by BPC or GU staff).

2.2.2.4 Crop washing

~14% of respondents (holding ~20% of the crop reported in this section) indicated that crop is washed on-site. Most of this crop was held in stores at ≥ 8°C, so this is likely to represent crop washed prior to delivery to processors rather than packing operations.

2.3 Results from second survey questionnaire

A copy of the second, more detailed questionnaire can be found in Appendix 2. This time, fewer questionnaires were sent out, mainly to individuals who had completed the original survey and indicated their interest in participating in a more detailed survey.

117 responses were collected for this part of the survey. The total tonnage held by respondents was 481,002 tonnes, which equates to approximately 7% of the total UK production in 1999/2000 [Anon (2001a)]. However, 13 respondents gave no details of the tonnage they held, so the actual storage capacity surveyed will be higher than stated.

2.3.1 General information on storage practice

2.3.1.1 Business nature

Approximately 90% of the respondents (holding ~70% of the total crop) identified themselves as producers rather than merchants or 'other' on the form.

2.3.1.2 Store building design

49% of the total tonnage was held at facilities including both purpose-built and converted stores. 23% was held on sites with stores converted from other uses, and 28% on sites with only purpose-built, modern stores.

More sophisticated storage buildings are generally easier to manage, and allow greater control of variables such as temperature, humidity and ventilation, making it easier to maintain crop quality over longer storage periods.

Of the tonnage described, 64% was held in boxes, with 36% in bulk. Only 3% of respondents had both bulk and box stores at their facility.

Overall, only 4% of crop was held in stores with no ventilation, and the majority of these were bulk stores. Almost half the crop was held where the circulation of ambient air is the only method for cooling or ventilating the store. One-third of the total tonnage was held in stores where both ambient air and refrigeration can be used to control store temperature.

Table 3 Temperature control and ventilation systems in described stores.

Store type	Tonnes in boxes	% of total	Tonnes in bulk	% of total
Without fan ventilation	4,600	1.0	16,500	3.4
Ambient cooling only	77,730	16.2	145,750	30.3
Refrigeration only	62,000	12.9	0	0
Ambient and refrigeration	166,272	34.6	8,150	1.7

Base = 104 responses (481,002 tonnes)

2.3.1.3 Insulating materials

Table 4 Insulating materials used in described stores, and associated tonnages.

Insulating material	Tonnage	Tonnage (%)	Responses
Polyurethane sprayfoam	203,880	43.1	59
PU foam and PS	154,172	32.6	19
PU, PS and straw	53,500	11.3	5
Polystyrene (PU)	26,350	5.6	15
PS and panelling	13,500	2.9	1
PU and straw	8,700	1.8	7
PU and panelling	7,300	1.5	3
Composite panelling	3,200	0.7	1
Straw	2,650	0.6	3

Base = 113 responses (473,252 tonnes)

By far the most common insulating material is polyurethane spray foam, with some 90% of the reported tonnage held in stores containing it (either alone or in combination with other materials). 77% of respondents indicated that insulation is exposed in their stores, as has been common practice in the past where spray foams are used. In the more modern stores, foam insulation is often sandwiched between layers of board.

Exposed porous polymer surfaces like polyurethane or polystyrene foam may absorb CIPC onto their surfaces, resulting in a loss of effective chemical from the store and potential contamination problems at a later date. Polyurethane has been used as an adsorbent for pesticide vapours in a number of studies [Kearney and Kontson (1976); Turner and Glotfelty (1977); Turner *et al* (1978)] so it is possible that significant amounts of CIPC

could be absorbed onto insulating material, given the large surface area of the walls and roof of a store.

2.3.1.4 Store filling and storage period

60% of the reported crop was held in stores that are filled within 2 weeks, but almost one quarter of respondents said their stores take more than 3 weeks to fill. Ideally, stores should be filled as quickly as possible to minimise the stress on the crop and allow store conditions to stabilise as soon as the crop is in.

The major movement of crop out of store occurred after 4 to 7 months of storage, with less than 5% held for less than one month. However, this situation should not be considered as representative of the industry as a whole – these questionnaires were distributed to registered users of CIPC. As a result, short-term storage of crop is unlikely.

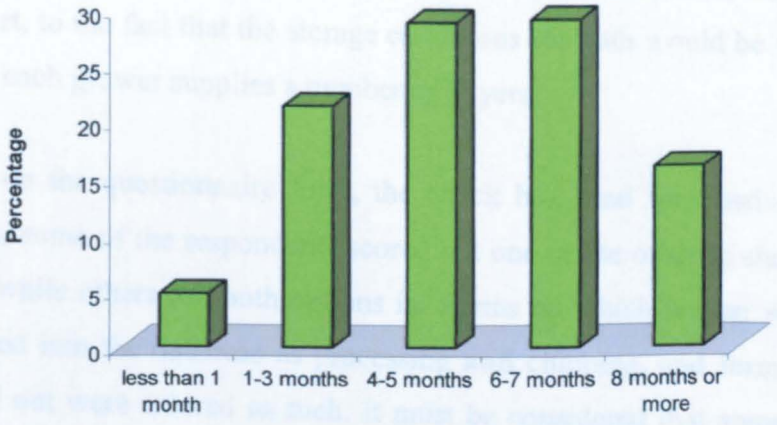


Figure 7 Percentage of total tonnage held for different storage periods

What they do show, however, is the trend towards longer storage periods because of year-round demand for quality produce.

2.3.1.5 End-use of stored crop

Seven main markets for crop were identified on the questionnaire form. Respondents were given the option of selecting more than one. Table 5 shows the number of responses for each end-use. Since more than one option was often selected, the percentage responses total over one hundred, and the cumulative tonnage is more than the base tonnage for this question.

Table 5 End-uses of stored crop as described by respondents, shown with cumulative storage capacity for each.

End use	Respondents	Storage capacity (tonnes)
Processing	88	390,780
Chipping	82	308,030
Washed pre-pack	46	30,190
General ware	18	129,850
Dry brushed pre-pack	7	46,272
Seed	7	85,300
Other	0	0
Base 113 responses (477,402 tonnes)		

This question was another in which the phrasing of the question or the format of the form dictated particular difficulties with data collation and analysis. For example, the combination of processing and chipping was a very common one, which could be due, at least in part, to the fact that the storage conditions for both would be very similar and it is likely that each grower supplies a number of buyers.

However, on the questionnaire form, the check box read 'processing/chipping' – when filling it in, some of the respondents scored out one or the other to show which applied in their case while others left both options in. Forms on which neither entry was scored out were entered into the database as processing **and** chipping, and forms where one option was scored out were entered as such. It must be considered that some of the 'processing and chipping' responses are not intended as such, and are a result of the respondent not completing the form correctly (or me not making it clear what response I was looking for).

Only a small proportion of respondents (6%) are storing for seed. Previous applications of CIPC can cause problems with the germination and growth of seed tubers in stores, even if the chemical has not been used for years, as a result of contamination of store materials (e.g. insulating material). Therefore it is unlikely that applications of CIPC will commonly be carried out on a site where seed crop is held, even if it is stored in a separate building.

Before these data can be used for any other purpose, it must be realised that it comes from a very biased sample population. No inferences can be drawn from the proportions of crop held for each end-use and extrapolated to the industry as a whole.

The tonnages stored for each individual purpose cannot be determined because of the way the questionnaire was structured, but it can be said that respondents supplying crop to only one area of the market hold only one quarter of the total tonnage. Respondents storing for 2 markets held approximately half of the total crop, while almost one quarter is intended for three or more different markets. This suggests that at any one storage location, individual stores may often be operating under different store management conditions during the same season.

2.3.1.6 Sprout suppressant use

Chlorpropham is by far the most widely used chemical, either alone or in combination with pre-harvest maleic hydrazide. Maleic hydrazide use was indicated by 46% of respondents, but seldom on its own. Applied in the field, maleic hydrazide is effective at controlling volunteers, and also has some sprout suppressant effect, but its efficacy is largely determined by conditions in the field at the time of application. As a result, post-harvest CIPC treatment is often necessary to maintain sprout control throughout the season.

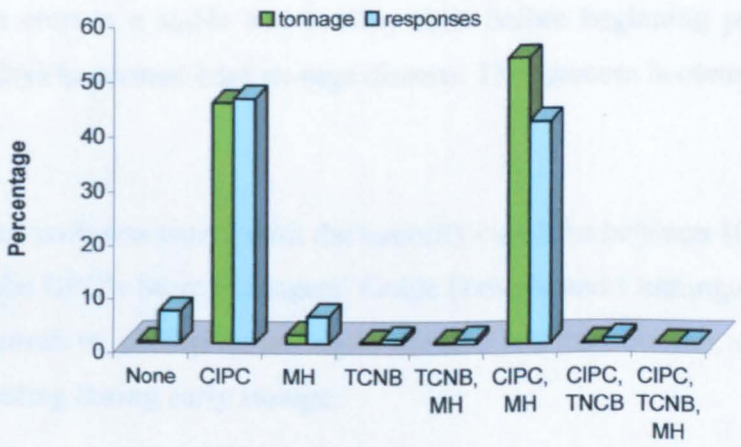


Figure 8 Combinations of sprout suppressant chemicals used by respondents

The graph above shows the percentages of the total described tonnage held by respondents indicating general use of different combinations of chemicals on their crop. It does **not** show the tonnages actually receiving treatments during 1999-2000.

Chlorpropham was used on 97.3% of the reported crop during 1999-2000. On average, those using CIPC applied it to 77.3% of crop held in their stores.

CIPC and MH are the only two chemicals used to any significant degree, which is hardly surprising considering the withdrawal of tecnazene from use (banned after 2001/2 season).

Storage of crop without chemicals is uncommon on a commercial scale, although the particularly low response in this study could be a result of the survey being aimed at CIPC users in particular, rather than at growers in general.

2.3.2 Specific store details

For the remainder of the questionnaire, respondents were asked to provide answers based on the individual store where crop was held longest in 1999-2000 storage season. The total storage capacity of the described stores was 138,223 tonnes (~2% of UK total that year).

2.3.2.1 Store type

Approximately 60% of the tonnage described in this section was held in boxes, with 40% in bulk stores. Only one respondent had both box and bulk stores at their facility.

2.3.2.2 Curing of crop

After a store is filled, it is normally maintained at a fairly high temperature (regardless of intended holding temperature) for a period to allow suberization of the skin to occur. It is necessary to have crop in a stable and healthy state before beginning pull-down (at no more than 0.5°C/day) to prevent later storage disease. This process is commonly known as curing.

93% of the reported crop was cured, with the majority cured for between 10 and 14 days as recommended in the BPC's Store Managers' Guide [Pringle and Cunnington (2001)]. Any less than this can result in incomplete setting of the skin and later disease, while any longer may result in sprouting during early storage.

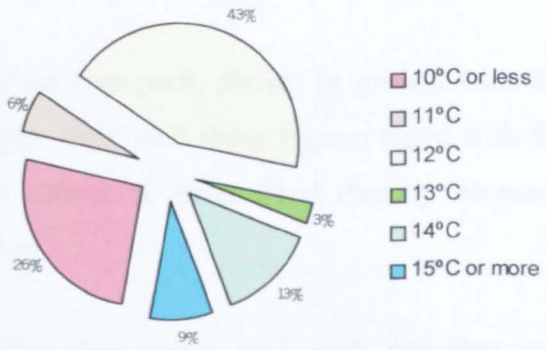


Figure 9 Curing temperature and associated proportions of tonnage

Figure 9 shows that the majority of crop was cured at between 12°C and 15°C as recommended by the BPC.

2.3.2.3 Holding temperature

The temperature set point of a store during the season will be dependent on i) the end-use of the crop and ii) the anticipated length of storage (e.g. higher temperatures for shorter storage times). For example, pre-pack crop will generally be held at≤5°C to maintain tuber quality and prevent sprouting in-store; while processing and chipping crop requires a higher temperature (≥8°C) to prevent the low-temperature conversion of starch into sugars, which causes an undesirable sweet flavour and dark colour in processed (e.g. fried) products.

Store temperatures ranged from 2°C to 11°C, as shown in Figure 10 below, reflecting the use of crop for both pre-packing and processing

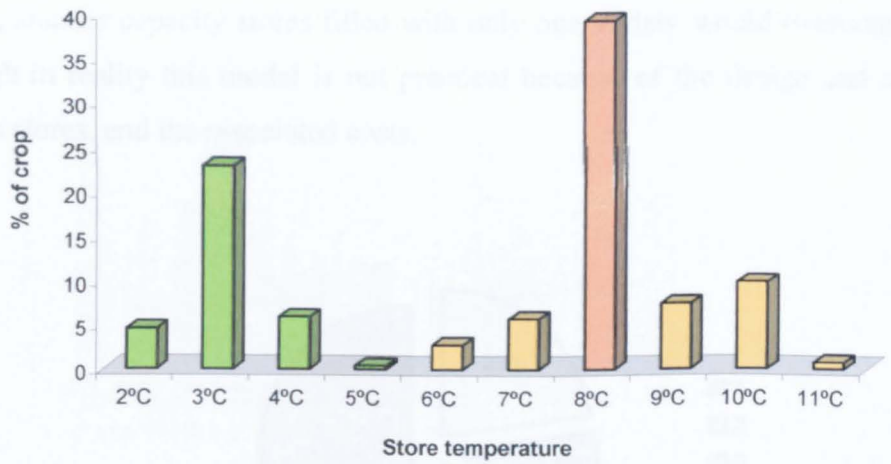


Figure 10 Percentages of total tonnage stored at temperatures between 2°C to 11°C

34% was held at 5°C or below (pre-pack, shown in green), with 66% at 6°C or above (processing, shown in orange). How well these figures agree with the end-uses reported earlier in the questionnaire cannot be determined directly because no tonnages were collated for the earlier question.

However, it can be said that they agree well with end-uses reported in the short questionnaire, where 26% of the tonnage was held at 5°C or less, and 74% at higher temperatures. In general terms at least, the proportion of stored crop held for pre-pack and

processing seems to match, with approximately one-third pre-pack and two-thirds processing. This relationship holds for this particular survey, but cannot be assumed to be representative of the industry as a whole because of bias introduced by the fact that registered CIPC users only were chosen to participate in the study.

2.3.2.4 Varieties

No information was gathered on the actual cultivars or combinations of cultivars stored in the described stores. However, respondents were asked to detail how many cultivars they held in the store during 1999-2000.

In industrial stores with capacities for thousands of tonnes, several different cultivars are often held in the same store. This can create problems where the dormancy characteristics and tendency to sprout of the cultivars are different (e.g. King Edwards in store with more quiescent varieties like Estima) and can lead to over-treatment of some crop with CIPC in order to keep control of sprouting in another.

Ideally, smaller capacity stores filled with only one variety would overcome this problem although in reality this model is not practical because of the design and management of modern stores, and the associated costs.

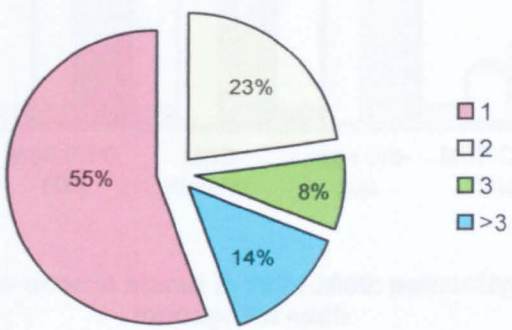


Figure 11 Number of varieties held in store, and associated proportion of tonnage

More than 50% of the crop was held in a store containing only one variety, in which situation chlorpropham treatment can be tailored to the needs of the crop fairly easily. In contrast, 14% of the reported tonnage came from stores in which more than three varieties were stored together. It is almost certain that some of the crop in such a store will receive more chlorpropham treatments than necessary to maintain sprout control because the

chemical must be applied on the basis of the worst-case scenario (i.e. going on the condition of that crop most likely to sprout).

Where possible, it is good management practice to keep only one variety in a single store, but the increased year-round demand for quality produce has driven the trend towards larger storage facilities making this virtually impossible to implement. Storing cultivars on the basis of their dormancy period or sprouting tendency would lead to reductions in the number of chemical applications necessary, although storage costs would almost certainly be higher.

2.3.2.5 Chlorpropham formulations

MSS Warefog (CIPC in methyl pyrollidone), Luxan Gro-Stop (CIPC in dichloromethane) and MSS 50M (CIPC in methanol) were the most commonly used formulations, although 27 respondents (28% of total) did not know which formulation(s) was applied to their crop.

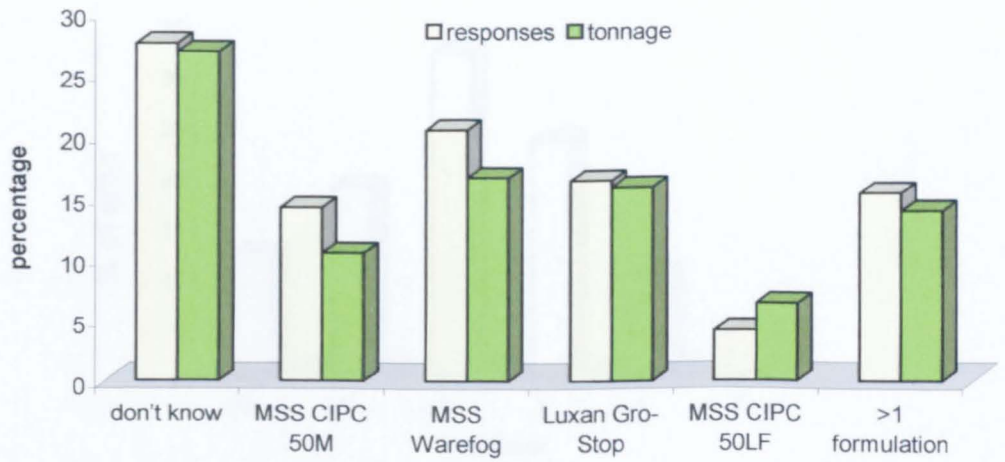


Figure 12 CIPC formulations used in stored in 1999-2000: percentage of total responses and tonnage for each

What is most interesting about the responses to this question is the number of respondents indicating the use of more than one formulation in this store in 1999-2000.

15% of the reported crop (19,394 tonnes) was treated with more than one formulation during the 1999-2000 season, while 30% was treated with an unknown formulation or combination of formulations. In addition, several respondents chose not to answer this question, so dual-labelling could be more widespread than it appears in the data.

However, it is also possible that the question was incorrectly answered, and the intention was to indicate what formulations were used on site in general, rather than in that one store. Again, had the survey been conducted as a series of site visits, this uncertainty would have been avoided. On the other hand, experience has shown that growers tend to favour one formulation over another (e.g. because they have used it in the past with good results) and will use it in all their stores, so the mixing of formulations without good reason seems unlikely. One 'good reason' for doing this would be to get around maximum dose rate regulations.

2.3.2.6 Number of chlorpropham treatments

The number of treatments received by crop ranged between 0 and 6 during the 1999-2000 storage season. Figure 13 below shows the distribution of treatments. Only 0 to 5 treatments are shown on the figure because the respondent indicating 6 treatments did not give any indication of the tonnage held in their store.

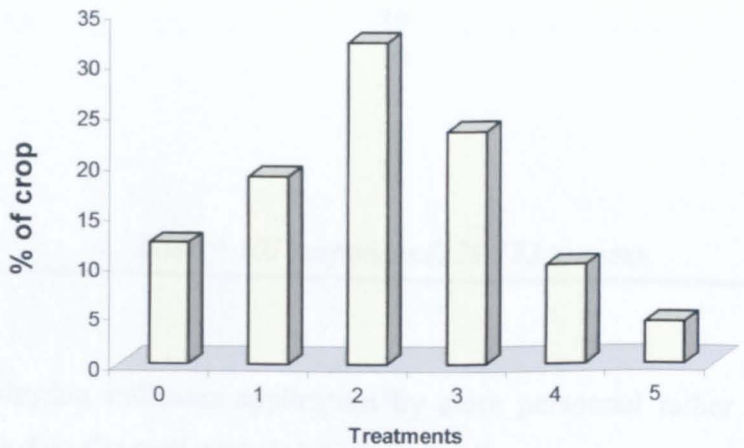


Figure 13 Number of treatments received by crop during 1999-2000

There was no clear relationship between the holding temperature of the store and the number of CIPC treatments made.

Most crop (85%) was treated three times or less, in line with label recommendations for most formulations. With 15% of the crop treated 4 or more times, it seems reasonable to suggest that some growers used more than one formulation. Indeed, these figures fit well with those from the section on which formulations are used: around 15% of respondents

specified two or more formulations that were used in their store. While dual labelling may appear to give an advantage in terms of sprout control, in terms of achieving an MRL in crop and minimising losses of chemical to the environment it is highly undesirable.

2.3.2.7 The application process

Professional contractors carried out applications to 81% of the reported crop, with 19% treated by store personnel. Where untrained or inexperienced personnel make applications, problems such as uneven distribution and reduced efficacy are more likely to occur as a result.

Respondents were asked for details of the fogging equipment used to make the application. The information is shown in Table 6 below

Table 6 Fogger types used in applications 1999-2000

Fogger	Responses	Tonnage (%)
Don't know	39	38.1
SAM Unifog	10	10.3
Superfog	22	24.7
Swingfog	18	17.1
Unifog	12	9.8
Base = 101 responses (129,173 tonnes)		

The use of Swingfog indicates application by store personnel rather than professional applicators. This data fits well with that from the earlier question regarding who carried out the application. The type of fogger used with be largely dependent on which contractor carried out the applications: details of individuals carrying out specific applications was supplied by respondents but will not be discussed here.

Air circulation during application

Around 30% of the total tonnage was held in stores where air was re-circulated to some degree during the application. However, the way in which this was carried out (e.g. fans running continuously during application vs. short pulses) was not specified. Although some formulations (e.g. Luxan Gro-Stop products) recommend running fans during application to aid distribution around the store, this is not known to be common practice. Indeed, the perception of increased fire risk as a result of the switching on and off of store

machinery makes most in industry unwilling to use fans during application. It is likely that some of these responses relate to short pulsing of the fans to clear fog out of ducts immediately after the application.

BPC funded work (as reported elsewhere in this thesis) has shown that gentle movement of the store air during the application can have a beneficial impact on how the chemical is distributed around the store, but also that if done incorrectly (i.e. with a forceful movement of air) circulation during application can have a very negative effect and result in unacceptably high residues at certain locations in the store. Miller *et al* (2001) suggested that short periods of ventilation at rates of 0.005 $m^3 s^{-1} t^{-1}$ could be beneficial in assisting the distribution of fog around the store, while more forceful movement could encourage precipitation onto metal surfaces e.g. fan units. This advice is also incorporated into BPC storage advice pamphlets [Anon (2000)] where air movement at rates of <0.01 $m^3 s^{-1} t^{-1}$ are recommended.

2.3.2.8 Timing of initial application and re-application(s)

The timing of the first application of chlorpropham in the described stores is shown in Table 7 below.

Table 7 Timing of initial CIPC application, with associated tonnage and number of responses

Time	Responses	Tonnage as %
2-4 weeks	13	22.1
4-6 weeks	25	23.4
6-8 weeks	22	22.4
10-12 weeks	1	0.7
12-13 weeks	1	1.1
4 months	1	0.9
at eyes open	29	29.4
	Base 92 responses (110,425 tonnes)	

The first chlorpropham application to 68% of the reported crop was carried out within 8 weeks of store loading. Almost 30% of the crop was left untreated until signs of crop movement were observed. If CIPC application is carried out too early, it can interfere with the setting of the skin, and lead to later problems of disease during storage. If left too late, it can be difficult to maintain sprout control, particularly in processing type stores where

the store temperature and conditions are more conducive to growth. Ideally, frequent inspection of crop condition followed by application at the first signs of eyes opening is the most efficient way of applying chemical.

Criteria for re-application

The need for repeat applications of chlorpropham during the season should be based on the condition of the crop and the likelihood of dormancy break and sprout initiation. However, commercial contractors are known to be booked months in advance, suggesting that in some cases the frequency of treatment may be decided before crop goes into store, and certainly before the treatment becomes necessary.

78% of respondents indicated that repeat applications in 1999-2000 were commissioned on the basis of crop condition, with 17% working on a calendar basis. 5% indicated that they timed their CIPC applications based on both the condition of the crop and the anticipated length of storage.

The high figures for crop condition being the most important factor when deciding if/when to re-apply are very encouraging, as this is the most efficient way of using the chemical, and will most often result in fewer applications than where it is applied at regular intervals irrespective of need.

2.3.2.9 Pre-application store management in cold stores

Those storing crop at lower than 5°C were asked whether they pre-warmed their stores prior to carrying out a CIPC application. Label recommendations seem to suggest that low temperature is undesirable (although giving no basis for this advice). In terms of crop condition, increasing air and crop temperature once it has stabilised at the holding point is potentially harmful, as it will only serve to 'waken' a quiescent crop, and encourage it to become active at an early point in storage. This could lead to problems later on in the season when maintaining sprout control can be difficult.

11% of respondents indicated that stores held at less than 5°C were warmed to at least 5°C for application. Initially, this figure seems surprisingly low since information to date suggests that applicators themselves are unwilling to apply chemical at low temperature if not allowed by the label (because of potential insurance claims if problems arise as a result of the application).

On closer inspection, only 32% of those completing the questionnaire held crop in cold stores, so based on these figures around 40% of cold stores were warmed up for application. Based on knowledge of working practice, these figures seem more likely.

Respondents were asked to give a brief explanation of why they warmed their stores – the main reasons stated are shown below:

- Label/contractor recommendation
- To improve distribution
- To keep crop temperature below air temperature to improve the deposition
- Label requirement or manufacturer's advice

Most growers indicated that they themselves are unsure of why this is done, but confirm that contractors and/or manufacturers advised them to do so. The feeling seems to be that the even distribution of chemical will not be achieved at low temperatures. While it is possible that the behaviour of the chemical may change with temperature, there is no scientific basis, at present, for claiming that a difference of only a few of degrees in air temperature is likely to make a significant difference.

Previous BPC-funded work had tended to suggest that the efficiency of deposition may in fact be improved at lower air temperatures. However, work carried out as part of this study (but not reported in this thesis) found no conclusive link between air temperature and deposition pattern in experimental stores – results of this work are published elsewhere [Park (2001a)].

Overall, it would seem that increasing store temperature will only have a detrimental effect on the tubers, and may encourage dormancy break. The application process itself already causes significant stress to the crop (as a result of temperature increase and the introduction of exhaust gases to the store atmosphere) so keeping conditions as stable as possible before and after application is recommended.

Where low air temperature is believed to present a problem, one alternative to re-warming the store for application would be to carry out CIPC application when air temperature reaches around 5°C during pull-down. This practice is already carried out in some

commercial cold stores [P.Coleman, personal communication], but means that an early application of CIPC will be made regardless of whether the crop needs it or not.

Application instructions on some labels state that air and crop temperature should be at least 7°C at the time of application (e.g. MSS SproutNip). No reason is given for this advice.

2.3.2.10 Post-application store management

Respondents were asked how long their stores remained switched off following chlorpropham application. Figure 14 below shows the percentage of the total tonnage held in stores switched back on at times from 6 to 72 hours post-application. Traditionally, most formulation labels have recommended that store control systems remain off and no personnel enter the stores for 24 hours following application. However, in recent years it has become clear that crop condition can be adversely affected as a result of the application process [Dowd (2001)]. Work has also been done that suggests that fog settles within 8 hours of application [Briddon and Jina (2000)], and that no advantage in terms of efficacy will be gained from leaving stores sealed any longer. This has led to recent advice that stores be vented a few hours after application to flush out combustion products present in the store.

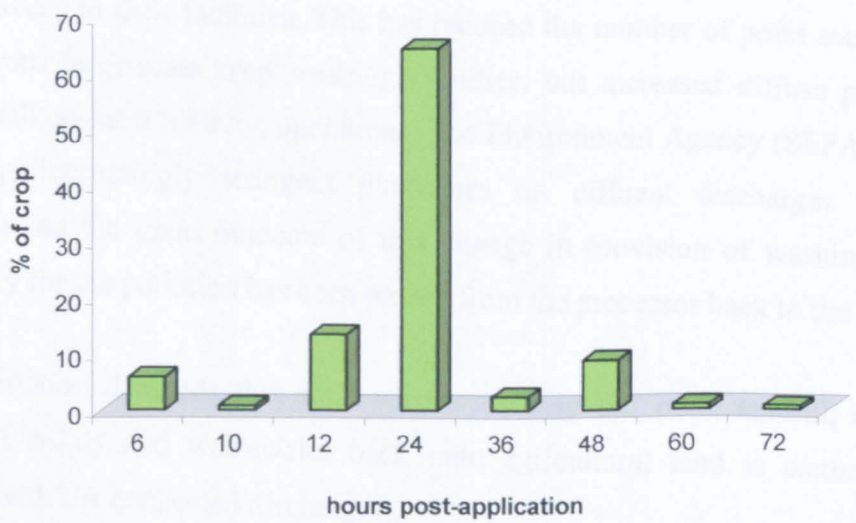


Figure 14 Percentage of total tonnage held in stores switched on at 6 to 72 hours post-application

By far, the most common practice was to leave stores sealed and switched off for 24 hours after application, following label guidelines.

In stores that are vented within 6 hours of application, it is possible that significant amounts of chlorpropham could be lost from the store, which (in addition to being an environmental concern) could cause later problems in terms of efficacy.

Where stores remain sealed for over 24 hours, crop condition will undoubtedly be affected. During the application process, products from the combustion of petrol are ducted into store along with the chemical. As a result, the store atmosphere becomes contaminated with high levels of ethylene and carbon dioxide (relative to background – both compounds are produced naturally in the crop as a result of respiration or stress), which can have a negative impact on the fry colour of processed products. This is less of an issue in stores holding ware crop, but in general the removal of any contaminants from the storage atmosphere is recommended as soon as possible post-application.

In recent years, product labels have been amended to incorporate this new advice e.g. the MSS CIPC 50M label now recommends venting the store 6 hours after application. It is still advisable, though, to keep personnel out of the treated area for 24 hours, so remote control of store systems is recommended.

2.3.2.11 Crop washing

It is becoming increasingly common for larger processors to require that crop is washed prior to delivery to their facilities. This has reduced the number of point sources of water pollution from large-scale crop washing facilities, but increased diffuse pollution as a result of small on-farm washing operations. The Environment Agency (SEPA in Scotland) is imposing increasingly stringent guidelines on effluent discharges into surface watercourses, so the main outcome of this change in provision of washing is that the responsibility for the pollution has been passed from the processor back to the farmer.

Current legislation demands that solid wastes are disposed of to landfill, although the spreading of solids and wastewater back onto agricultural land is commonplace (in compliance with EA consented discharges).

Respondents were asked whether crop was washed prior to leaving their site. If they answered yes, they were asked to provide some detail on the treatment and disposal of the washing effluent.

15 respondents, holding 20% of the total tonnage, indicated that crop is washed on-site at their facility. This figure is likely to include both processing crop washed prior to delivery and also pre-packers storing and packing on the same premises.

On the questionnaire (and in the Access database), this question took the form of a yes/no tick box. As a result, no differentiation can be made between those answering 'no' and those not answering the question at all. It is possible then that some respondents do in fact wash crop, but given the very sensitive nature of the effluent issue chose not to provide details.

Of those who did disclose their crop-washing operations, the most common treatment for the effluent was settlement to remove any solid material, which was done either alone or in combination with other processes e.g. filtering and digestion. The liquid effluent was commonly spread back on land.

The solid waste produced by the washing of 50% of the crop was disposed of to landfill by contractor. 20% is stored on site, and the chemical hazard represented by this material (and by any liquid spread back onto land) will depend very much on the persistence of the chemical in the soil, which will depend in turn on the conditions in the soil (e.g. moisture, temperature, chemical composition, presence of micro organisms capable of degrading residues).

The volume of washing water produced varied from 1,000 to 10,000 litres per day. The amount of chlorpropham present in the effluent will vary depending on how much crop has been washed in it, and the treatment(s) the crop has received. It would have been useful to be able to link the volumes of washing waste produced with the tonnage washed, but this was not possible due to the format of the questionnaire.

2.3.2.12 Applications in partially filled stores

Instructions on the label of CIPC formulations provide dose rates for individual applications and also a total dose for the season based on the tonnage of crop treated. These dose rates are independent of the capacity of the store being treated. In practice, stores are usually full at the time of application but occasionally stores are partly empty, for example when short-term storage crop has been removed, but crop for longer-term supply requires a further treatment.

19% of respondents indicated they do not apply CIPC to stores that are only partly full. A further 19% carry out standard applications, as required by the label. The remaining 60% indicated that they alter their application procedure in some way. The way in which the application was altered varied considerably.

Misinterpretation of the question was common in this case. A 'standard application' as referred to on the questionnaire form was intended to represent an application carried out at the usual dose rate per tonne. Where a store is part empty, both the time taken and the weight of chemical introduced to the store would be less than for a full store. However, many of those stating a change in the procedure indicated that the change amounted to reduction in chemical tailored to the tonnage left in store. In terms of following label instructions, this is the correct policy to adopt.

Another common response was that empty areas in the store were sealed off to prevent chemical dispersal into those areas in an attempt to maintain the same airspace-to-crop ratio as would be found in a full store. In terms of chemical losses from store, where a greater percentage of the store volume is free air, less chemical might be expected to be lost through leakage at the time of application (see Chapter 8).

In some cases, the amount of chemical added to the store was actually increased by up to 10% to account for the extra air space in the store. However, other work described in this thesis has shown that losses from a store with a large volume of empty airspace relative to crop may be less than in a tightly-filled store, so a 'normal' treatment with chlorpropham would be likely to result in a higher dose than usual. Increasing the amount of chlorpropham added to the store will further increase the dose received by the crop, and make it difficult to achieve MRLs consistently in treated crop. In practice, it might be better in terms of residues and efficient use of chemical to work on a slightly reduced dose rate in stores that are not full.

2.4 Summary of findings from the survey questionnaires

In the UK, storage in boxes is more common than in bulk piles. Despite increasingly sophisticated storage facilities, the vast majority of stored crop requires treatment with CIPC to maintain control of sprouting during storage.

Multiple applications of chlorpropham are often necessary, and it appears that the use of more than one formulation in the same store during the same season is commonplace.

Although not against the law, this practice cannot be considered to be good agricultural practice, and does not demonstrate responsible use of post-harvest chemicals. What it does show is that the application process is inefficient and there is significant scope for improving the process. After all, three applications at a dose rate of ~14ppm should be more than sufficient to keep control of sprouting, assuming that most of the chemical can be made to reach the target crop.

The majority of applications are carried out by licensed applicators. This is considered the most appropriate way to ensure a good-quality application with satisfactory results in terms of both efficacy and efficiency of application.

Washing effluent often receives only remedial treatment prior to release to drain or into surface watercourses. Only a small number of storage facilities have sophisticated clean-up plants (e.g. with settlement, digestion and filtration) capable of reducing chemical residues to similar levels to the Environmental Quality Standard (EQS) for surface and drinking water (10μg l^{-1} and 0.1μg l^{-1} respectively). Controls on releases to the environment are becoming ever stricter, and the handling of washing effluent (although less complicated than the handling of processing wastes) is likely to pose a significant challenge to the industry.

In addition to environmental legislation, the increasing cost of maintaining a fresh water supply means that the ability to re-use water on site is desirable. Reducing chemical residues to virtually zero is required in order to achieve this.

Chapter 3

DISTRIBUTION OF CIPC IN COMMERCIAL BOX STORES FOLLOWING THERMAL FOG APPLICATION

3.1 Introduction

CIPC is applied to potato stores as a thermal fog composed of fine particles a few microns in diameter. For a conventional thermal fogging, all fans in the store are switched off prior to application and are left off for the following 24 hours (following label recommendations). Thus, during and after the application, the only factors influencing the movement and distribution of the fog throughout the store are the properties of the fog itself e.g. high temperature, application force and air turbulence. This can result in an uneven distribution of chemical throughout the store, particularly in a box store. Non-uniform deposition can result in excessive chemical residues in crop from some parts of the store, while efficacy can be impaired in parts of the store where little chemical reaches. A number of studies that aimed to address this problem are described in this chapter. All were carried out in box stores rather than bulk.

Previous studies have investigated the problem of uneven distribution of chemical in box stores. Burfoot *et al* (1996) and Xu and Burfoot (2000) used mathematical modelling to predict deposit levels throughout the store, and compared their predictions with experimentally determined levels. Although their predictions were in general agreement with the experimental values, there were a number of limitations to their model. Their original study considered that fog would flow only downward around the boxes and assumed losses due to degradation of CIPC in the air (e.g. thermal degradation during application) and through leakage to be zero. These are over-simplifications of what is actually happening in a store during application. For example, 3-chloroaniline, a product of the thermal degradation of CIPC, has been found in air sampled from CIPC treated stores (see Chapter 4). Significant quantities of fog escape through louvres and vents during application, particularly in older buildings with no refrigeration, which tend to be less airtight than modern temperature-controlled stores.

In box stores, the highest deposits are usually found on the top boxes, with progressively lower levels towards the bottom box [Burfoot *et al* (1996); Khan (1999)]. This pattern of distribution is consistent with fog that rises to the roof space at high temperature, and

subsequent settling of larger particles onto top surfaces. It has also been noted that residue levels on crop are usually higher at the far end of the store from the application port than at the near end, because the large amount of force produced by the fogging equipment means the fog tends to accumulate there. The volume of air produced by a commercial fogger (Unifog) was determined experimentally (as described elsewhere in this thesis) to range from ~700-1000 m^3 per hour under normal operating conditions.

It is considered desirable to produce a buoyant, dry fog that will move freely around the store. To achieve this, combustion chamber temperature and the flow of air through the fogger must be high. A lot of fuel is consumed to generate the high burner temperature, resulting in large amounts of combustion products entering into the store. Components of the exhaust gases can have an adverse effect on the quality of the crop and cause fry colours to be dark. This effect has been largely attributed to the accumulation of ethylene in the store [Wang and Pritchard (1997), Dowd (2003)]. Other products of combustion, including carbon dioxide and water, are also introduced to the store and may have an effect on the crop.

During a 1-hour application under standard operating conditions, several litres of fuel are consumed [Dowd (2003)]. Formulation passes through the fogger at the rate of ~1 litre/min (~500g CIPC/minute), so a commercial application takes approximately 1 hour for every 2,000 tonnes treated. All exhaust gases are blown into store.

Label recommendations state that all store controls should be switched off prior to application, and should remain off for 24 hours following application. Some formulations (e.g. Luxan Gro-Stop, BL500) allow fans to be switched back on 12 hours post-application to assist with distribution around the store. Recent BPC funded work has shown that the deterioration in fry colour associated with the build-up of exhaust gases into the store can be reduced if stores are vented at 12 hours or less, instead of the standard 24 hours [Dowd (2003)]. Since the effect of the exhaust gases is cumulative, store managers advocate fewer, high dose applications over several applications at a lower rate [Coleman (Ed.) 2001].

Each formulation label gives a maximum dose rate for each application and a total dose for the season. These dose rates are legally binding, and should not be exceeded under any circumstances. However, store managers often find that sprout control cannot be maintained throughout the season, even at the maximum allowable dose, and the use of more than one formulation ('dual-labelling') in individual stores is commonplace. This is

likely due to shortcomings in the application process, rather than because the amount of CIPC applied is not enough. Corsini *et al* (1979) suggested that a peel concentration of 20ppm is necessary in the peel for complete inhibition of sprouting, which equates to around 2ppm on a whole tuber basis. The need for repeat treatments at dose rates of ~16ppm suggests that not much of the chemical applied into the store actually reaches the crop. If evenly distributed around the store, the maximum dose allowed by one formulation should be more than adequate to control sprouting throughout the season.

Where repeat applications are made during the season, they are usually carried out in exactly the same way as the first, resulting in the same pattern of distribution. This can lead to two types of problem. Crop in sensitive places in the store (e.g. in top boxes) can have unacceptably high residues – a Maximum Residue Level (MRL) for CIPC is imminent, and is expected to be in the range 5-10 mg kg^{-1} (ppm), on a washed, whole tuber basis. In 1995, the Scientific Committee for Pesticides of the Commission of the European Union reviewed the toxicology of CIPC and suggested a temporary Acceptable Daily Intake (ADI) of 0.1mg kg^{-1} b.w, based on a NOEL of 50mg kg^{-1} body weight and a safety factor of 500 [Lentza-Rizos and Balokas (2001)]. Chlorpropham has still to be cleared by the FAO/WHO JMPR (Joint Meeting for Pesticide Residues) and as such a permanent ADI has not yet been established. It is likely that, on paper at least, some of the residues found in crop from treated stores may result in this level being exceeded, particularly in children. However, MRLs and ADIs are determined on a whole potato basis and do not take into account any preparation prior to consumption e.g. peeling. Peeling a potato has been shown to remove up to and in excess of 90% of the residue [Lentza-Rizos and Balokas (2001); Conte and Imbroglini (1995)] and thus the amount consumed by the individual can be significantly less than that measured on the tuber.

The other problem created by uneven distribution is one of efficacy. Crop held at the bottom of the store, or in any 'dead-spots' where air does not move freely, may not receive an adequate amount of CIPC for effective sprout control, and may start to sprout. Where a mixture of cultivars with different sprouting pressures are held in the same store, there may be a similar effect. Often the decision to re-treat a store is based on visual inspection of crop condition, and the presence of sprouts on some of the crop might trigger another application of chlorpropham. This raises problems in terms of efficacy for the under-treated crop, and creates high chemical residues in the over-exposed crop.

Trials were carried out over 3 storage seasons with the aim of improving the distribution of fog around a store by modifying the patterns of air circulation in the stores. In each year,

two stores at QV Foods Ltd's facility at Holbeach (Lincs) were used. The stores were identical in size, with similar CIPC treatment histories. The stacking pattern of boxes was different in each, but was kept as similar as possible wherever practicable. However, work was carried out within the limitations of commercial practice, which had implications for temperature control, box stacking pattern and sample availability.

3.1.2 Season 1999-2000

Although the UK storage season begins in September, work on this project did not begin until November 1999. As a result, crop was already in store by the time the described study began. In order not to miss out on one season's work, two commercial trials were conducted in 1999-2000 on a limited scale as a range-finding exercise. The results from this work were used as the basis for the next 2 years' full-scale commercial trials.

3.1.2.1 Store conditions 1999-2000

Two stores with identical dimensions were used. Applications of chlorpropham were made with a Unifog fogging machine, and MSS Warefog 25. This formulation is 60% (w/v) CIPC in methyl pyrrolidone, which both the store manager and applicator felt would give good results in terms of distribution and efficacy. Although stores were held at 3°C throughout the storage season, the refrigeration systems were switched off one week prior to application to allow crop to reach 5°C for application, in line with label recommendations. Although low-temperature applications of chlorpropham are discouraged, there appears to be no scientific basis for this advice. Many in industry feel that applying below 3°C can impede the movement of fog around the store, and result in crystallisation of chlorpropham onto the surface of the crop [Clutterbuck, personal communication; Coleman (Ed), 2001].

Both stores were stacked 8 boxes high according to the pattern in Figure 15 overleaf, although the actual tonnages were different. In the control store, chlorpropham application was carried out under normal conditions i.e. all store machinery was switched off prior to application and remained off for the following 24 hours, in line with label recommendations. In the trial store, the large overhead fans were left running on full power during application and for the following 24 hours. The aim was to encourage air movement around the store and prevent the accumulation of fog at the top of the store, and to lessen the effect of gravitational settling out of particles on the top surface of the crop.

In each store, only one row of boxes was accessible for sampling, shown as Row J in the diagram below.

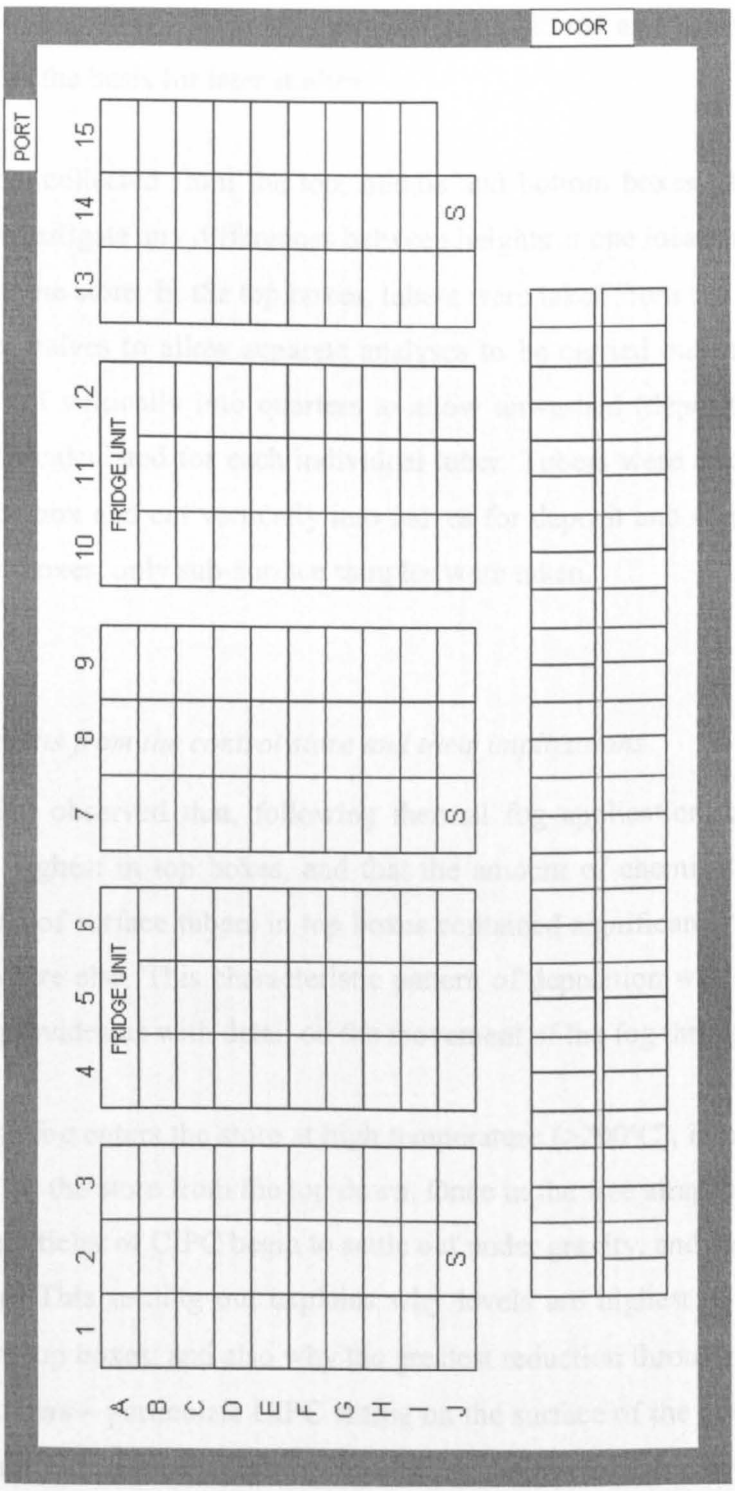


Figure 15 Plan view of the layout of two stores used in 1999-2000 storage season (not to scale)

3.1.2.2. Sampling and analysis

Proper statistical replication of sampling was not performed in these stores, as they were only designed to be range-finding exercises to highlight the problems encountered when distributing chemical around a box store. As such, the results of the analyses will not be presented in any detail. Instead, the main observations and patterns in the data will be discussed, as the basis for later studies.

Tubers were collected from the top, middle and bottom boxes (8, 4, and 1) of stacks in Row J to investigate any differences between heights at one location, and between different locations in the store. In the top boxes, tubers were taken from the surface and cut into top and bottom halves to allow separate analyses to be carried out on each half. The halves were then cut vertically into quarters to allow unwashed (deposit) and washed (residue) values to be calculated for each individual tuber. Tubers were also collected from ~20cm depth in the box and cut vertically into halves for deposit and residue analysis. In middle and bottom boxes, only sub-surface samples were taken.

3.1.2.3. Results from the control store and their implications

Khan (1999) observed that, following thermal fog application, chlorpropham levels on crop were highest in top boxes, and that the amount of chemical decreased with height. The top half of surface tubers in top boxes contained significantly more CIPC than tubers from anywhere else. This characteristic pattern of deposition was also seen in our control store, and provides us with detail on the movement of the fog through the store.

Because the fog enters the store at high temperature (>200°C), it tends to rise into the roof space and fill the store from the top down. Once in the free airspace at the top of the store, the larger particles of CIPC begin to settle out under gravity, and accumulate on the surface of the crop. This settling out explains why levels are highest in the top half of surface tubers from top boxes, and also why the greatest reduction through washing is also seen on these top tubers – particulate CIPC sitting on the surface of the potatoes is easily removed by washing or brushing. Any chemical that reaches lower down in the store (i.e. the smaller particles that remain in suspension and can move around the store) tends to be held more strongly by the waxes in the periderm, and is therefore more difficult to remove. The force with which the fog enters the store (the volume of air introduced to the store during application has been calculated to be ~1000m^3 hr^{-1} in a study discussed elsewhere in this

thesis) drives it to the far end, resulting in higher chemical residues in crop at this end of the store.

In the control store the ranges of measured CIPC concentrations were as follows:

- Deposit (unwashed) 0.8 – 38.3 mg kg^{-1}
- Residue (washed) 1.4 – 27.4 mg kg^{-1}

At some locations, more chemical was found on washed samples than on unwashed. Contamination of tubers during the washing process was considered to be negligible under laboratory conditions. This effect may be a result of the way in which sampling and preparation for analysis were carried out, although the highly variable nature of the crop might have some influence. Since one discrete half (or one quarter if the tuber came from the surface of the top box) of a single tuber was analysed, the starting concentration of CIPC in each portion of the tuber may be influenced by how it was lying in the store, for example, if all CIPC landed on one side. Preparing the whole tuber and analysing a representative sub-sample would reduce this type of variability, but would mean that deposit and residue values could not be obtained from the same tuber.

The top halves of surface samples contained significantly more chemical than samples from elsewhere in the same box, including the bottom half of the same tuber.

The greatest reduction through washing was seen in these surface samples, which is consistent with the removal of larger particles that settle out onto the surface under gravity. Similar effects have been noted by other workers [Boyd (1988), Khan (1999)]. However, the effect of washing the crop might be masked as a result of the way in which samples were collected.

The high level of variability in the results can be explained in a number of ways. Firstly, the tubers themselves are highly variable with regard to size and weight. Different cultivars exhibit different characteristics in terms of tuber shape and dimensions (e.g. round vs long tubers; small vs large), skin type (physical and chemical qualities) and surface area (e.g. a rough surface provides a greater surface area on which CIPC particles might land and/or from which the chemical can volatilise).

Experiments were carried out in a commercial environment, rather than under the more controlled conditions of the laboratory. Working within the limitations of a commercial set-up meant that close control of variables such as air temperature, humidity and air movement (all of which might affect the transport of chemical around the store) was not feasible. In addition, the wooden boxes in which crop was held might contribute to the variability in the store since, for example, some have slatted sides, some are solid; some have been CIPC treated before and some are new.

In the full-scale commercial trials carried out in seasons 2000-1 and 2001-2, statistical analysis of the data was made possible by the collection and analysis of 5 'replicate' tubers from each location. However, the design of the experiments made the handling of the data quite complicated, as discussed in later sections.

3.1.2.4. Results from the store with fans running and their implications

In this store, the large overhead roof fans remained on (operating on full power) during application and for the following 24 hours. The aim was to keep the fog mobile for as long as possible and try to prevent the accumulation of chemical at the top of the store.

On re-entering the store 24 hours after application, visual inspection of the crop revealed a black tarry material on the surface of the crop in some of the top boxes. Damage was limited to the boxes in the vicinity of the fans, but extended down to depth in each affected box. Analysis of the contaminated tubers showed them to contain CIPC in concentrations of >450mg kg^{-1} in several cases. These levels are unacceptably high, and render the crop unsaleable.

The tarry material was seen to track across the surface of the boxes in the direction of air movement, and it is likely to be a result of the use of the fans in this store. With large fans operating on full speed, the high-speed impact of fog on the blades and casing of the fan units resulted in condensation of CIPC and solvent, and subsequent dripping onto the crop. Either the speed of the fans, or the volume of air they were moving (or a combination of both), could be responsible for this effect. In addition, there may be a formulation effect: methyl pyrrolidone is not very volatile at the low temperature at which application was carried out (~5°C). In spite of this, Warefog is a popular choice of formulation in pre-pack stores [C. Herkes, personal communication], as confirmed in responses to the CIPC survey described elsewhere in this thesis. In my opinion, the use of another more volatile solvent or formulation (e.g. MSS CIPC 50M, methanol; Luxan Gro-Stop, dichloromethane) might be more appropriate in cold-store situations.

Excluding the grossly contaminated samples in some top boxes, the ranges of measured CIPC concentrations in this store were as follows:

- Deposits (unwashed) <0.1 – 9.05 mg kg^{-1}
- Residues (washed) 2.12 – 6.84 mg kg^{-1}

In this store, the ranges of values for both washed and unwashed samples were significantly less than in the other store that received a conventional CIPC application. Whether this is because there has been an improvement in terms of chemical distribution, or because so much of the chemical condensed out leaving relatively little elsewhere in the store cannot be determined.

3.1.2.5 Summary of findings from Season 1999-2000

Although very limited in their scope, the two trials carried out in this first season offered a lot of useful information on the movement of chemical around a box store. Patterns and trends in the data were used to indicate what treatments might be successful in improving the distribution of CIPC around the store. The main points arising from this work taken forward into the full-scale commercial trials are:

- Sample numbers need to be increased to allow statistical handling of the data to be carried out satisfactorily
- Overhead fans generate too much forceful movement of air, and may contribute to the problem of high crop residues in top boxes by forcing air down onto the surface of the crop.
- A gentler 'stirring' of the air using smaller auxiliary fans might show more success. Slower movement should not promote condensation and should help to keep fog moving around the store for longer.
- The formulation itself might be causing problems under cold-store conditions. Our recommendation was to use a different formulation with a more volatile solvent (e.g. MSS CIPC 50M). However, it is a common misconception in industry that the use of methanol in potato stores presents an explosion risk due to its low flash point (13°C). However, the lower and upper explosion limits for methanol in air are 6 and 36 % respectively. It is difficult to imagine any circumstances under

which concentrations of this order would be present in the air in a potato store, even during application. Provided that the fogging equipment is functioning efficiently there shouldn't be any risk. A more likely source of explosion is the CIPC dust itself. Modern thermal fogging equipment produces a very fine dry particulate fog, which, if distributed evenly, has a concentration in air of 5-10 mg l^{-1} [Duncan (1999)]. Minimum explosive concentrations for other dry powders have been reported in the range 15-100 mg l^{-1}, which is fairly close to the value for CIPC expected during application. Any restriction of the movement of fog could conceivably result in an increase in concentration of particles at one point in the store. Figure 16 below shows an explosion resulting from a very simple experiment where CIPC dust was placed in a sealed container with a lighted candle. Air was blown into the tube to create turbulence, which dislodged the CIPC dust and caused it to ignite in contact with the flame. No solvent was present at any time.

Figure 16 Controlled explosion of CIPC dust

However, the store manager and CIPC applicator involved with this trial remained reluctant to use any product other than Warefog, which they have found most acceptable in terms of consistent results on crop and for insurance purposes in the past.

As a result, Warefog was the formulation applied in all the following studies.

3.1.2.6 Approaches for 2000-1 and 2001-2 studies

Modifications to the patterns of air movement may improve the distribution of chemical around the store, and increase the efficiency of deposition i.e. get more of the chemical to the target crop.

In the following sections, studies are described where the main aims were to prevent the accumulation of fog at the top of the store and to encourage lateral movement around the store. The approaches adopted were as follows:

1. **Year 2 Study A:** Control store receiving conventional CIPC application.

2. **Year 2 Study B:** Store with fans moving air horizontally at the top of the store.

3. **Year 3 Study A:** Store with fans moving air vertically down from the top of the store.

4. **Year 3 Study B:** Store with a plenum chamber to encourage lateral movement.

The set-up and results for each store will be described in turn, and any changes or improvements to the distribution assessed through statistical analysis and also by graphical plotting of the data sets.

For each store, an approximation of deposition efficiency was calculated based on the deposits calculated at different locations in the store.

Studies are presented in the order in which they were carried out in seasons 2000-1 and 2001-2.

3.2 Experimental methods

The studies described were carried out over the 2000-2001 and 2001-2002 storage seasons in commercial box stores at QV Foods Ltd at Holbeach Hurn, Lincolnshire. All stores operated at low temperature and contained crop intended for the pre-pack market. Although the methods of application and sampling varied, the aim of each study was to investigate the distribution of chemical following thermal fog application. Details of each particular study are provided in the relevant sections.

Experimental procedures common to a number of experiments are detailed in this section. Further information about individual studies can be found in later sections.

3.2.1. Sampling

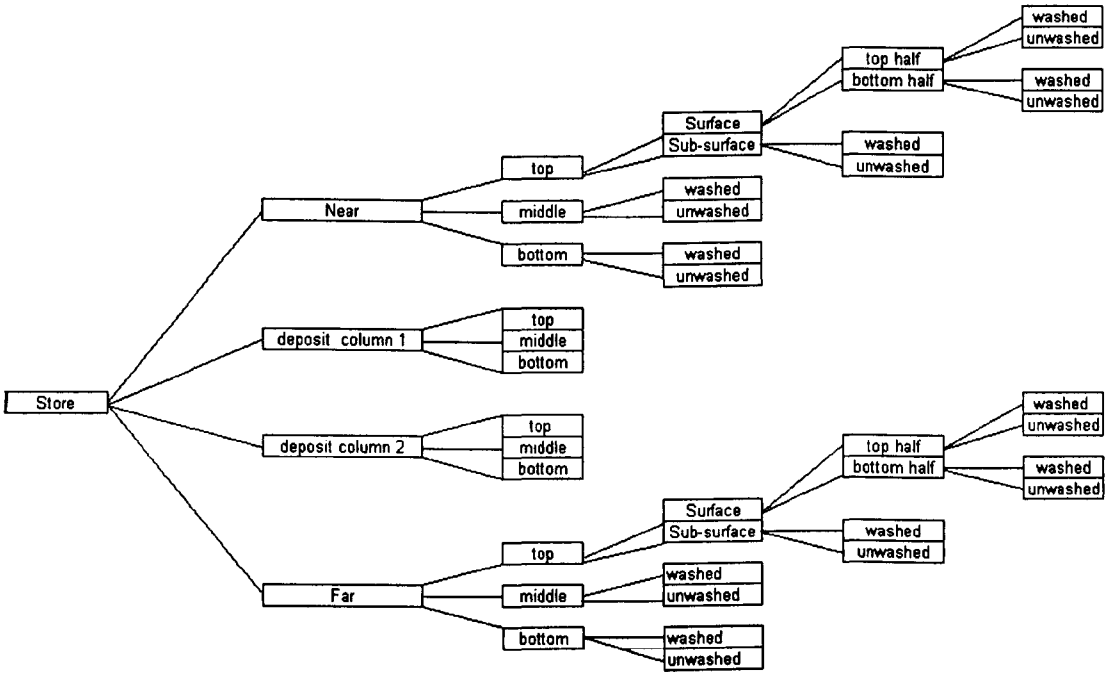
In all distribution experiments, samples were removed from the store 24 hours post-application. Tubers were collected from 3 heights in the store (top, middle and bottom of the stacks) at two or more locations to determine the 3-dimensional distribution of CIPC throughout the box store.

Analysis was carried out on an individual tuber basis to establish the degree of tuber-to-tuber variability at each location, rather than on the bulked samples common in other work. Combining several tubers and analysing a sub-sample can provide a result that is more repeatable and representative of the situation in the box as a whole. However, working on an individual tuber basis means that the distribution of chemical at one location can be investigated, and variables such as tuber size and weight can be associated with particular residue values.

In top boxes, tubers were collected from the surface, and also from the sub-surface at ~20cm depth. The surface samples were halved horizontally *in situ* to allow separate analysis of the exposed top half and the bottom half of the same tuber. In middle and bottom boxes, only sub-surface tubers were sampled. In some studies, separate tubers were collected for residue and deposit analysis, while in others a single tuber was halved vertically *in situ* and both analyses carried out on it. Details on the method of sampling employed in each study can be found in the relevant sections.

Diagrams of the layout of each sampled store and the locations of the sampling points are shown for each study in their individual sections. However, in each store, the pattern of

sampling was based on Figure 17 below, where each store is split into a number of locations; each location into three heights, and each height into deposit (unwashed) and residue (washed) analysis. Surface samples are further divided into top and bottom halves



prior to deposit and residue analysis.

Figure 17 Sampling pattern for distribution studies

3.2.2. Extraction

CIPC was extracted from tubers following the method of Khan (1999), which has been shown to have an average recovery of 93.1%. The results of this work are presented uncorrected for the recovery factor.

Most analytical methods (and Codex Alimentarius guidelines) recommend that a sample of several kilograms is bulked and sub-sampled in order to obtain a value that is representative of the sample as a whole, and to reduce the variability among replicate analyses. However, with the imminent introduction of an MRL, and increasing public awareness of food safety, the amount of chemical present on an individual tuber basis is coming under more scrutiny. There are concerns that where residue levels are high, the Acceptable Daily Intake (ADI) level might be exceeded, particularly in vulnerable individuals like young children. As a result, analysis was carried out on individual potatoes in this study to ascertain the amount of tuber-to-tuber variability.

Deposit: The tuber was rubbed lightly to remove any adhering soil, then diced into ~0.5cm^3 cubes. A sub-sample of approximately 30g was added to a cellulose extraction thimble with ~10g anhydrous sodium sulphate. The thimble was plugged with cotton wool, and placed in the Soxhlet apparatus. *n*-hexane was added (~100ml) and the sample extracted for 2 hours on half heat. Once cool, the siphon was rinsed with 3 volumes of hexane and the washings added to the flask. The volume of extract was reduced to <2ml on a rotary evaporator (keeping the temperature <40°C to prevent loss of CIPC by volatilisation), then made up to volume in a 2ml volumetric flask.

Residue: Samples were washed in cold running water then prepared and Soxhlet extracted with hexane following the procedure outlined above.

3.2.3. Analysis

Quantitative analysis of the hexane extracts was carried out on a Pye Unicam PU 4500 gas chromatograph, equipped with a 1m packed column (3% OV-17 on Gaschrom-Q; Supelco) and a flame ionisation detector. Daily calibration of the system was carried out by injection of appropriate standards of CIPC made up in HPLC grade *n*-hexane (Riedel-de-Haen).

GC conditions for analysis were as follows:

Temperatures:

Oven	180°C isothermal
Injector	220°C
Detector	250°C

Gas flows:

N_2 carrier	30ml/minute
Flame H_2	30ml/minute
Flame air	180ml/minute

Injection volume: 5µl

Under the described conditions, CIPC had a retention time on the column of ~3 minutes.

3.2.4. Results and data handling

3.2.4.1 Chemical levels

Results are expressed as parts per million (mg kg^{-1}) on a whole tuber basis. Where Maximum Residue Levels (MRL) are in operation, these are also expressed in parts per million, but on a washed tuber basis. Although there is currently no MRL established in the

UK, other European countries commonly have a 5mg kg^{-1} limit. A legally binding EU-wide MRL is pending, and is anticipated in late 2003.

3.2.4.2 Statistical analysis

Data analysis was carried out using Minitab statistical software for Windows (Version 13). The nature of the experiment made statistical analysis of the results rather complicated. Each set of data consists of 5 values obtained from 5 separate tubers. As a result, none of the data can be considered outliers and rejected because the 5 analyses are not true replicates. In contrast, had the same 5 tubers been collected, combined and sub-sampled 5 times, any unusual values could have been justifiably rejected. In our studies, the mean and standard deviations for the data set could be skewed by one extraordinary data point, which may give a false impression of the variability among samples. As a result, raw data are presented for each study in Appendix 1 in addition to the statistical summaries.

In addition, the complicated sampling pattern and differences in store layout make it impossible to compare directly the different treatments. Instead, the distribution of chemical was examined in each store individually using Analysis of Variance (ANOVA) techniques. General Linear Model (GLM) was selected as the most appropriate procedure to give an indication of what is happening in the very broadest terms. For each set of data, 3 fixed factors were assumed to affect the results:

Surface samples

- The location in the store
- The half of the tuber (top or bottom)
- Whether the sample is washed

Sub-surface samples

- The location in the store
- The height of the box
- Whether the sample is washed

In a Minitab worksheet, data were separated out into surface and sub-surface sets, since each set would be considered separately. All data for each set were stacked into one column, with subscripts for location, half and wash (for surface samples) and location, height and wash (for sub-surface samples) in the following three columns. GLM was carried out using the model below for surface and sub-surface samples respectively:

```
GLM  'CIPC' = column! half(column) wash(half)

GLM  'CIPC' = column! height(column) wash(height)
```

Because of the way in which samples were collected (see Section 3.2.1 and Figure 17 for a full description of the sampling procedure), some factors were nested within others, as indicated by the parentheses. Nesting the factors enables the model to look for differences between locations; between heights at a single location; between washed and unwashed at each height at each location, as well as for any interactions among the factors (denoted by "!" in the models).

The Minitab output for GLM is shown in the relevant sections for each study. The printed output displays 3 types of data – first, it gives the table of factors and levels, then the analysis of variance table and finally a list of any unusual observations. Unusual observations are those with a large residual (i.e. a poor fit with the rest of the data). These values are generally those that would have been discarded as outliers had that been an appropriate way to deal with the data.

Although this kind of statistical analysis will indicate whether any significant differences exist in the data, it will not show **where** the differences lie. To determine where significant differences lie, the data were separated out in Minitab into its simplest form, then analysed by one-way ANOVA with Tukey's multiple comparisons tests. Tables of values for the differences between pairs of means are given in Appendix 1.

Because of differences in the stacking pattern of boxes, and alterations made to the CIPC application process and tuber sampling procedures as the studies progressed, direct comparison of individual stores is inappropriate. The distribution and levels of chlorpropham in each store will therefore be discussed separately.

3.2.4.3 Estimation of deposition efficiency

A simple model of each store was employed in order to estimate how much of the chemical applied could be recovered on the crop. Deposit values were used because they indicate not only how the chemical is dispersed around the store, but also how much lands on crop at various locations in the store.

Data from the 2000-1 control store is used in the worked calculation below. Mean values for other stores were calculated following the same procedure using the relevant figures.

Top boxes were considered to be different from all others in the store, because they are affected by the settlement of large particles from above. The average deposit on crop in top

boxes was estimated by finding the mean of the means of each sample type in each box e.g.

A14 **Top box** top half = 7.92 bottom half = 2.26
sub-surface = 4.12

J2 **Top box** top half = 25.84 bottom half = 3.84
Sub-surface = 14.79

Top box average deposit = (7.92 + 4.12 + 2.26 + 25.84 + 14.79 + 3.84) / 6

= **9.80** mg kg^{-1}

This mean deposit was multiplied by the number of top boxes to give a weight of CIPC assumed to be present on the crop. The number of top boxes was calculated from the layout of boxes in each store (as shown in figures in each section).

All boxes other than top boxes were considered as being the same, but different to top boxes. CIPC deposits in these boxes were assumed to be the product of finer particles and vapour that remain airborne for longer than the large particles. To estimate the mean deposit in all boxes other than top boxes, deposits from middle and bottom boxes were used e.g.

A14 middle box sub-surface = 1.71
bottom box sub-surface = 1.51

J12 middle box sub-surface = 1.16
bottom box sub-surface = 1.34

Average deposit in boxes other than top boxes = (1.71 + 1.51 + 1.16 + 1.34) / 4

= **1.43** mg kg^{-1}

This mean deposit was multiplied by the number of boxes not located at the top of a column to estimate the weight of CIPC present on the crop in these boxes.

The total amount of CIPC added into the store was estimated by multiplying the tonnage in store by the dose rate of the application (assumed to be 18g/tonne in all cases). To estimate the efficiency of deposition, the weight recovered on the crop was expressed as a percentage of the total introduced to the store.

3.3 Year 2 Study A: Control store

3.3.1 Store layout

This study was carried out in a 2000-tonne modern box store, equipped with temperature and humidity control equipment, designed for long-term storage of potatoes at ~3°C for the pre-pack market. Crop was held in 1-tonne wooden boxes, stacked up to 8 boxes high. Store temperature control was switched off one week prior to application to allow crop temperature to reach 5°C by the time of application (in line with formulation manufacturer's label recommendations).

A full control store was sampled in Year 2 to provide information on CIPC distribution in a box store following conventional application. Year 1's results had given some indications of what may be happening, but more detail was required.

Figure 18 overleaf shows the plan view of the layout of boxes in the store. Rows A-C were stacked 7 boxes high because the roof sloped at that point in the store. Stacks were 8 boxes high in all other rows.

CIPC application (the first of the season) was carried out on 30th November 2000, using a Unifog fogger and MSS Warefog 25 [60% (w/v) CIPC in methyl pyrollidone], at a dose rate of 30ml/tonne. Block 13-15 as shown in Figure 18 was not complete, and the total tonnage in the store was 1,150 tonnes. Samples were collected 24 hours post-application, immediately before the store control systems were switched back on.

3.3.2 Sampling

Samples were collected from 2 locations in the store. One was at the same end and side of the store as the application port (position A14) and the other at the opposite side and far end (J2).

Tubers were collected from ~20cm depth within boxes at 3 heights (top, middle and bottom boxes) in each sampled column. 5 tubers were collected from each location, and cut vertically in half *in situ* to allow deposit (unwashed) and residue (washed) analysis to be carried out on each tuber. In top boxes only, a further 5 tubers were collected from the surface of the box, and cut into top and bottom halves. Each half was cut in half again (i.e.

into quarters) so both types of analysis could be carried out on each individual half. Samples were individually labelled and stored in polythene bags at ~4°C until analysis.

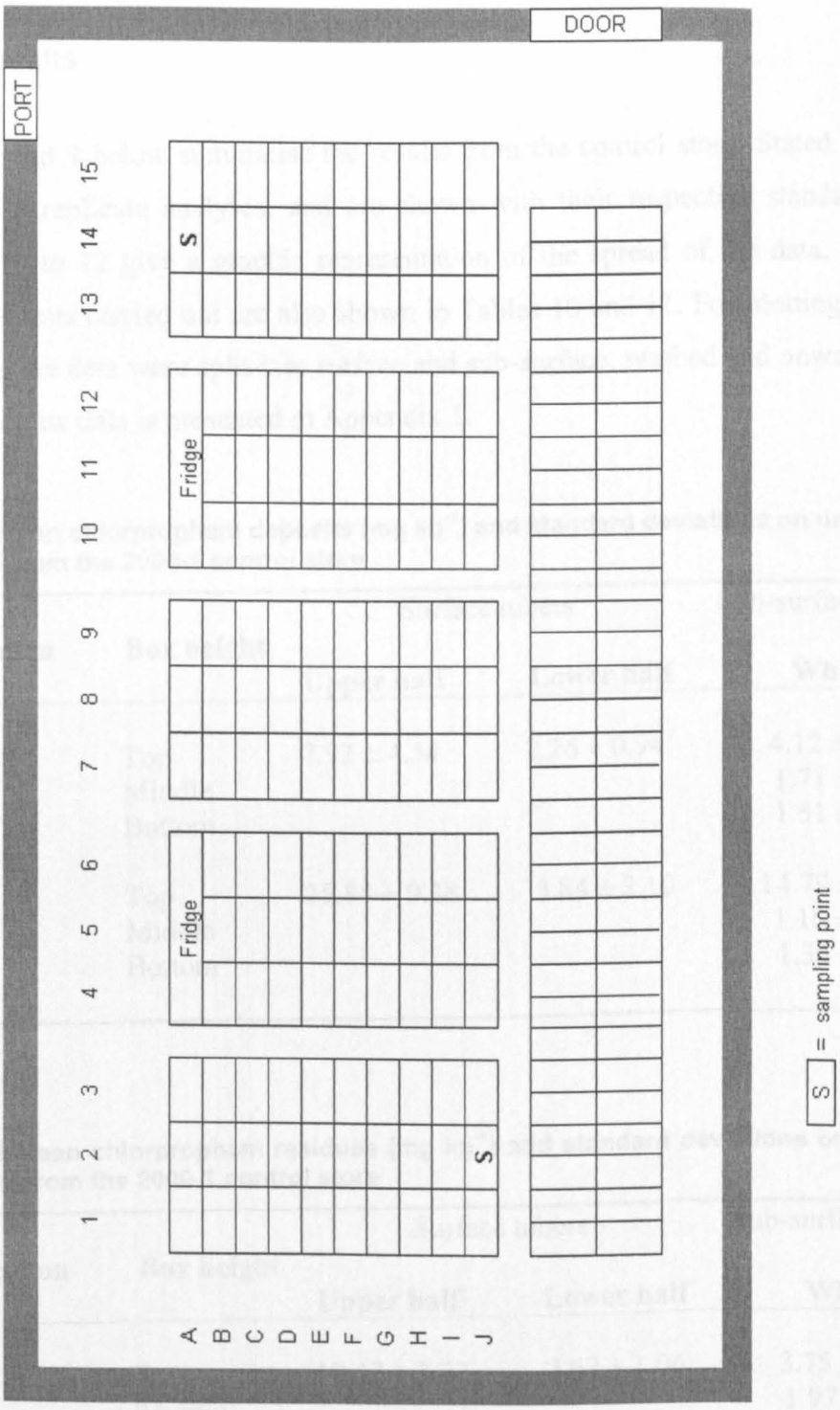


Figure 18 Plan view of the layout of the 2000-1 control store (not to scale)

3.3.3 Analysis

Deposit and residue samples were prepared and Soxhlet extracted in hexane as detailed in Section 3.2.2 and analysed by GC-FID as in Section 3.2.3.

3.3.4 Results

Tables 8 and 9 below summarise the results from the control store. Stated values are the mean of 5 replicate analyses, and are shown with their respective standard deviations. Figures 19 to 22 give a graphic representation of the spread of the data. Results of the statistical tests carried out are also shown in Tables 10 and 11. For plotting and statistical handling, the data were split into surface and sub-surface, washed and unwashed sets. The full set of raw data is presented in Appendix 1.

Table 8 Mean chlorpropham deposits (mg kg^{-1}) and standard deviations on unwashed tubers sampled from the 2000-1 control store

Location	Box height	Surface tubers		Sub-surface tubers
		Upper half	Lower half	Whole
A14 (near)	Top	7.92 ± 4.54	2.26 ± 0.94	4.12 ± 1.40
	Middle			1.71 ± 0.52
	Bottom			1.51 ± 0.38
J2 (far)	Top	25.84 ± 9.38	3.84 ± 2.10	14.79 ± 3.99
	Middle			1.16 ± 0.48
	Bottom			1.34 ± 0.60

Table 9 Mean chlorpropham residues (mg kg^{-1}) and standard deviations on washed tubers sampled from the 2000-1 control store

Location	Box height	Surface tubers		Sub-surface tubers
		Upper half	Lower half	Whole
A14 (near)	Top	10.42 ± 3.22	2.67 ± 1.06	3.75 ± 1.18
	Middle			1.97 ± 0.61
	Bottom			1.69 ± 0.50
J2 (far)	Top	13.89 ± 6.29	4.99 ± 2.57	9.62 ± 4.87
	Middle			2.02 ± 1.28
	Bottom			1.69 ± 0.72

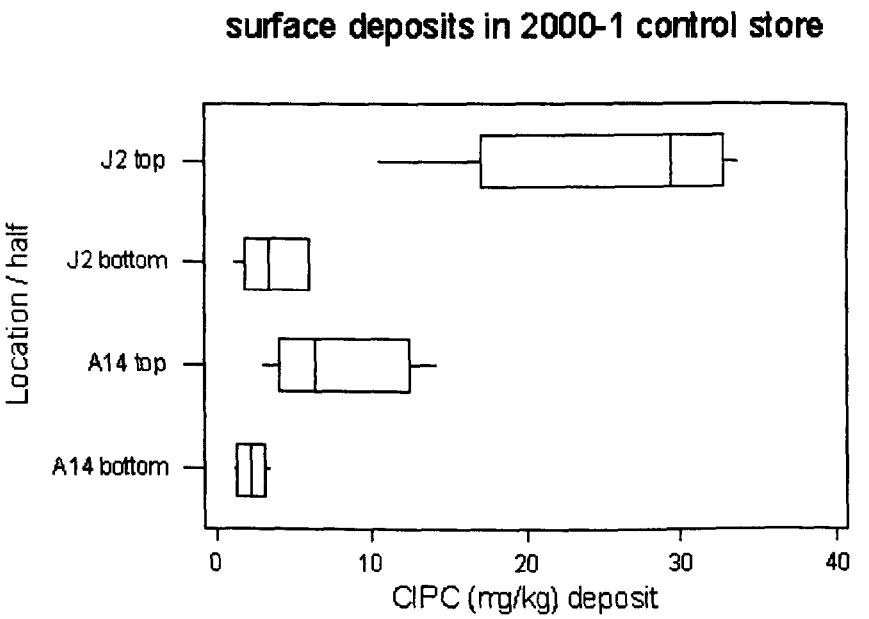


Figure 19 Boxplot showing chlorpropham deposits on top and bottom halves of tubers taken from the surface of top boxes at two locations in the 2000-1 control store

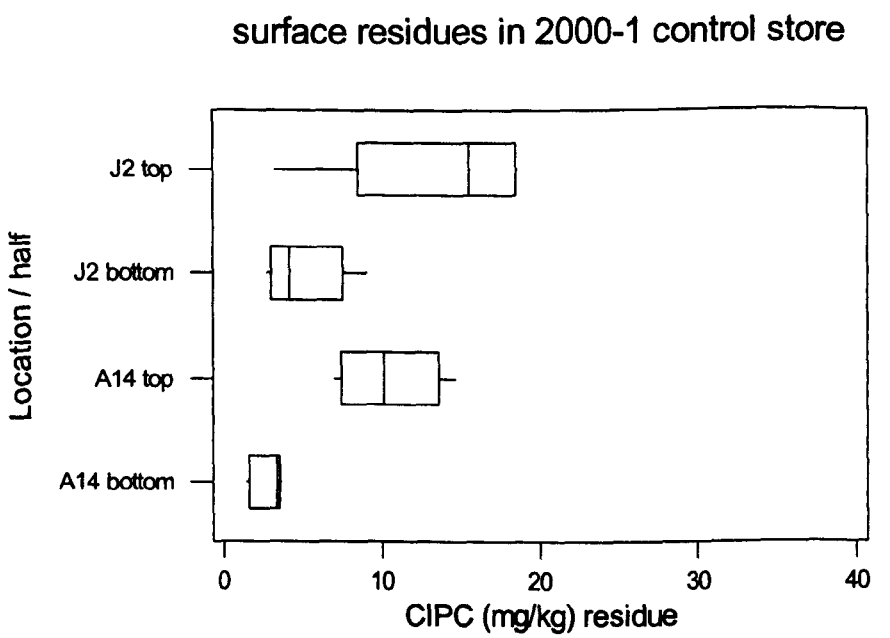


Figure 20 Boxplot showing chlorpropham residues on top and bottom halves of tubers taken from the surface of top boxes at 2 locations in the 2000-1 control store

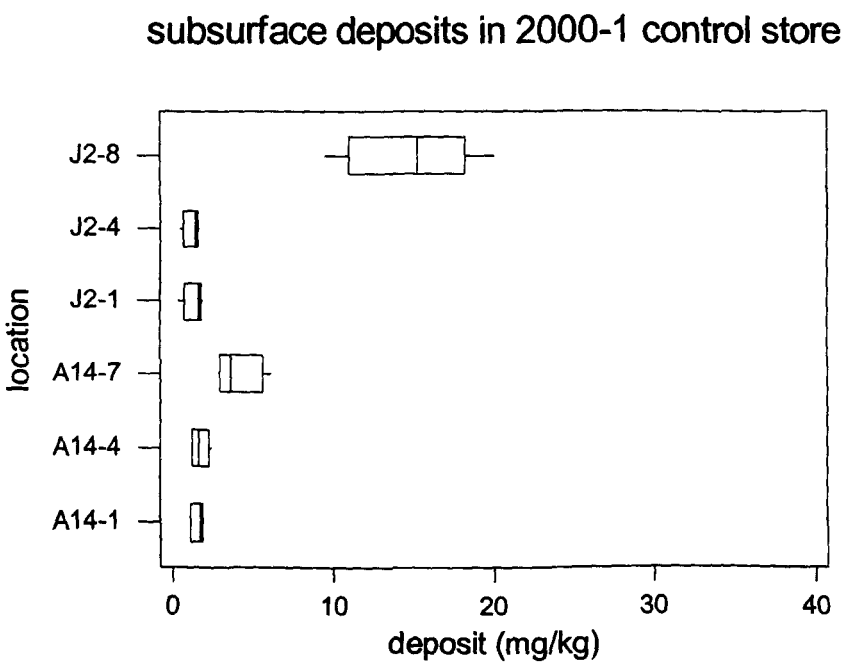


Figure 21 Boxplot showing chlorpropham deposits (unwashed values) on tubers taken from the sub-surface of boxes at 2 locations in the 2000-1 control store

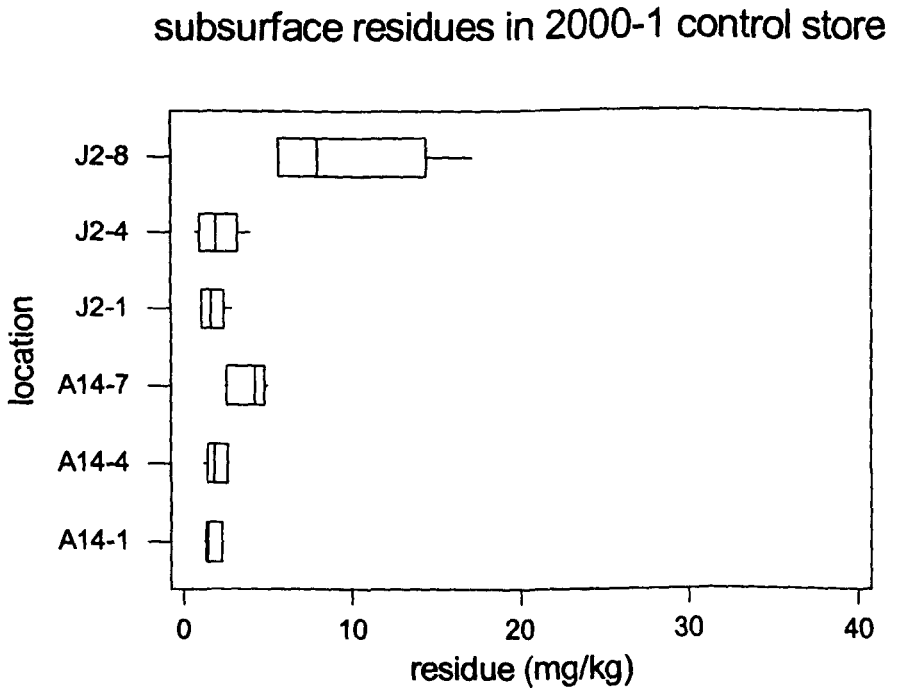


Figure 22 Boxplot showing chlorpropham residues (washed values) on tubers taken from the sub-surface of boxes at 2 locations in the 2000-1 control store

Table 10 Minitab 13.0 output for ANOVA (General Linear Model) carried out on surface data from the 2000-1 control store

General Linear Model: control store 2000-1 surface samples

```
Factor                 Type Levels Values
column                 fixed      2 A14        J2
surface(column)        fixed      4 bottom top    bottom top
type(column surface)   fixed      8 unwashed washed   unwashed washed   unwashed
                                   washed   unwashed washed

Analysis of Variance for CIPC, using Adjusted SS for Tests

Source                 DF      Seq SS      Adj SS      Adj MS       F      P
column                  1      399.61      399.61      399.61   18.64  0.000
surface(column)         2     1417.72     1417.72      708.86   33.06  0.000
type(column surface)    4      376.53      376.53       94.13    4.39  0.006
Error                  32      686.19      686.19       21.44
Total                  39     2880.06

Unusual Observations for CIPC

Obs      CIPC       Fit      SE Fit  Residual   St  Resid
  3   10.4700   25.8400      2.0709  -15.3700     -3.71R
  7    3.2300   13.8880      2.0709  -10.6580     -2.57R

R denotes an observation with a large  standardized residual.
```

Table 11 Minitab 13.0 output for ANOVA (General Linear Model) carried out on sub-surface data from the 2000-1 control store

General Linear Model: control store 2000-1 sub-surface samples

```
Factor                 Type Levels Values
column                 fixed      2 A14 J2
height(column)         fixed      6 bottom middle top    bottom middle top
wash(column height)    fixed     12 unwashed washed   unwashed washed   unwashed
                                    washed   unwashed washed   unwashed washed
                                    unwashed washed

Analysis of Variance for CIPC using Adjusted SS for Tests

Source                 DF      Seq SS      Adj SS      Adj MS       F      P
column                  1     101.185     102.831     102.831   25.91  0.000
height(column)          4     788.996     789.120     197.280   49.71  0.000
wash(column height)     6      69.689      69.689      11.615    2.93  0.017
Error                  47     186.523     186.523       3.969
Total                  58    1146.393

Unusual Observations for CIPC

Obs  CIPC (mg       Fit      SE Fit  Residual   St Resid
  3     9.5400   14.7920      0.8909   -5.2520    -2.95R
  4    20.0200   14.7920      0.8909    5.2280     2.93R
  6    17.1100    9.6180      0.8909    7.4920     4.20R
  9     5.6400    9.6180      0.8909   -3.9780    -2.23R
 10     5.6700    9.6180      0.8909   -3.9480    -2.22R

R denotes an observation with a large standardized residual.
```

To determine where these statistical differences lie, pairwise comparisons of the data were carried out using Tukey's multiple comparisons test. Data were first separated into surface and sub-surface sets (because tubers lying at the top of the store are considered to be held under different conditions to crop elsewhere) then one-way ANOVA with Tukey's pairwise comparisons was carried out. The table below shows surface data from the control store for the purposes of illustration. Tables for the rest of the data set from this and other distribution studies can be found in Appendix 1.

Table 12 Table showing Tukey's 95% confidence interval for the difference between pairs of means for surface samples from 2000-1 control store.

2000-1 control store all surface samples

	A14 BD	A14 BR	A14 TD	A14 TR	J2 BD	J2 BR
A14 BR	-10.64 8.33					
A14 TD	**-31.49** **-12.52**	**-30.33** **-11.36**				
A14 TR	**-19.54** **-0.57**	-18.38 0.59	**2.47** **21.44**			
J2 BD	-7.91 11.06	-6.76 12.22	**14.09** **33.06**	**2.14** **21.11**		
J2 BR	-9.32 10.65	-7.16 11.81	**13.68** **32.65**	**1.73** **20.70**	-9.89 9.08	
J2 TD	-13.57 5.41	-12.41 6.56	**8.44** **27.41**	-3.52 15.46	-15.14 3.83	-14.73 4.24
J2 TR	-16.07 2.90	-14.91 4.06	**5.94** **24.91**	-6.02 12.95	-17.64 1.33	-17.23 1.74

D = deposit R = residue T = top half of tuber B = bottom half of tuber

Yellow shading indicates pairs of means that are considered statistically different (i.e. the range of values for the difference does not include zero

3.3.5. Discussion

3.3.5.1 Surface samples

Results show that chlorpropham deposits on top halves of tubers are significantly higher and more variable than the corresponding bottom halves. In general, residue levels are lower and less variable than the corresponding deposit, with less of a difference between

the two locations. These effects can be seen most clearly in the box plots (Figures 19-21), which show the levels and variability for each sample type.

Top and bottom halves: CIPC deposits were generally higher at position J2 than at A14, although the differences are not always statistically significant (see Table 12 for details). Column J2 was at the opposite end and far side of the store from the application port, while A14 was very near the port (see Figure 18). This pattern of deposition has been reported by other workers, and is thought to be related to the conditions under which the fog is applied. A great deal of force is used to propel fog into store, and a large volume of air is introduced (up to ~1000m^3 hr^{-1} under experimental conditions), which encourages the fog to rush to the far end of the store. Its high temperature means that once in the store, the fog rises rapidly to the roof. Once at the top of the store, larger particles begin to settle out under gravity, and deposit onto the surface of crop in the top boxes. Because the fog tends to accumulate at the far end of the store, this effect is greater at that end than the near end.

Effect of washing: Other than on the top half of tubers from J2, washing did not result in a significant reduction in chemical levels. This reduction may reflect the influence of deposition of dry particles on top surfaces at this location. Bottom halves are somewhat sheltered from this effect, and behave more like the bulk of the store. Chemical reaching crop within the boxes is likely to be held on the skin, rather than just sitting on it, and is therefore not as easily removed by brushing or washing.

However, since individual analyses were carried out on discrete quarters of the tuber, any significant effect of washing would be masked if all the CIPC landed on one side of the tuber. Thus, the trends seen in the data with regard to washing might be more an artefact of the sampling procedure rather than a true measure of the effectiveness of washing at reducing chemical levels.

Deposit (unwashed) values are the best indicator of how chemical gets distributed around the store. Residue (washed) levels are more interesting in terms of the dose of chemical received by the consumer, or in determining whether crop meets the requirements of MRL guideline levels. Codex Alimentarius guidelines (Vol 2A Part 1, 2000) state that pesticide residue analysis should be carried out on root and tuber vegetables as follows for determination of compliance with MRL:

> "..whole commodity after removing tops. Wash the roots or tubers in cold running water, brushing gently with a soft brush to remove loose soil and debris, if necessary, and then dab lightly with a clean tissue paper to dry."

In this instance, a bulked sample is used. Depending on where and how a sample was collected, and whether individual locations were investigated or the store as a whole, crop from this store may or may not meet future MRL requirements. Even after washing, most of the surface samples from this study would still exceed the 5ppm expected as the UK MRL. However, crop from lower boxes would be well within limits.

3.3.5.2 Subsurface samples

Top boxes: Even at 20cm depth within the box, levels at J2 are generally higher than at A14, presumably because of the influence of airflow and particle deposition in the top box. Levels are, however, lower and less variable than at the surface of the same box.

Middle and bottom boxes: There is a significant height effect within a column of boxes, which is related to the fact that the hot fog accumulates at the top of the store during application. Levels are lower further down the stack, and show less variability than the top boxes. However, low variability in this instance does not necessarily indicate evenness of distribution – consider that the most 'even distribution' of chemical we could find would be where no chemical is applied at all, and no residue is found anywhere. The fact that residue levels are low in these boxes (<3ppm in most cases) but so high at the top of the store suggest that chemical is in fact poorly circulated around the store, and that very little is actually reaching into boxes and getting to the crop. The narrow spread of data might be the result of very little chemical reaching these boxes at all.

Where levels are so low, there may be an issue regarding the efficacy of the treatment i.e. effective sprout control might not be achieved with very little chemical on the crop. Poor efficiency of deposition on the crop (as well as uneven distribution) can result in re-applications being necessary to maintain sprout control throughout the store. It has been suggested that a concentration of around 1ppm on the tuber is all that is required for sprout control [H. Duncan, personal communication] but the position of the chemical on the tuber is also important. CIPC has been shown to be active in the vapour phase [van Vliet and Sparenberg (1970)], so having one large crystal land on the tuber surface may not result in complete sprout control if it is located too far from the eyes for the vapour to reach. This explains why tubers have been observed to sprout in spite of crystalline deposits on their skin. In that sense, the total concentration in the tuber is not the most important factor. What is more crucial is getting the chemical within effective range of the eyes.

3.3.5.3 Statistical analysis of data by ANOVA (General Linear Model)

Tables 10 and 11 show the Minitab output when data (split into surface and sub-surface sets) was analysed by ANOVA. Where there are two or more factors to be considered in a model, either balanced ANOVA or General Linear Model (which does not require a balanced design) can be used for data analysis. General Linear Model (GLM) was selected as the most appropriate statistical procedure in this instance because of the complicated sampling pattern in the stores [T. Aitchison, personal communication]. This analysis will provide a very general view of the situation in the store and determine whether there are any statistically significant factors at work in the store.

GLM will identify whether there are any statistically significant differences in the data, but will not show where the differences lie. For example, in Table 10 $p = 0.000$ for column effect, which means there is a statistically significant difference between the two columns in some part of the data. However, this may occur only at one height, or all three; in just the unwashed or washed data, or in both; at one sampling point or in all instances. Pair-wise comparison of the means is necessary to determine which samples are statistically different to which. Table 12 shows the data from surface samples presented in this way for illustration. Tables of the differences between means for the sub-surface data (and all data from other studies) are given in Appendix 2.

Results of GLM:

Surface samples: The analysis of variance table indicates that all factors (location, half and wash) are significant at a 99% confidence level ($p<0.01$ in all cases).

Subsurface samples: The analysis of variance table shows that all the factors are significant at a 95% probability level ($p<0.05$). Column and height effects are significant at a 99% confidence level ($p = 0.000$).

3.3.5.4 Estimation of deposition efficiency and chemical recovery from crop

In order to estimate the amount of chemical that may be lost from store or adsorbed onto the various fabrics within the store, an approximation of the percentage of applied chemical recovered on crop was calculated, based on levels determined in this study. Calculations were based on a number of assumptions, as detailed below.

Boxes at the top of the columns (8 or 7 high depending on location) are considered to be different from all the others. Deposition of particles from above is assumed to account for

the high levels seen in top boxes, and to have a significant effect through the whole box. At all other heights, where less chemical is expected to reach crop, the boxes were considered as being the same, though different to the top.

From the experimental data, an estimate for the mean deposit in top boxes was calculated (using top and bottom halves and whole tuber values) to be 9.71mg kg^{-1}. An estimate for the mean concentration in all the other boxes was calculated from middle and bottom box values as 1.43mg kg^{-1}.

The store held 1,150 tonnes at time of application, so 20.7kg of CIPC would have been added to the store (for a dose rate of 18g/tonne). From the plan layout, 198 tonnes were held in top boxes, with 952 tonnes elsewhere.

Weight of CIPC accounted for in this model:

- 198 tonnes at 9.71 g/tonne = 1.923kg
- 952 tonnes at 1.43 g/tonne = 1.362 kg

Thus, the percentage of the applied chemical estimated to be on the crop is **15.9%.** This figure is only a rough approximation, given the large differences in concentrations seen in individual tubers from the same location, and among the different locations and heights in the store.

3.3.5.5 Summary of results

The main trends in the data can all be explained as a result of the way in which the fog is expected to behave and move around the store:

- Surface levels in top boxes are significantly higher than sub-surface levels
- Values are higher in top boxes, and very low in middle and bottom boxes
- More chemical found at the far end of the store than near the application port

All these trends are consistent with the idea of hot fog entering the store and rapidly rising and moving to the far end of the store, followed by settling out of larger particles on the top surface of the crop.

The low levels (except in top boxes) suggest poor efficiency of deposition, that is, only a small proportion of the chemical introduced to the store reaches the target crop. Variability is low in most sampled boxes, but this does not necessarily imply even distribution.

Following conventional application, very little chemical penetrates into the boxes near the bottom of the store, which might mean sprout control becomes a problem over longer periods of storage. This may lead to repeated re-application of CIPC throughout the season.

In contrast, top box tubers (in particular, those lying at the surface) contain very high levels of chemicals, which might raise concerns in terms of MRL or Acceptable Daily Intake (ADI).

The poor recovery of chemical from the crop is also a problem in environmental terms. Although human exposure in the diet is important, non-target organisms and/or crops in the environment might be affected by large amounts of chemical lost from the store. Significant losses of chemical from the store are expected, through leakage at the time of application, and during routine venting. Materials in the store (e.g. boxes, insulating foam, walls, floor etc) may become contaminated with CIPC, which might cause problems during later use of the store. Impaired growth of seed held in CIPC treated stores has been reported by many in industry [Duncan, personal communication], and other types of sensitive seed and grain could also be affected.

Two key objectives were identified for future work: firstly, to prevent accumulation of the fog in the roof space, and secondly to encourage downward and lateral movement of air into boxes. In achieving these, more chemical may reach the crop in the first instance, and a more even dose will be received by crop in all locations in the store. Improvements to the application process could result in fewer applications being made, and lower residue levels on crop. Contamination of the environment (air through leakage, and water as a result of washing) and of store materials would also be reduced, in addition to production costs.

3.4 Year 2 Study B: Store with fans

3.4.1 Store layout

This study was carried out in a 2000-tonne modern box store, equipped with temperature and humidity control equipment, designed for long-term storage of potatoes at ~3°C for the pre-pack market. Crop was held in 1-tonne wooden boxes, stacked up to 8 boxes high. The potatoes were sampled on 1st December 2000, 24-hours after the first application of CIPC. Store temperature control was switched off one week prior to application to allow crop temperature to reach 5°C by the time of application (in line with formulation manufacturer's label recommendations).

Figure 23 overleaf shows the plan view of the layout of boxes in the store. Boxes were stacked 8 high in all rows except A-C, which were only 7 high because of the sloping roof at that part of the store.

4 oscillating desk fans were positioned in the top boxes of 4 columns of boxes (locations D3, D13, J3 and J13) at the four corners of the main block of boxes. When in use, the fans rotated through 90° to blow air towards the outer corners of the store and the end walls (see Figure 23). Air was blown out to the sides of the stack of boxes, and then fell down to the floor to be pulled back up through the columns of boxes. The surface of boxes immediately in the path of air blown by the fans were covered with polythene sheeting during application and for the following 24 hours in case of any condensation of the formulation – in Year 1, the use of overhead fans to move air during application resulted in gross contamination of crop in some top boxes, and CIPC concentrations >450ppm. On contact with the fans (which were operating on full power) the formulation condensed and dripped onto the crop below. This year, small desk fans were used, because of their large blades and slow revs, to encourage a gentle 'stirring' of the store air rather than a forceful movement.

CIPC application (the first of the season) was carried out on 30th November 2000, with a Unifog fogger and MSS Warefog 25 (60% CIPC in methyl pyrollidone), at a dose rate of 30ml/tonne. The total tonnage in the store was approximately 1300 tonnes, requiring ~39 litres of formulation at the maximum dose permitted on the label. The fans were switched on immediately before the application began, and left on for the following 24 hours while

all other store machinery remained off. Samples were collected 24 hours post-application, and then the store control systems were switched back on.

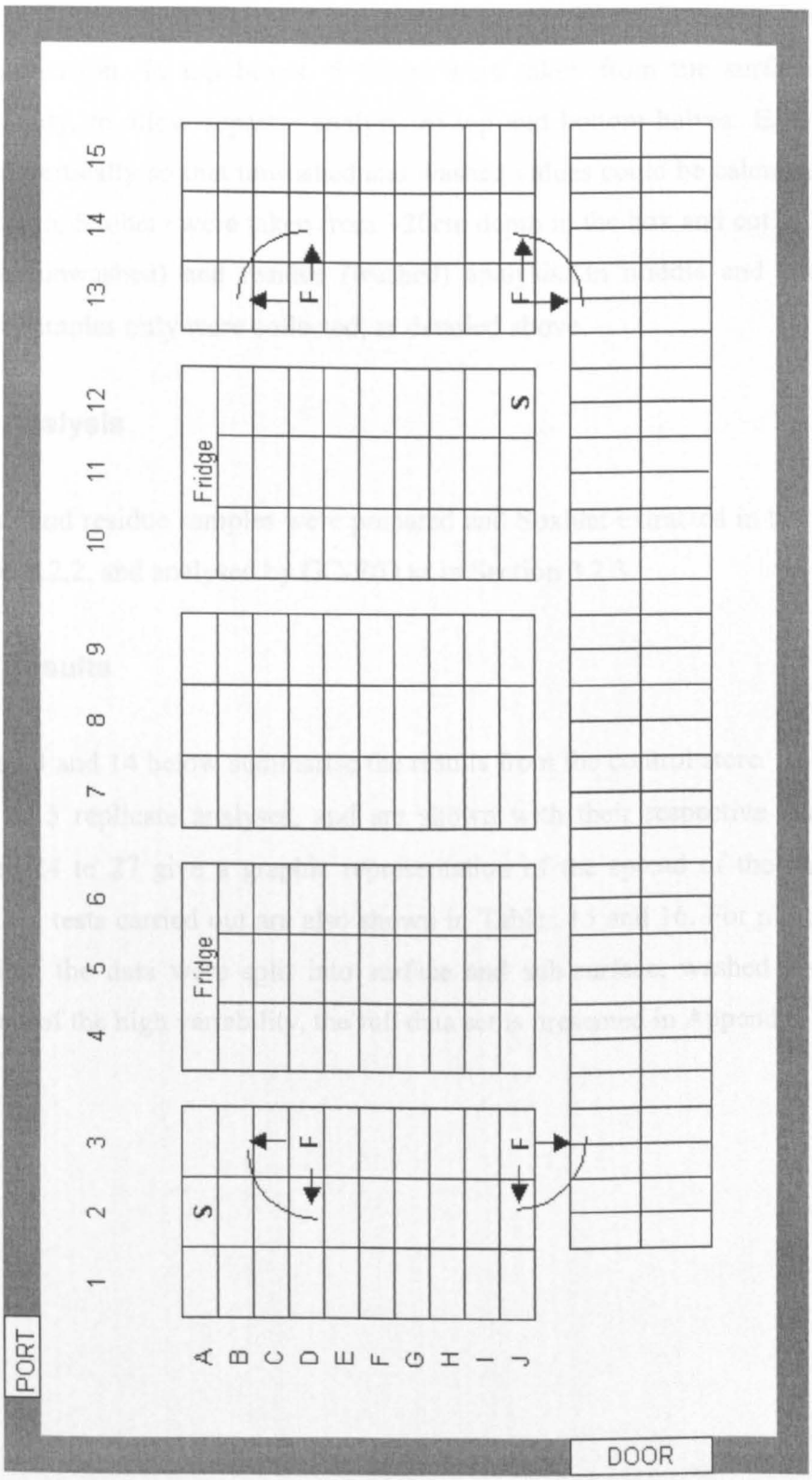


Figure 23 Plan view of layout of the 2000-1 fan store (not to scale)

3.4.2 Sampling

Tubers were collected from top, middle and bottom boxes in sampled columns 24 hours post-application. In top boxes, 5 tubers were taken from the surface and cut in two horizontally, to allow separate analysis of top and bottom halves. Each half was further divided vertically so that unwashed and washed values could be calculated for each tuber. In addition, 5 tubers were taken from ~20cm depth in the box and cut in half vertically for deposit (unwashed) and residue (washed) analysis. In middle and bottom boxes, sub-surface samples only were collected, as detailed above.

3.4.3 Analysis

Deposit and residue samples were prepared and Soxhlet extracted in hexane as detailed in Section 3.2.2, and analysed by GC-FID as in Section 3.2.3.

3.4.4 Results

Tables 13 and 14 below summarise the results from the control store. Values given are the mean of 5 replicate analyses, and are shown with their respective standard deviations. Figures 24 to 27 give a graphic representation of the spread of the data. Details of the statistical tests carried out are also shown in Tables 15 and 16. For plotting and statistical handling, the data were split into surface and sub-surface, washed and unwashed sets. Because of the high variability, the full data set is presented in Appendix 1.

Table 13 Mean chlorpropham deposits (mg kg^{-1}) and standard deviations on unwashed tubers from the 2000-1 fan store

Location	Box height	Surface tubers		Sub-surface tubers
		Upper half	Lower half	Whole
A2 (near)	Top	12.35 ±3.22	3.84 ± 0.91	4.80 ±1.32
	Middle			3.44 ± 1.88
	Bottom			2.11 ± 0.86
J12 (far)	Top	17.24 ± 6.10	4.41 ± 1.32	7.77 ± 2.70
	Middle			1.86 ± 0.76
	Bottom			3.65 ± 1.52

Table 14 Mean chlorpropham residue (mg kg^{-1}) and standard deviations on washed tubers sampled from the 2000-1 fan store

Location	Box height	Surface tubers		Sub-surface tubers
		Upper half	Lower half	Whole
A2 (near)	Top	17.59 ± 6.06	3.57 ± 1.05	8.59 ± 1.19
	Middle			4.75 ± 0.74
	Bottom			2.12 ± 0.32
J12 (far)	Top	16.69 ± 9.00	4.09 ± 0.42	7.03 ± 1.15
	Middle			1.83 ± 0.74
	Bottom			2.14 ± 1.82

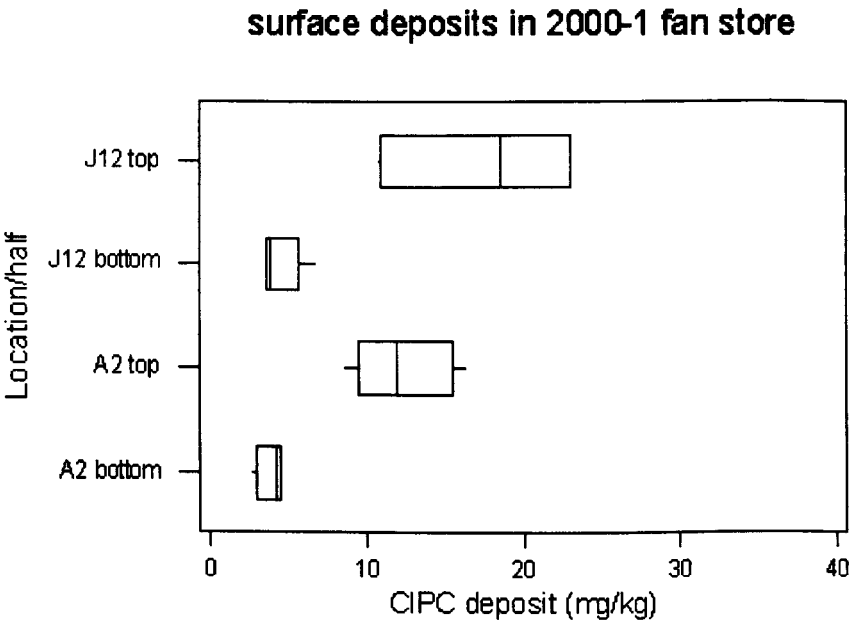


Figure 24 Boxplot showing deposits of chlorpropham on top and bottom halves of tubers taken from the surface of top boxes at two locations in 2000-1 fan store

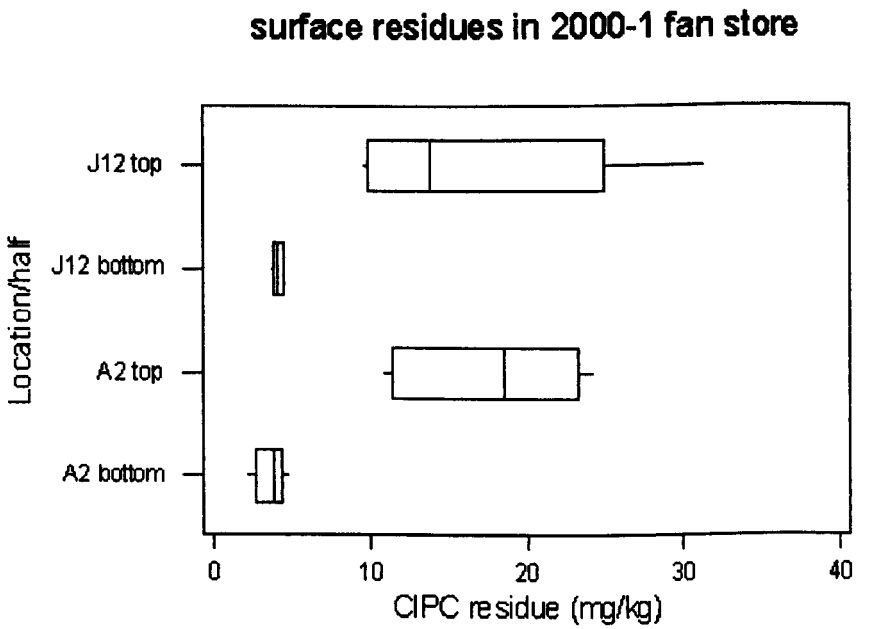


Figure 25 Boxplot showing residues of chlorpropham top and bottom halves of tubers taken from the surface of top boxes at two locations in the 2000-1 fan store

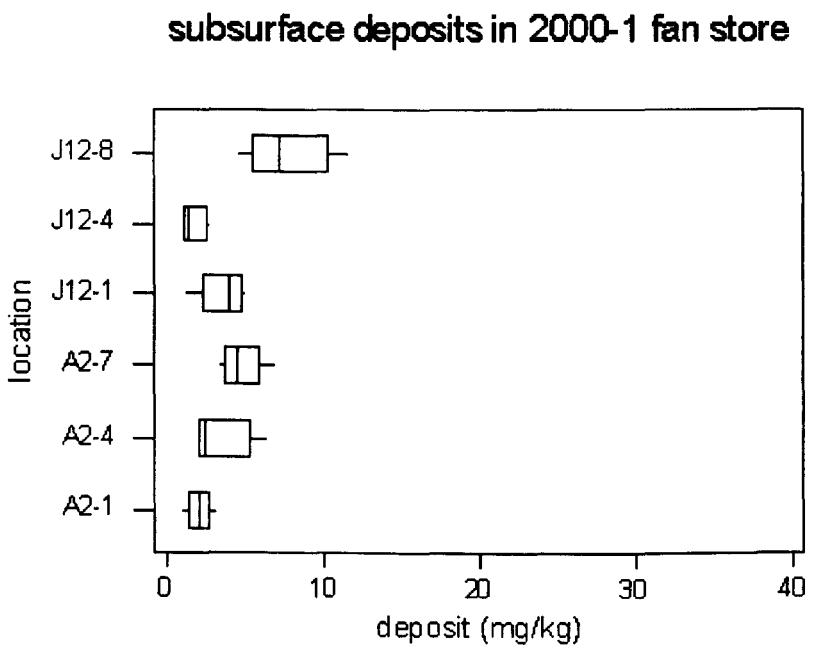


Figure 26 Boxplots of deposits of chlorpropham on tubers taken from ~20cm depth in boxes from the 2000-1 fan store

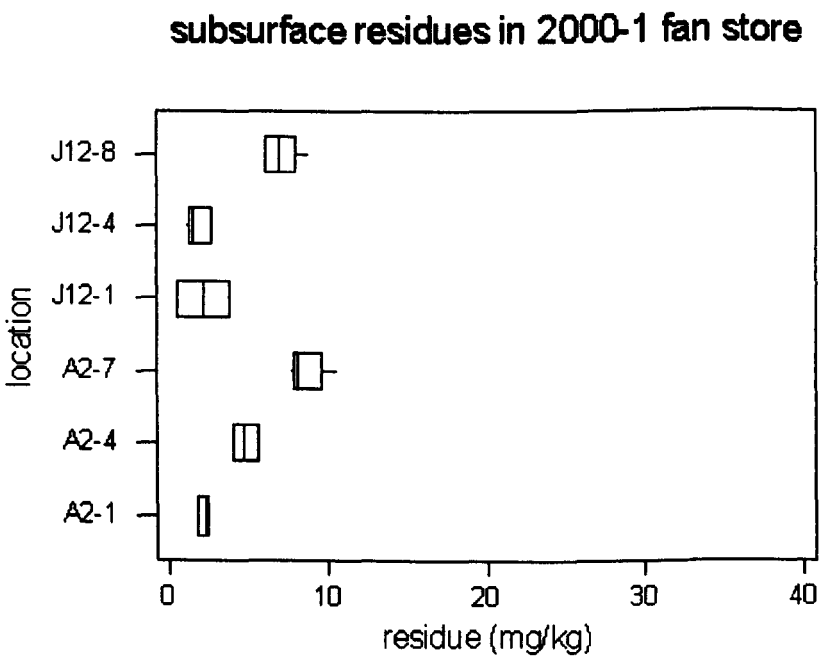


Figure 27 Boxplot of residues on tubers taken from ~20cm depth in boxes from the 2000-1 fan store

Table 15 Minitab 13.0 output for nested ANOVA General Linear Model carried out on surface data from the 2000-1 fan store

General Linear Model: Fan store 2000-1 surface samples

```
Factor                   Type Levels Values
Location                 fixed      2 A2          J12
Half (Location)          fixed      4 bottom top     bottom top
wash(Location half)      fixed      8 unwashed washed   unwashed washed
                                      unwashed washed   unwashed washed

Analysis of Variance for CIPC_1, using Adjusted SS for Tests

Source                    DF     Seq SS     Adj SS     Adj MS     F      P
Location                   1       9.35      15.62      15.62    0.72  0.403
half_(location)            2    1410.31    1404.82     702.41   32.26  0.000
wash (location half)       4      69.72      69.72      17.43    0.80  0.534
Error                     31     674.89     674.89      21.77
Total                     38    2164.27

Unusual Observations for CIPC_1

Obs     CIPC_1       Fit      SE Fit  Residual   St Resid
 29    31.4600   16.6860      2.0867   14.7740      3.54R

R denotes an observation with a large standardized residual.
```

Table 16 Minitab 13.0 output for nested ANOVA General Linear Model carried out on sub-surface data from the 2000-1 fan store

General Linear Model: 2000-1 fan store sub-surface samples

```
Factor                 Type Levels Values
column                 fixed      2 A2  J12
height(column)         fixed      6 bottom middle top    bottom middle top
wash(column height)    fixed     12 unwashed washed   unwashed washed   unwashed
                                    washed   unwashed washed   unwashed washed
                                    unwashed washed

Analysis of Variance for CIPC (mg, using Adjusted SS for Tests

Source                  DF     Seq SS     Adj SS     Adj MS       F      p
column                   1      0.528      0.954      0.954    0.50  0.483
height(column)           4    276.517    278.108     69.527   36.50  0.000
wash(column height)      6     46.577     46.577      7.763    4.08  0.002
Error                   47     89.527     89.527      1.905
Total                   58    413.149

Unusual Observations for CIPC (mg

Obs  CIPC (mg       Fit      SE Fit  Residual   St Resid
 13    6.4200    3.4420      0.6172    2.9780      2.41R
 33   11.6600    7.7740      0.6172    3.8860      3.15R
 34    4.5200    7.7740      0.6172   -3.2540     -2.64R
 55    1.1800    3.6500      0.6172   -2.4700     -2.00R
```

3.4.5 Discussion

3.4.5.1 Surface samples:

Top half deposits and residues are significantly higher and more variable than the corresponding bottom half values ($p = 0.000$)

There was less of a difference between locations in this store than in the control store. Levels at J12 were slightly higher than at A2, but this effect is much less pronounced than in the control store. ANOVA (GLM) shows no significant difference between the two columns ($p = 0.403$).

Washing appeared to make little difference to the amount of chemical on crop ($p = 0.534$), but as previously discussed in Section 3.3.5 any effect might be masked because of the way in which samples were collected and prepared for analysis. Individual tubers were cut into quarters in the store, so if the surface of the tuber was unevenly exposed to CIPC (e.g. if chemical only landed on one side) this might introduce bias into the results and conceal any reductions through washing.

In both deposits and residues, levels of chemical on the bottom halves are much lower and less variable than the top halves because they are sheltered from the deposition of particles from above. Levels are often more similar to tubers from middle and bottom boxes than to the top half of the same tuber.

3.4.5.2 Sub-surface samples:

Deposits in sub-surface samples are lower and less variable than at the surface of the top box. Residue values are significantly lower and less uneven than the deposits ($p = 0.002$).

General Linear Model analysis of sub-surface data showed no difference between the two locations ($p = 0.483$), so it appears the use of fans has reduced the tendency for the fog to accumulate at one end of the store.

Significant differences remain between samples collected from different heights at the same location ($p = 0.000$). Again, GLM analysis does not show where these differences do lie – tables of significant differences are given in Appendix 2. Because of the high variability seen in the store, emphasis was not placed on these in the discussion of the results. Generally, the top half of surface tubers are assumed to be different from those everywhere else in the store.

In this store, middle and bottom box deposits and residues are higher than in the control store, suggesting that more of the applied chemical is reaching into these boxes. Height differences are also less pronounced, so it appears there is an improvement both in terms of distribution and also application efficiency.

In bottom boxes, residue levels are often <2ppm, which may not be enough for effective sprout control throughout the season, depending on how it is distributed around the tuber.

3.4.5.3 Estimation of application efficiency

An estimation of the proportion of applied chemical reaching the crop was calculated in the same way as for the control store (see Section 3.3.5.4).

Top boxes were considered to be different to all others in the store, and to be affected by the settling out of particles of fog. CIPC was assumed to reach crop in all other boxes by lateral movement of the fog, and levels assumed to be less influenced by the larger particles of chlorpropham.

A mean deposit was calculated for top boxes using all values (top half, bottom half and whole tuber) to be 7.9ppm.

A mean deposit for all boxes other than top boxes was calculated (using middle and bottom box values) to be 2.8ppm.

The tonnage in store was 1,300 tonnes. From the layout of the store, 198 tonnes were held in top boxes, with 1,102 tonnes elsewhere. At a dose rate of 18g per tonne, 23.4 kg CIPC was applied to the store.

The amount recovered on crop was estimated at

- 198 tonnes * 7.9 g/tonne = 1.56 kg
- 1,102 tonnes * 2.8 g/tonne = 3.09 kg

The percentage of applied chemical recovered was **19.9%**. Although this may not represent a significant improvement in the efficiency of deposition, the pattern of distribution has been altered.

3.5 Year 3 Study A: Box store with fans

3.5.1 Store layout

This study was carried out in a modern box store, equipped with temperature and humidity control equipment, designed for long-term storage of potatoes at ~3°C for the pre-pack market. Crop was held in 1-tonne wooden boxes, stacked up to 8 boxes high. The potatoes were sampled on 17th January 2002, 24-hours after the first application of CIPC. CIPC was applied as a methyl pyrrolidone formulation (MSS Warefog) with a modified Unifog fogging machine. Store temperature control was switched off one week prior to application to allow crop to reach 5°C by the time of application.

6 auxiliary fans were incorporated into this trial, attached to the side of top boxes of stacks at positions A3, A9, F1, F12, J3 and J9 (see Figure 29). The fans were aimed directly down towards the floor, as shown in Figure 28 below. Their purpose was to introduce a downward air current to counteract the accumulation of fog in the free air space at the top of the store, and reduce the effect of gravitational settling out of particles. Boxes in the store were stacked 8 high, except rows A-C, which were 7 high because of the sloping roof at that point in the store. Samples were taken from 4 locations: 2 at each side and end of the store.

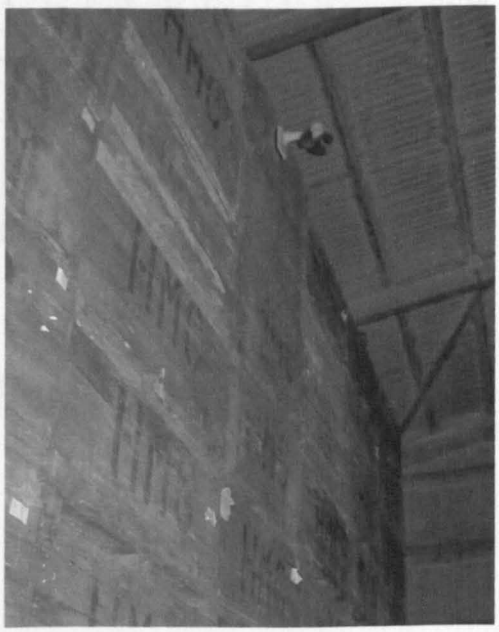


Figure 28 Position of fan on the side of a column of boxes

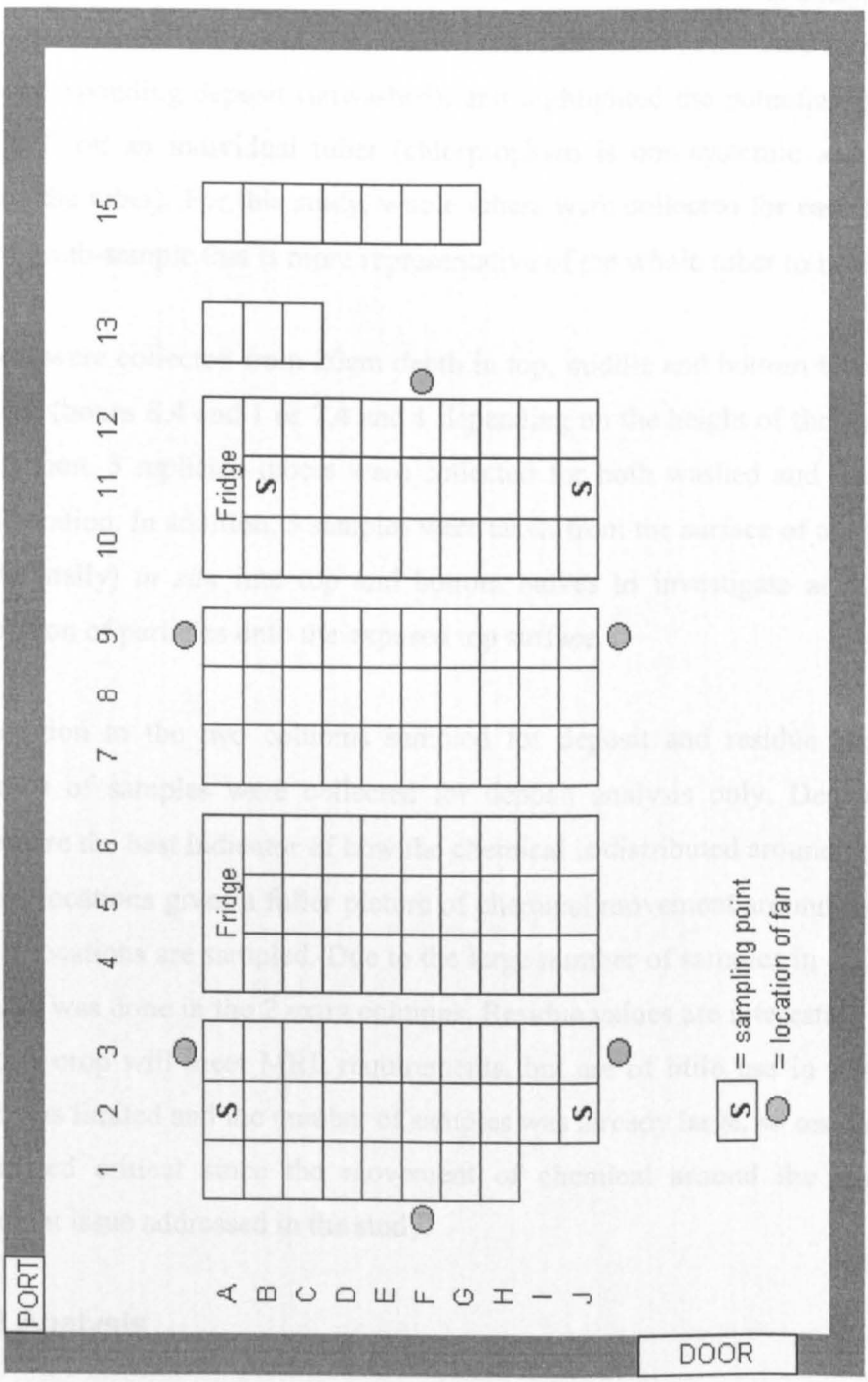


Figure 29 Plan view of the layout of the 2001-2 fan store (not to scale)

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3.5.2 Sampling

In previous work, deposit and residue analyses were carried out on the same tuber by cutting it vertically in half *in situ*. Thus, one side of the tuber was analysed washed and the other unwashed. This resulted in residue (washed) values that were sometimes higher than the corresponding deposit (unwashed), and highlighted the potential for uneven dispersal of CIPC on an individual tuber (chlorpropham is non-systemic and is not transported within the tuber). For this study, whole tubers were collected for each type of analysis, to allow a sub-sample that is more representative of the whole tuber to be extracted.

Tubers were collected from 20cm depth in top, middle and bottom boxes in each sampled column (boxes 8,4 and 1 or 7,4 and 1 depending on the height of the stack) 24 hours post-application. 5 replicate tubers were collected for both washed and unwashed analysis at each location. In addition, 5 samples were taken from the surface of top boxes and were cut (horizontally) *in situ* into top and bottom halves to investigate any differences due to deposition of particles onto the exposed top surface.

In addition to the two columns sampled for deposit and residue analysis, a further 2 columns of samples were collected for deposit analysis only. Deposit (i.e. unwashed) values are the best indicator of how the chemical is distributed around the store, and values from 4 locations gives a fuller picture of chemical movement around the store than where only 2 locations are sampled. Due to the large number of samples in each store, no residue analysis was done in the 2 extra columns. Residue values are interesting when determining whether crop will meet MRL requirements, but are of little use in terms of distribution. Time was limited and the number of samples was already large, so residue analysis was not considered critical since the movement of chemical around the store was the most important issue addressed in the study.

3.5.3 Analysis

Deposit and residue samples were prepared and Soxhlet extracted in hexane as detailed in Section 3.2.2 and analysed by GC-FID as in Section 3.2.3.

3.5.4 Results

Tables 17 and 18 below contain the summarised results of all analyses. The figures shown represent the means of 5 replicate analyses, and are given along with their corresponding

standard deviations. The full data set is presented in Appendix 1. Figures 30-33 show the spread of the data, and Tables 19 and 20 the results of statistical analysis.

Table 17 Mean chlorpropham deposits (mg kg^{-1}) and standard deviations on unwashed tubers sampled from the 2001-2 fan store

Location	Box height	Surface tubers		Sub-surface tubers
		Upper half	**Lower half**	**Whole**
A2	Top	24.12 ± 13.88	5.41 ± 5.34	13.99 ± 4.52
(near)	Middle			3.23 ± 2.66
	Bottom			4.04 ± 2.40
J11	Top	49.50 ± 27.4	11.23 ± 13.85	16.15 ± 10.07
(far)	Middle			3.17 ± 1.79
	Bottom			2.19 ± 0.68
B11				
(extra column)	Top			12.26 ± 5.37
	Middle			11.19 ± 6.31
	Bottom			1.31 ± 0.37
J2				
(extra column)	Top			11.45 ± 4.35
	Middle			13.81 ± 10.19
	Bottom			7.54 ± 3.83

Table 18 Mean chlorpropham residues (mg kg^{-1}) and standard deviations on washed tubers sampled from the 2001- 2 fan store

Location	Box height	Surface tubers		Sub-surface tubers
		Upper half	**Lower half**	**Whole**
A2	Top	12.01 ± 4.54	6.88 ± 3.27	5.08 ± 2.93
(near)	Middle			2.87 ± 0.99
	Bottom			3.02 ± 1.85
J11	Top	23.38 ± 17.87	7.73 ± 4.03	6.25 ± 3.49
(far)	Middle			2.38 ± 0.53
	Bottom			1.46 ± 0.42

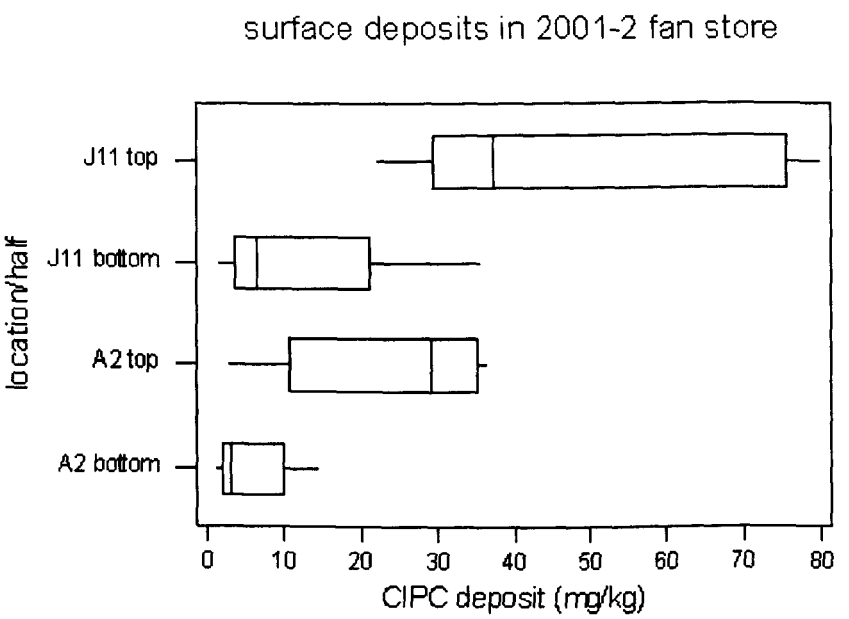


Figure 30 Boxplot showing deposits of chlorpropham on top and bottom halves of tubers at the surface of top boxes at two locations in the 2001-2 fan store

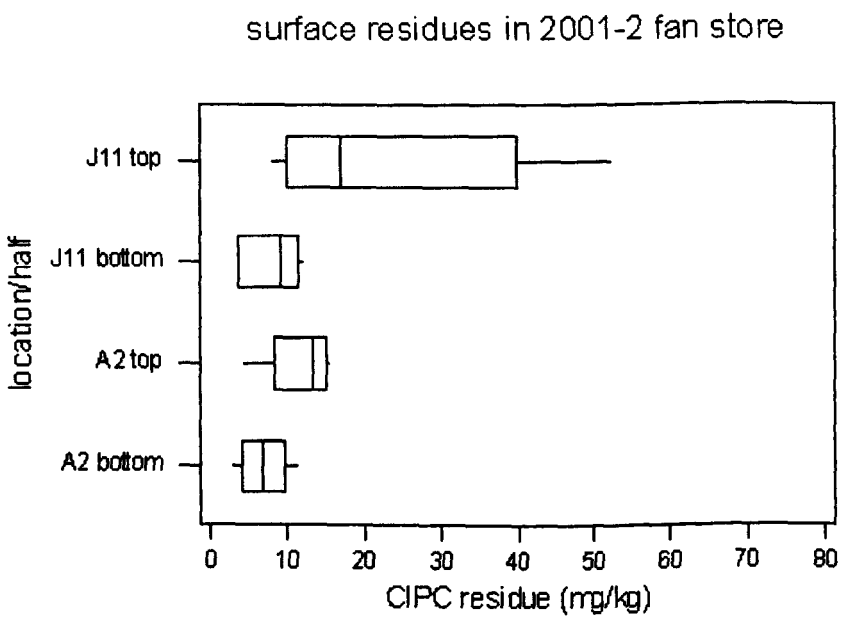


Figure 31 Boxplot showing residues of chlorpropham on top and bottom halves of tubers at the surface of top boxes at two locations in the 2001-2 fan store

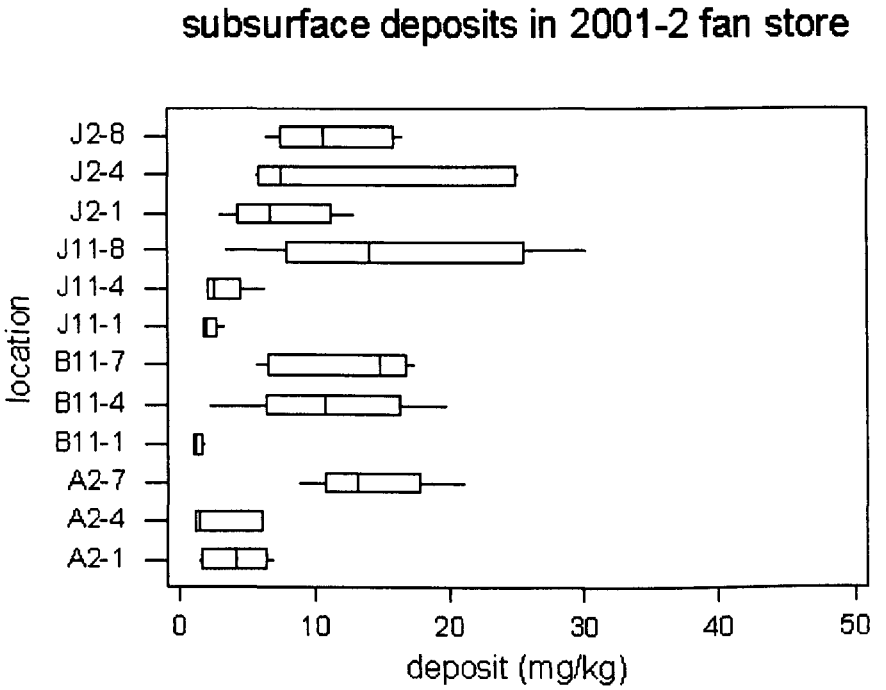


Figure 32 Boxplot showing deposits of chlorpropham on tubers taken from ~20cm depth in boxes from the 2001-2 fan store

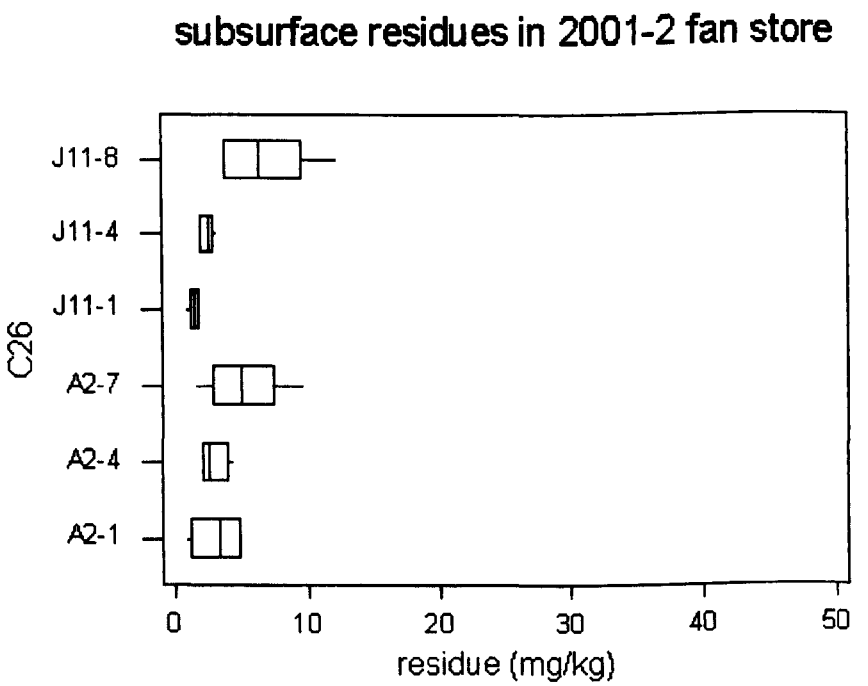


Figure 33 Boxplot showing residues of chlorpropham in tubers taken from ~20cm depth in boxes from the 2001-2 fan store

Table 19 Minitab 13 output for GLM carried out on surface data from 2001-2 fan store

General Linear Model: 2001-2 fan store surface samples

```
Factor                  Type Levels Values
location                fixed      2 A2  J11
half(location)          fixed      4 bottom top    bottom top
wash(location half)     fixed      8 unwashed washed   unwashed washed
                                     unwashed washed   unwashed washed

Analysis of Variance for CIPC using Adjusted SS for Tests

Source                  DF     Seq SS     Adj SS     Adj MS       F      P
location                 1     1176.0     1176.0     1176.0    6.14  0.019
half (location)          2     4343.9     4343.9     2171.9   11.34  0.000
wash (location half)     4     2104.7     2104.7      526.2    2.75  0.045
Error                   32     6128.7     6128.7      191.5
Total                   39    13753.2

Unusual Observations for CIPC

Obs  CIPC          Fit      SE Fit  Residual   St Resid
 23   92.5800   49.4800      6.1890   43.1000      3.48R
 25   21.7200   49.4800      6.1890  -27.7600     -2.24R
 28   52.5200   23.3820      6.1890   29.1380      2.35R
```

Table 20 Minitab 13 output for GLM carried out on sub-surface data from 2001-2 fan store

General Linear Model: 2001-2 fan store sub-surface samples

```
Factor                  Type Levels Values
column                  fixed      4 A2  B11 J11 J2
Height(column)          fixed     12 bottom middle top    bottom middle top
                                     bottom middle top    bottom middle top
wash(column Height)     fixed     18 unwashed washed   unwashed washed   unwashed
                                     washed   unwashed unwashed unwashed unwashed
                                     washed   unwashed washed   unwashed washed
                                     unwashed unwashed unwashed

Analysis of Variance for CIPC, using Adjusted SS for Tests

Source                  DF     Seq SS     Adj SS     Adj MS       F      P
column                   3     414.82     414.82     138.27    6.72  0.000
Height(column)           8    1276.79    1276.79     159.60    7.76  0.000
wash(column Height)      6     434.83     434.83      72.47    3.52  0.004
Error                   72    1480.58    1480.58      20.56
Total                   89    3607.02

Unusual Observations for CIPC

Obs      CIPC       Fit      SE Fit  Residual   St Resid
 31    3.1900   16.1520      2.0280  -12.9620     -3.20R
 34   30.2500   16.1520      2.0280   14.0980      3.48R
 66   19.8000   11.1860      2.0280    8.6140      2.12R
 67    2.1300   11.1860      2.0280   -9.0560     -2.23R
 81   24.6600   13.8120      2.0280   10.8480      2.67R
 82   25.2300   13.8120      2.0280   11.4180      2.82R
 83    5.5000   13.8120      2.0280   -8.3120     -2.05R
```

3.5.5 Discussion

3.5.5.1 Surface samples

Top half deposits are higher and more variable than the bottom halves ($p = 0.000$).

GLM analysis suggests there is a difference between surface samples in top boxes at the two locations ($p = 0.019$), but doesn't give any indication of where in the data the difference lies. Tables of values from Tukey's pairwise comparisons are given in Appendix 1 to show which samples were identified as being significantly different from which. In this study, fans were attached to the sides of boxes, pointing downward. In effect there was nothing to prevent the accumulation of fog at the far end of the store from the application port (last year's horizontal fanning helped reduce this effect, resulting in no difference between the two locations).

Washing reduced the amount of chemical on tubers, and also reduced the variability among samples, but there are still significant differences between the top and bottom half of the tuber.

In this study, washing did significantly reduce the amount of chemical present on the crop, both at the surface and in the sub-surface of boxes. This can be attributed to the altered sampling procedure and way in which samples were prepared for analysis: in previous studies, 5 tubers were collected from each sampling point, and were subsequently cut into sections to allow washed and unwashed analysis to be carried out on the same tuber. This year, 10 tubers in total were collected from each sampling point, allowing analysis of a more representative sub-sample of a whole tuber, rather than a sub-sample of one particular half or one quarter. In this way, a more random sub-sample of 30g is analysed, reducing any influence of uneven dispersal around the surface of the tuber.

Table 19 shows the Minitab output when a nested General Linear Model analysis of variance was carried out on surface data. In this store, several data points are identified as unusual observations, in both the surface and sub-surface data sets. These values are the ones that would have been discarded as outliers had that been considered an appropriate way to deal with the data, since unusually high or low values can have a significant effect on the calculated means and standard deviations of the sample. All the unusual observations in this set of surface data occur at position J11, and are likely to be a result of the deposition of particles leading to high and unpredictable chemical levels.

The most significant effect is the difference between top and bottom halves (p =0.000) in each top box. Differences between surface and sub-surface values within the top box can be explained by considering the boxes of crop as porous media through which the fog moves. Larger particles will have a higher rate of deposition than smaller particles [Xu and Burfoot (2000)], and so greater deposits are expected on the outer surfaces of the porous medium (i.e. on top tubers) with a much-reduced concentration of particles penetrating to the inside of the box. This explains the gradient of CIPC levels within the top boxes seen in this work, and also as reported by other workers. The gradient of deposits in boxes from different heights can largely be explained by the temperature gradient in the store as a result of thermal fog application, and the fact that the predominant movement of air was in a downward direction. As such, there was no real incentive for lateral movement into the boxes. (This issue is addressed in the following study).

3.5.5.2 Subsurface samples

Deposits in the sub-surface of boxes (particularly in middle and bottom boxes) are generally more variable and much higher than in the previous studies, e.g. in the control store and store with fans 2000-1.

The height difference is much less pronounced than in the store with horizontal fanning from 2000-1. In that store, there was little location effect, but significant height differences. In the current work, height differences were reduced but there were location effects. The fans are having an effect in each case, albeit a small one.

Residues are generally higher and more variable than in the control store, suggesting that although the dispersal of fog around the store is still uneven more of the chemical is reaching into the boxes.

Again, most of the unusual observations listed in Table 19 come from location 11 (columns B and J), which could be symptomatic of fog accumulating towards this end of the store.

When pairwise comparisons were carried out using Tukey's test, this store generated the highest number of significant differences. It also contained the highest deposit and residue levels. Variability has been increased as a consequence of more chemical penetrating into boxes.

3.5.5.3 Deposition efficiency

A simplified model of the store was used to estimate the proportion of the applied chemical recovered from the crop, as described in Section 3.2.4.3.

Top boxes were considered to be different from all other boxes in the store because they are affected by particle deposition from above. Location differences were assumed to be negligible. A mean CIPC deposit level for top boxes was calculated using all the data from the sampled boxes (top and bottom halves, and whole tuber data from 4 locations) to be 16.5ppm.

Every box other than the top box of each column was considered as being the same, although different to the top boxes (i.e. CIPC was assumed to reach them by the movement of small particles around the store in the airstream, rather than by deposition of particles from above). Location differences were again considered negligible for the purposes of this model. A mean deposit level of 5.45ppm was calculated from data from middle and bottom boxes at 4 locations in the store.

This store was fairly empty at the time of application, because crop had been moved into another store (see next section for details). The total tonnage in store was 946 tonnes, of which 122 tonnes was assumed to be in top boxes (according to the stacking pattern in Figure 29) and 824 tonnes in other boxes.

At a dose rate of 18g/tonne, 17.03kg of CIPC would have been added to the store. That recovered on crop was estimated to be

- $122 * 16.5 mg\ kg^{-1}$ = 2.013 kg
- $824 * 5.45\ mg\ kg^{-1}$ = 4.491 kg

Thus, 6.504 kg of CIPC was recovered on the crop, which amounts to **38.2%** of that applied.

This is a significant improvement on the recoveries calculated for the 2000-1 control store (~16%) and the 2000-1 horizontal fanning store (~20%). Although the prevention of the vertical movement of fog is thought to be a significant factor in this improvement, there is another possible angle. This was a 2,000 tonne store, but was only approximately half full. As a result, there was a lot of free air space in the store, much more than is usual under

commercial conditions. During CIPC application, fog is lost through leakage as the volume of air in the store is replaced with fog. If the volume of fog introduced is greater than the volume of free air in the store then some loss is guaranteed, as the store does not pressurise during application. A simple modelling exercise carried out as part of this work (see Chapter 8) estimated that up to 40% of the chemical applied could be lost in this way from a store assuming ~40% of the volume is free air space. The mathematical model of Xu and Burfoot (2000) calculated that some 32% was lost from the store during a 30-second application carried out in an experimental store with 3 tonnes crop.

The smaller the volume of free air space in the store, the less air there is to be replaced by fog, and the quicker the fog will begin to escape through the vents. Consequently, more chemical is lost from the store. In a store like this one, where most of the volume is air, less of the fog may be lost during application, and as a result more remains in the store to deposit on the crop.

The improved application efficiency in this store is likely to be a result of a combination of the modified air circulation and the large volume of free air space within the store. As reported elsewhere in this thesis (see Chapter 2) industry opinion on how to deal with part-filled stores is divided. Label instructions state that the amount of CIPC applied to the store must be calculated on the basis of the tonnage in store, and not on store volume. However, some store managers will not apply when stores are part-filled; some add less CIPC per tonne while some apply extra because of the empty space in the store. These results suggest that dose rate should in fact be reduced when a store is not full, on the basis that less chemical will be lost through leakage. Free air circulation, and more even distribution of chemical, is more easily attained when the store is less full.

3.6 Year 3 Study B Store with artificial plenum

3.6.1 Store layout:

This study was carried out in a modern box store, equipped with temperature and humidity control equipment, designed for long-term storage of potatoes at ~3°C for the pre-pack market. Crop was held in 1-tonne wooden boxes, stacked up to 8 boxes high. The potatoes were sampled on 17th January 2002, 24-hours after the first application of CIPC that season. CIPC was applied as a methyl pyrrolidone formulation (MSS Warefog) at a dose rate of 30ml/tonne. Store temperature control was switched off one week prior to application to allow crop temperature to reach 5°C by the time of application, in line with label recommendations.

Figure 34 overleaf shows the plan view of the store. The store was identical in dimensions to the store in the previous study, although the layout of the boxes was very different. In order to construct the plenum in this store, it was important that all columns in the affected part of the store were the same height (8 boxes high). No empty boxes could be used to fill out this part of the store, as they would have been unsafe to work on. As a result, crop was transferred from the fan store into this one, resulting in significant differences in both stacking pattern and tonnage.

CIPC application was carried out on 16th January 2002, using MSS Warefog 25 and a Unifog fogging machine. Samples were collected 24 hours later. In this store, the metal ducting pipe from the fogger was not inserted through the application port as for conventional applications, but was instead run under the roller door to introduce the fog directly into the plenum chamber, constructed from polythene sheeting (see Figure 34).

The purpose of the plenum chamber was to provide a physical barrier to the upward movement of the fog. Forcing air to travel through boxes full of crop before reaching the free airspace at the top of the store may reduce the very large deposits often found in top boxes because of the settling out of fog particles from above. Movement of fog through boxes will become the dominant process, rather than the usual rise and fall in free air space during conventional application.

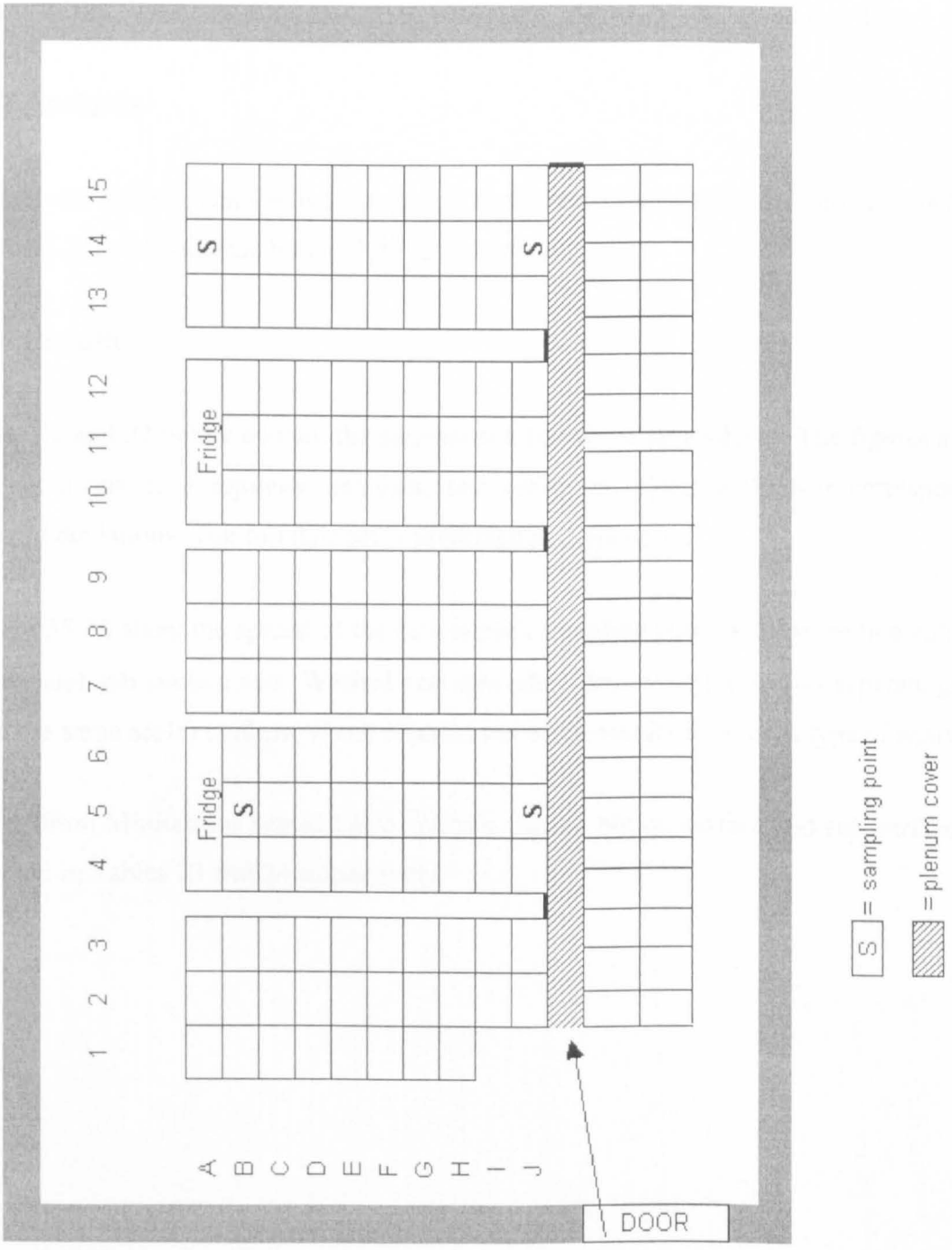


Figure 34 Plan view of layout of boxes in the 2001-2 plenum store (not to scale)

3.6.2 Sampling:

Sampling was carried out as described in Section 3.5.2, 24 hours post-application. Whole tubers were collected from 20cm depth, so no cutting was carried out *in situ*, except at the surface of top boxes where tubers were cut into top and bottom halves as they lay.

3.6.3 Analysis:

Deposit and residue samples were prepared and Soxhlet extracted in hexane as detailed in Section 3.2.2 and analysed by GC-FID as in Section 3.2.3.

3.6.4 Results:

Tables 21 and 22 below contain the summarised results of all analyses. The figures shown are the means of 5 replicate analyses, and are given along with their corresponding standard deviations. The full data set is presented in Appendix 2.

Figures 35-38 show the spread of the data at each sampling point. Data were first split into surface and sub-surface sets. Washed and unwashed data were plotted on separate graphs (with the same scale) to allow visual comparison of the results from each type of analysis.

Output from Minitab for nested GLM analysis carried out on surface and sub-surface data is shown in Tables 23 and 24 respectively.

Table 21 Mean chlorpropham deposits (mg kg^{-1}) and standard deviations on unwashed tubers sampled from the 2001-2 plenum store

Location	Box height	Surface tubers		Sub-surface tubers
		Upper half	Lower half	Whole
A2	Top	27.94 ± 15.15	11.01 ± 16.42	16.04 ± 8.29
(near)	Middle			3.93 ± 2.85
	Bottom			2.11± 0.85
J11	Top	19.28 ± 6.64	3.95 ± 1.21	7.34 ± 0.79
(far)	Middle			5.29 ± 3.43
	Bottom			2.29 ± 1.67
B11				
(extra column)	Top			9.95 ± 3.28
	Middle			7.25 ± 11.01
	Bottom			3.49 ± 2.70
J2				
(extra column)	Top			4.11 ± 2.02
	Middle			5.19 ± 0.53
	Bottom			6.30 ± 8.59

Table 22 Mean chlorpropham residues (mg kg^{-1}) and standard deviations on washed tubers sampled from 2001-2 plenum store.

Location	Box height	Surface tubers		Sub-surface tubers
		Upper half	Lower half	Whole
A2	Top	16.85 ± 2.74	3.83 ± 0.90	7.53 ± 4.19
(near)	Middle			3.21 ± 2.15
	Bottom			1.44 ± 0.14
J11	Top	9.15 ± 7.60	1.86 ± 1.29	3.72 ± 1.93
(far)	Middle			4.10 ± 1.58
	Bottom			1.39 ± 0.65

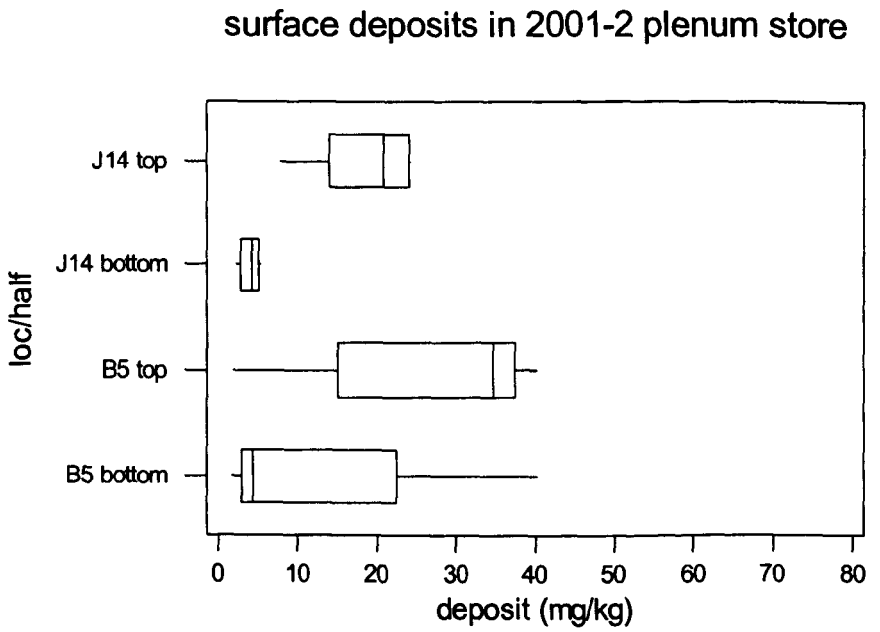


Figure 35 Boxplot showing chlorpropham deposits on top and bottom halves of tubers taken from the surface of top boxes in the 2001-2 plenum store

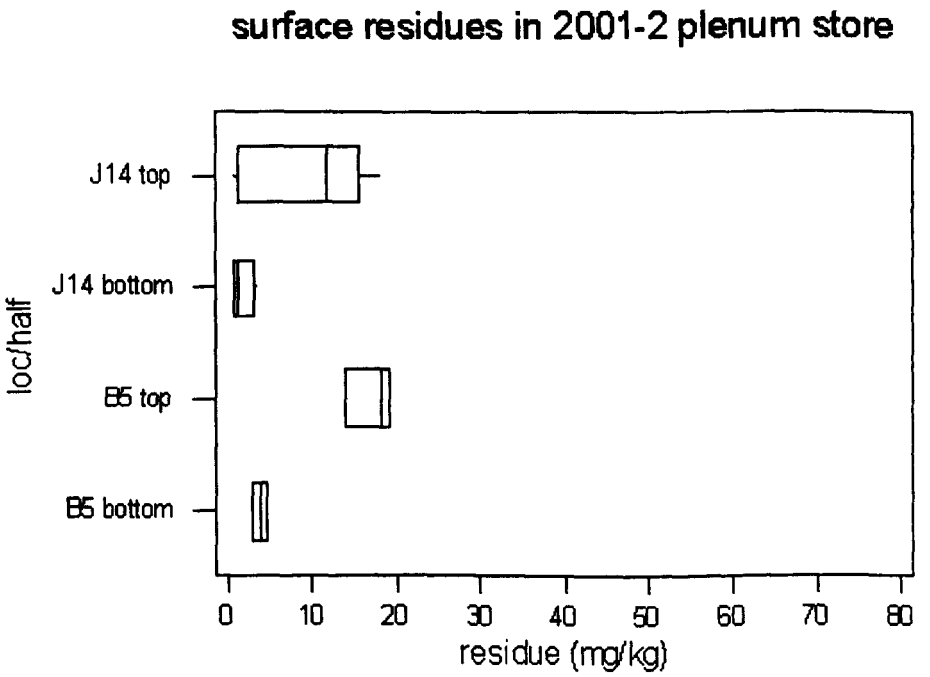


Figure 36 Boxplot showing chlorpropham residues in top and bottom halves of tubers taken from the surface of top boxes in the 2001-2 plenum store

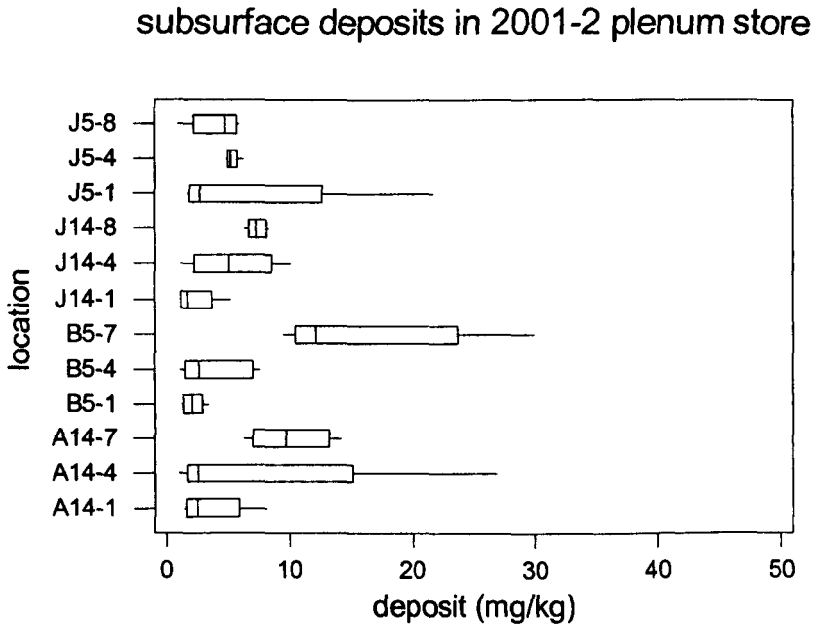


Figure 37 Boxplot showing chlorpropham deposits on tubers taken from ~20cm depth in top boxes in the 2001-2 plenum store

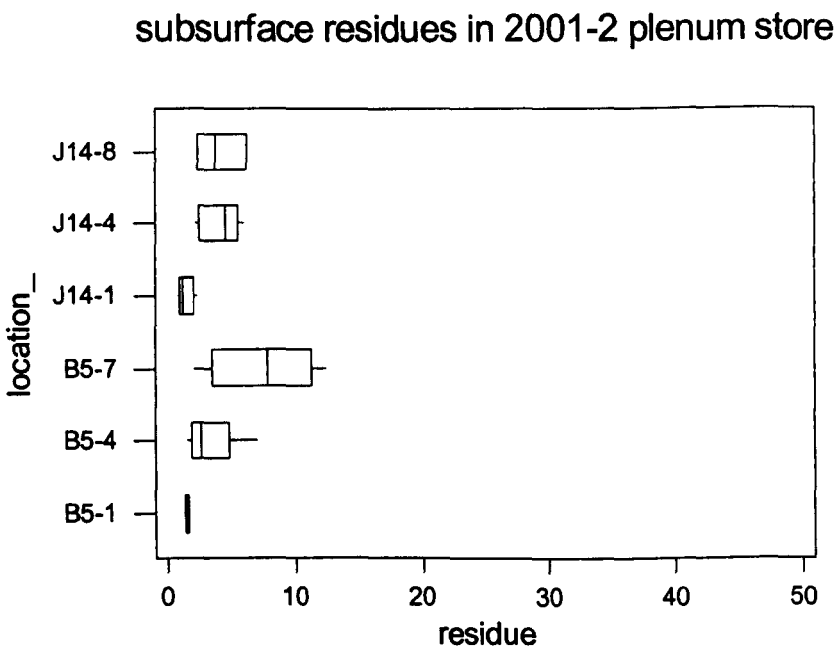


Figure 38 Boxplot showing chlorpropham residues in tubers taken from ~20cm depth in top boxes in the 2001-2 plenum store

Table 23 Minitab output for GLM carried out on surface data from 2001-2 plenum store

General Linear Model: 2001-2 plenum store surface samples

```
Factor                  Type Levels Values
location                fixed      2 B5  J14
half-p(location)        fixed      4 bottom top    bottom top
wash(location half-p)   fixed      8 unwashed washed   unwashed washed
                                     unwashed washed   unwashed washed

Analysis of Variance for CIPC (mg, using Adjusted SS for Tests

Source                  DF     Seq SS     Adj SS     Adj MS       F      P
location                 1     424.92     379.19     379.19    4.65  0.039
half-p(location)         2    1625.62    1658.09     829.05   10.16  0.000
wash(location half-p)    4     688.22     688.22     172.06    2.11  0.104
Error                   30    2447.87    2447.87      81.60
Total                   37    5186.63

Unusual Observations for CIPC (mg

Obs  CIPC (mg       Fit      SE Fit  Residual   St Resid
  5    1.9600   27.9400      4.0397  -25.9800     -3.22R
 13   40.3200   11.0100      4.0397   29.3100      3.63R
```

Table 24 Minitab output for GLM carried out on sub-surface data from the 2001-2 plenum store

General Linear Model: 2001-2 plenum store sub-surface samples

```
Factor                  Type Levels Values
column                  fixed      4 A14 B5  J14 J5
Height(column)          fixed     12 bottom middle top    bottom middle top
                                     bottom middle top    bottom middle top
wash(column Height)     fixed     18 unwashed unwashed unwashed unwashed
washed
                                     unwashed washed   unwashed washed
unwashed
                                     washed   unwashed washed   unwashed
washed
                                     unwashed unwashed unwashed

Analysis of Variance for CIPC (mg, using Adjusted SS for Tests

Source                  DF     Seq SS     Adj SS     Adj MS       F      P
column                   3      63.83      78.67      26.22    1.33  0.271
Height(column)           8     773.30     702.43      87.80    4.46  0.000
wash(column Height)      6     188.28     188.28      31.38    1.59  0.163
Error                   67    1319.38    1319.38      19.69
Total                   84    2344.78

Unusual Observations for CIPC (mg

Obs  CIPC (mg       Fit      SE Fit  Residual   St Resid
  1   29.8800   16.0380      1.9846   13.8420      3.49R
 67   26.8900    7.2520      1.9846   19.6380      4.95R
 86   21.6200    6.3040      1.9846   15.3160      3.86R
```

3.6.5 Discussion

Constructing the artificial plenum across the main alley in the store was intended to present a physical barrier to the upward movement of fog, and to promote the lateral spread of chemical through the boxes. Not all gaps between columns of boxes were covered, and as a result some accumulation of fog at the top of the store was anticipated. Nevertheless, the pattern of distribution in this store was very different from the previous three studies.

3.6.5.1 Surface samples

None of the very high deposits (up to 80 mg kg^{-1}) found in the previous studies were seen in this store. This suggests that the influence of particle deposition has been reduced. However, the amount of chemical reaching top halves is still significantly higher ($p = 0.000$) than that reaching the bottom halves, so chemical settling out from above is still having an effect. Since crop in top boxes is most likely to cause concern in terms of MRL/ADI requirements following conventional application, this can be considered a significant improvement.

Although the plenum was constructed by covering the alleyway with polythene sheeting, gaps between columns of boxes were not covered. As a result, once fog was introduced into the plenum, a substantial proportion may have taken the easiest route and moved out into the body of the store through the gap between columns 3 and 4.

B5 is located at the end of the store where the application was made, but at the far side of the 10 columns of boxes (i.e. the fog had to pass through 9 columns to reach it) and deposit levels there are higher and more variable than at position J14. For more chemical to reach B5 than J14 (the first column of boxes at the far end of the plenum) suggests that the fog does not travel evenly along the length of the plenum, and that a significant proportion moves out into the main stack of boxes through the gaps between the first few. Because of the large amount of force used to generate the fog, it tends to accumulate at the far side of the store, creating higher and more variable deposits as the larger particles settle out. This effect results in a statistically significant difference between the 2 surface sample locations ($p = 0.039$).

Washing surface tubers causes no significant reduction in chemical levels ($p = 0.104$), although the large variability seen in deposits (particularly at position B5) is reduced.

3.6.5.2 Sub-surface samples

Deposit values for the four sampled locations, particularly in middle and bottom boxes, are higher and show more variability than in the two studies from Season 2000-1, suggesting that modifying the way air moves around the store allows more chemical to reach crop within the boxes.

Residues from the two sampled locations, particularly in middle and bottom boxes, are higher than in the earlier studies, which means impaired efficacy in this part of the store is less likely to be a problem. Although there is still a significant height effect ($p = 0.000$) it is less pronounced than in previous studies. Even though the distribution of chemical is still uneven, this trial has succeeded in altering the pattern of deposition. The higher deposits and residues suggest that the proportion of chemical actually reaching the crop has been increased relative to the industry standard control.

At the sub-surface level, no statistical difference was found between the 4 locations sampled ($p = 0.271$). Excluding surface effects in the top box, chlorpropham appears to be more evenly distributed around the body of the store when applied via the plenum.

No significant reduction in chemical level was seen following washing ($p = 0.163$), but variability was reduced considerably. Since light washing will only remove any particles sitting on the surface of the tuber, or those held on the associated soil, this effect was expected. In this store, the impact of particle settlement has been reduced, so it is less likely that washing will remove a large amount from the tubers.

3.6.5.3 Estimation of deposition efficiency

The same model of the store was used as in the other 3 stores to estimate the amount of applied chemical reaching crop in this store, even though the distribution pattern was significantly different here. Deposit (unwashed) data were used in the model because it gives the most useful picture of the way the chemical was spread around the store. Because four locations were sampled for deposits (as opposed to two for residues), the mean value calculated is more likely to be representative of the store as a whole.

Top boxes were considered to be different to all others because they are affected by significant particle deposition from above. Location differences were assumed to be negligible for the purposes of this calculation. A mean CIPC deposit in top boxes was

calculated using all the data (top and bottom halves and whole tuber data) to be 11.42 mg kg^{-1}.

All other boxes were considered as being the same, though different from the top boxes. Again, location effects were assumed to be negligible. A mean deposit level of 4.48ppm was calculated from middle and bottom box data at the four locations.

The tonnage in the store at the time of application was 1,457 tonnes (from Figure 34). There were 187 top boxes, and 1,270 others. At a dose rate of 18 grams per tonne, 26.23 kg of CIPC was applied into the store. The proportion recovered on the crop was estimated to be

- 187 tonnes * 11.42 mg kg^{-1} = 2.136 kg
- 1,270 tonnes * 4.48 mg kg^{-1} = 5.690 kg

Thus, 7.826 kg is assumed to be present on the crop, which amounts to **29.8%** of the total applied.

This is a significant improvement on the 16% recovery calculated following conventional application (see 2000-1 control store). This improvement can be attributed to preventing the accumulation of fog in the roof space of the store, which may increase the amount of chemical reaching the crop by a combination of two processes. Forcing the fog to pass through the boxes means that the chemical can be deposited on the crop before reaching the free air volume, reducing the concentration of chemical in the fog when it reaches the headspace.

Leakage of chemical from the store may also be reduced if the fog is kept at low level within the store, meaning more chemical is left in the store at the end of the application. As fog is introduced to the store, an equal volume of gas must be lost through louvres and vents to prevent the store becoming pressurised. Under ideal conditions, only air from the store would be lost, and the entire volume of fog would remain in the store. In reality, what is lost from the store is a mixture of air and fog. Most escapes through the eaves and vents at the top of the store, so keeping the fog at a low level in the store for as long as possible should mean that more air is lost and less fog. Leakage during application is accepted as being a significant loss from store, if not the most significant loss, so the more that can be kept within the store until the application is complete, the more chance of it depositing on

the crop. In addition to the improvement in terms of efficacy of treatment, environmental contamination is also minimised.

Keeping more chemical inside the store means that chemical residues on crop may increase. However, if the effectiveness of application can be improved and losses reduced, it may be possible to reduce either the number of repeat applications or the application rate necessary to maintain sprout control. It is important to note that the deposit and residue levels quoted in this chapter were calculated on samples taken 24 hours post-application. Over time, re-distribution of chemical may occur through volatilisation and the levels on crop can reduce [Lentza-Rizos and Balokas (2001)]. However, an adequate concentration must be maintained in the tuber or sprout control will be compromised.

3.7 Summary of findings from three years' distribution trials

Conventional application of CIPC as a thermal fog

- results in large deposits on top box crop, particularly at the opposite end of the store from the application port. These effects are related to the properties of the fog (i.e. high temperature, particle size) and the excessive force used to propel the chemical into store.

- The amount of chemical penetrating into boxes near the bottom of the store is low.

- Losses through leakage during application are high, and the amount of chemical actually recovered on the crop is low (~20%). The whereabouts of the remainder of the chlorpropham applied has not been determined.

Modified applications

- Small alterations to the pattern of air movement in the store can affect the way in which the chemical is distributed around the store.

- The use of small fans to generate a slow movement of air (gentle stirring as opposed to forceful blowing) can help get chemical to the more difficult to reach boxes by keeping fog mobile for longer.

- Forceful movement of air can cause condensation onto the surface of the boxes and gross contamination of affected crop.

- Preventing the accumulation of fog at the top of the store (using either physical barriers or by altering patterns of air movement) can reduce the effect of particle settling on top boxes and encourage the fog to move through boxes rather than circulating around them.

- More of the applied chemical is recovered on the crop following modified applications, as shown by the estimates of deposition efficiency.

- In spite of the small improvements seen, there are still significant differences between boxes at different heights in each store. These are attributed to the properties of the fog itself, and as a result might be very difficult to eliminate without completely revising the method of application.

- Keeping the fog at low level in the store may reduce the amount lost through leakage during application, resulting in more effective application. Environmental pollution is also kept to a minimum if the fog can be contained within the store.

- Increasing the volume of free air space in the store may also reduce losses during application and result in higher levels of chemical on the crop.

Chemical levels on crop

- The samples in these studies were collected 24 hours post-application, and as such can be considered to represent a worst-case scenario in terms of both chemical levels on crop and also any distribution differences between locations.

- Over time, re-distribution of chemical through volatilisation can reduce levels on crop and also minimise any differences between different locations in the store.

- The sampling time in these studies was deliberately selected to provide the greatest chance of locating and understanding any differences and the processes responsible.

- In terms of Acceptable Daily Intake, >90% of the CIPC residue has been shown to be removed by peeling, so assuming this level of preparation prior to consumption exposure should not exceed guideline levels.

The effect of washing

- Washing can remove significant amounts of chemical deposited on crop, but its effectiveness is dependent on a number of factors.

- In these studies, the effect of washing may have been masked as a result of the way in which samples were collected and prepared for analysis.

- Sub-sampling 30g from a whole tuber (as compared with a half or quarter tuber as in early work) will provide a more representative result and reduce any bias created by uneven distribution of chlorpropham over the tuber surface.

- >90% of the applied chemical remains on the skin, so perhaps extracting and analysing the whole peel and calculating back to a whole tuber concentration would be a better approach. However, this would rely on a number of assumptions i.e. that the peel to tuber weight ratio is the same in all cases, and that a defined percentage of the CIPC penetrates the flesh (e.g. 5%) in all cases. A representative sub-sample of the individual tuber should be the most reliable method, assuming a representative sample can be obtained.

Chapter 4

DETERMINATION OF CIPC IN AIR

4.1 Introduction

CIPC is applied to potato stores as a thermal 'fog' composed of fine particles a few microns in diameter. When introduced to the store, these particles rise (due to the high temperature of the fog) then gradually settle out under gravity. Once the fog has deposited (generally assumed to be within 24 hours of application) small amounts of CIPC remain in the air as vapour. Although not extremely volatile, measurable concentrations can be present in store air following application as a thermal fog.

For example, Boyd and Duncan (1986) reported concentrations in the range 0.3-1.3 $\mu g\ l^{-1}$ in a box potato store at the start of the storage season. Filmer and Land (1978) followed the concentration of various volatiles in potato store air over a period of 30 weeks, during which 4 applications of CIPC were made. The major component of the air samples was CIPC, the concentration of which accounted for 0.1% of the total chemical added after 2 applications. The measured concentration was always greatest immediately after an application, and gradually declined over time until the next application. Measured concentrations ranged from 0.01 $\mu g\ l^{-1}$ to 4.46 $\mu g\ l^{-1}$. Valange and Henriet (1973) quoted a saturated vapour pressure of $1*10^{-5}$ mm Hg at 25°C, equivalent to 0.12 $\mu g\ l^{-1}$. Boyd (1988) calculated the saturated vapour concentration of chlorpropham in air to be 0.54 $\mu g\ l^{-1}$ and 3.36$\mu g\ l^{-1}$ at 10°C and 25°C respectively. These figures were calculated using the vapour pressure measurement extrapolated from higher temperature and are thus liable to error. They also assume no interaction between the chlorpropham and the surface on which it is held. However, Coxon and Filmer (1985) determined the vapour pressure of chlorpropham adsorbed on filter paper to be $1*10^{-5}$mm Hg at 10°C, while the measured concentration was 15 times lower when the compound was applied to the surface of potatoes. They concluded that some adsorption of chemical onto the periderm must have occurred. Aleksandrova and Klisenko (1982) quoted the maximum vapour concentration of chlorpropham as 0.1$\mu g\ l^{-1}$ in air, and cautioned against other studies that may not have distinguished between tiny droplets or particles of dust and actual vapour molecules. Boyd (1988) also observed that fine particles trapped on Tenax columns during air sampling in dusty stores could greatly affect the measured concentration because the particles had adsorbed quantities of sprout suppressants applied in the store.

The presence of CIPC in air in potato stores is of interest for several reasons. Firstly, leakage during the application process can result in significant losses from the store. The degree of loss is dependent on a number of factors including the concentration of chemical in the fog, the 'leakiness' of the store, the rate of airflow from the fogger and the duration of the application. It is worth noting that loss at this point will be significant since CIPC is present in fog not only as vapour but also as discrete particles, and so the chemical concentration is likely to be in the mg/l range. Over an application period of approximately 1 hour, several kilograms of chlorpropham may be lost to the atmosphere. In addition to loss during application, routine venting and opening of doors throughout the storage season can result in losses of chlorpropham as vapour, although the concentration in air at this stage is only likely to be in the $\mu g\ l^{-1}$ range, meaning less chemical escape.

CIPC is active as a sprout suppressant in the vapour phase, although little is known about the minimum concentration required to have an effect. van Vliet and Sparenberg (1970) found that when cartridges impregnated with CIPC (located in air ducts) were used to treat crop instead of thermal fogging, sprout control and residue levels were broadly comparable to those found after conventional thermal fogging. Although they determined residue values on crop treated in this way, no measurement of the vapour concentration in air was made.

Following treatment with CIPC thermal fog, store fabric can become contaminated with chemical. This residue can volatilise back off affected surfaces and be found in the air several seasons after the last application, even after repeated cleaning and disinfections of the store. In stores where seed potatoes or other sensitive seeds and grain are held, this can result in problems with germination and growth. Where organically grown crop is held in previously treated stores, or transported in the same vehicles as CIPC treated material, there is concern that cross-contamination may result in uptake onto the crop. For example, measurable levels have been found in untreated potatoes held in new boxes at 3°C in a previously treated store [B. Coulson, personal communication]. Any detectable residues can result in rejection of crop and significant losses to the supplier.

The described studies were carried out in 12-tonne experimental stores at the BPC's Sutton Bridge Experimental Unit over a period of time from August 2001 to November 2002. The aim of the study was to investigate the concentration of chemical present in air over a range of temperatures. Several different methods of sample collection and analysis were used before a final protocol was developed.

4.2 Experimental methods

Experimental procedures common to a number of experiments will be described in this section, with more detail on individual experiments to follow in later sections.

4.2.1 Sample collection:

Air sampling pumps (Aircheck Sampler Model 224-PCXR8, SKC) were used to draw air through traps. Because these pumps are designed for monitoring the exposure of personnel to harmful compounds in air, they normally sample several litres of air per minute. To achieve the lower flow rates necessary in this work (100-500ml/minute) low-flow controllers were added online.

Two trapping mechanisms were employed in the course of the described work.

1.Solvent trap: Initially, CIPC was removed from air as it passed through a solvent trap. Methanol is a good solvent for CIPC (solutions of up to 75% CIPC in methanol can be achieved with ease) and is also suitable for injection into the GC. Both these factors were important in the selection of solvent for the trap. 25ml of HPLC grade methanol was used to fill the trap.

2. Adsorbent resin: In later work, air was pulled through a glass column packed with Tenax-GC resin. The use of this technique allowed sampling time to be reduced since a smaller sample volume was required.

4.2.2 Control of environmental factors

Control of the store environment was carried out using Cornerstone Systems Ltd hardware. Relative humidity was held at ~95%, and temperature maintained to within ±0.3°C of the set-point, which can be related to either crop or air temperature. Twelve temperature probes were located in the store: six recording air temperature, and six located inside tubers for crop temperature. There was no crop in the store other than the six probe tubers.

4.2.3 Preparation of samples and standards for analysis

After solvent samples arrived at Glasgow, the methanol was transferred to a flat-bottomed flask and the volume reduced to ~1ml on a rotary evaporator (Büchii, Switzerland). The sample was transferred to a 2ml volumetric flask and made up to volume with HPLC grade methanol. Samples were stored at 3-4°C until analysed.

A stock standard solution of 1000mg/l CIPC was prepared by dissolving the appropriate amount of CIPC in HPLC grade methanol. A range of standards of lower concentration were prepared by accurate dilution of the stock standard.

Tenax resin samples were stored at 3-4°C in the laboratory and analysed as received. For calibration of the GC, a standard containing 1000mg/l of both CIPC and 3-chloroaniline (3-CA) was prepared by dissolving appropriate amounts of each chemical in HPLC grade *n*-hexane. For calibration, a Tenax column was spiked with 1µl of this standard, which was then thermally desorbed on the GC.

4.2.4 Gas chromatography:

Quantification of CIPC was carried out by gas chromatography for both types of sample.

Solvent samples: A 5µl aliquot was injected into Pye Unicam PU4500 packed column gas chromatograph equipped with a column (1m length, 4mm i.d) packed with 3% OV-17 on Gaschrom-Q and a flame ionisation detector. The GC conditions are described below.

Temperatures:	Injector	220°C
	Column	180°C
	Detector	250°C
Gases	N_2 carrier	30ml/minute
	Flame H_2	30ml/min
	Flame air	180ml/min
Oven temperature:	180°C isothermal	

Tenax resin samples: Tenax precolumns were analysed by thermal desorption following the method of Boyd (1984). Quantification of CIPC was carried out on a Pye Unicam PU4500 gas chromatograph equipped with a 1m column (3% OV-17), flame ionisation detector and thermal desorption block. GC conditions were as follows:

Temperatures:	Injector:	220°C
	Detector:	250°C
	Desorption block:	240°C
Gases:	N_2 carrier	30ml/minute
	Flame H_2	30ml/minute
	Flame air	180ml/minute

Oven programme: 130°C for 7 minutes
12°C/minute to 180°C
Hold at 180°C for 5 minutes

An oven temperature programme was required to allow the separation and quantification of both 3-chloroaniline and CIPC in the samples: under standard operation conditions (180°C isothermal) 3-chloroaniline co-elutes with the solvent and cannot be distinguished on the chromatogram.

4.3 Collection of air from CIPC-treated stores using solvent traps located on the roof of the store

4.3.1 Sampling system

In August 2001, a combination of air sampling pumps and 10 litre aspirators was used to draw air from 6 experimental stores through methanol traps at flow rates of approximately 100ml/minute. Sampling time was 100 minutes, resulting in the collection of ~10 litres of air. Traps consisted of long-necked round-bottomed flasks, located on the roof of the stores, filled with 25ml HPLC grade methanol. Approximately 1m of PVC tubing was attached to the inlet of the trap to reach down into the store and collect the sample. Two filters were attached online before the trap – first a GF/C filter to remove larger particles, followed by a 0.45µm Acrodisc syringe filter (Pall Gelman) to ensure no particles reached the trap. Figure 39 overleaf illustrates the sampling system.

4.3.2 Store preparation

6 stores were sampled: 2 each at set-points of 6°C, 9°C and 12°C. An application of CIPC was carried out in the morning of Day 0 (Tuesday 28th August 2001) using a Swingfog applicator and MSS CIPC 50M at a dose rate of ~500ml/store. Two samples (A and B) were collected on the same day as the application (approximately 1-3 and 4-6 hours post application) and two more (C and D) on Day 1 (approximately 24-26 and 27-29 hours post-application).

4.3.3 Analysis:

Samples were prepared for analysis as detailed in section 4.2.3, then a 1µl aliquot was injected into a Hewlett-Packard 5890 gas chromatograph equipped with a 15m megabore column (DB1) and flame ionisation detector. The GC conditions were as follows:

Temperatures:	Injector	220°C
	Detector	250°C
	Oven	180°C isothermal

Gases:	N_2 make-up gas	30ml/min
	He carrier	
	Flame H_2	30ml/min
	Flame air	180ml/min

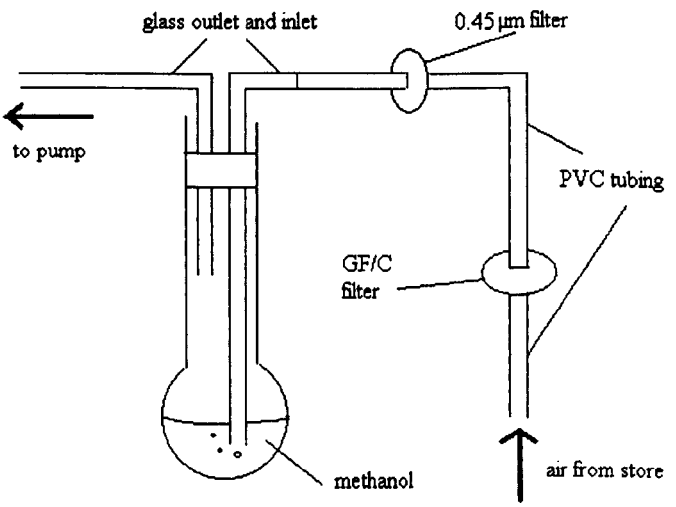


Figure 39 Schematic representation of first trapping system

4.3.4 Results and discussion:

No quantifiable chlorpropham was found in any of the samples from the methanol traps. However, the GF/C filters when soaked in methanol and analysed on the GC showed significant CIPC content, which decreased with increasing time since application.

Table 25 Weight of CIPC on GF/C filter after sample collection (µg)

Sample and time post-application (hr)	CIPC on filter paper (µg)					
	Store 31 (6°C)	Store 34 (6°C)	Store 32 (9°C)	Store 33 (9°C)	Store 35 (12°C)	Store 36 (12°C)
A (1-3 hours)	2537.5	2747.2	5318.2	5606.4	-	607.5
B (4-6 hours)	1451.7	353.2*	1065.8	-	465.2	79.3
C (24-26 hours)	16.0	8.4	55.9	7.5	8.2	39.3
D (27-29 hours)	4.1	ND	8.9	6.6	5.5	7.8

Particles of CIPC trapped on the filter paper during sampling result in the concentrations shown in the table above. That the amount of CIPC on the filters gets less the longer the time between application and sampling illustrates that in each store significant settling of fog particles occurs within a few hours. Although each set of results shows this effect clearly, none of the results can be used in any quantitative way, as there are likely to be significant variables not taken into account e.g. sorption onto the PVC tubing. Also, no replication of sampling was carried out. Determining concentrations in air where particles are present can be very difficult, as the presence of only one or two can significantly alter the result. What the results do suggest is that even >24 hours after application, some particles still remain in the air, which would affect any vapour phase measurement were the filters not present.

Following soaking in methanol, a sample of the PVC tubing was shown to contain significant CIPC. Initially, it was thought that the PVC had adsorbed all CIPC from the air, and that none reached the trap. However, considering the low concentrations reported by Boyd and Duncan (1986), it is likely that the amount of CIPC in a 10 litre sample of air is too low for quantitative analysis by this method, and that the presence of CIPC on the tubing is mainly due to particles landing on its surface.

4.4 Collection of air from CIPC-treated stores using re-designed solvent traps located inside the store

4.4.1 Sampling system

In September/October 2001, new traps were designed in an attempt to eliminate any problems caused by the length of PVC tubing required to reach into the stores. These traps were designed to fit through small ports (2.6cm diameter) in the roof of the store, to allow the tubing to be connected behind the traps i.e. to allow air to pass through the traps before reaching the tubing to remove any effect of sorption onto the plastic. Figure 40 below shows the design of the new traps. The inlet and outlet were re-designed to be vertical (rather than at 90° to the trap as in the conventional set-up) so the trap could fit fully through the 2.6cm diameter port. Traps were suspended from a cross-shaped support; long enough to bridge the open port, on 3 elastic strings to keep the weight balanced and ensure the trap remained upright during positioning, sampling and removal from the store. PVC tubing was attached to the outlet of the trap, fed through the port in the roof and connected to the pump situated on the roof of the store. Cling film was used to seal round all the equipment and minimise the amount of air leaking through the open port during sampling.

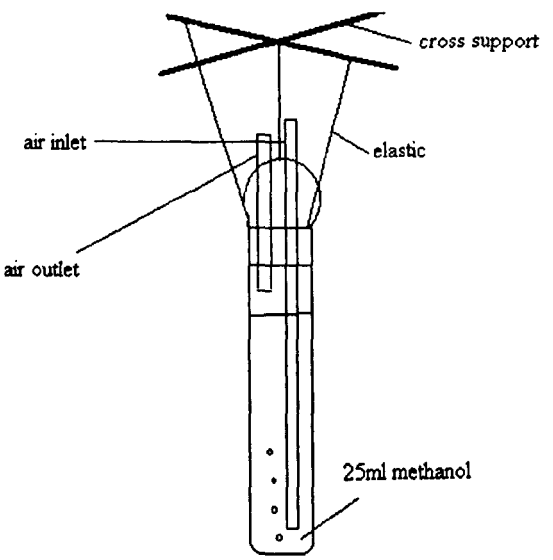


Figure 40 Trap designed to fit through 2.6cm diameter port in roof of stores.

In early November 2001, a set of samples were collected from one store at Sutton Bridge using the new design traps, and similar flow rates and sampling times as described previously.

4.4.2 Experimental methods

Samples were collected and prepared for analysis as outlined in Sections 4.2.1. and 4.2.3. Analysis by gas chromatography was carried out as described in Section 4.3.3.

4.4.3 Results and discussion:

Once again, no quantifiable CIPC was detected in any of the samples from the methanol traps.

Assuming levels in these experimental stores will be similar to those described previously for commercial stores, it may be that the volume of sample collected is too small for quantitative determination of CIPC. Boyd (1986) reported a highest concentration of CIPC in air in a commercial store of 1.39mg/m^3 at ambient temperature. The methanol traps will only contain a few μg of CIPC, and since a 5μl aliquot of the 2ml extract is used, only ~0.25% of the CIPC in the extract is introduced onto the GC column. The GC used for the analysis (H-P 5890 capillary GC with megabore column) was not optimised for this kind of analysis, and is not sensitive enough to detect very small quantities of chemical. The amount found in a 5μl aliquot will certainly be less than the limit of quantification under normal running conditions, and is probably close to the limit of detection. Although this experiment did not result in quantitative determination of CIPC, it did show that sorption onto the PVC tubing in the previous experiment was not (solely) responsible for the poor result, and demonstrates that the volume of air sampled needs to be increased to achieve a reliable result.

Once the results of the previous set of samples were known, another sample was collected by Ajay Jina (BPC Sutton Bridge) at a flow rate of ~100ml/minute for ~960 minutes. This sample gave a quantifiable concentration of 1.5μg/ml in the 2ml extract, or 0.03μg l^{-1} in the store air. However, significant evaporation of the methanol in the trap had occurred during sample collection, and the final volume in the trap as returned to Glasgow was ~10ml.

In the laboratory, a small study was conducted to determine the rate of evaporation of methanol at different flow rates for sampling times up to 3 hours. It was anticipated that sampling air at a rate of 500ml/minute for 180 minutes would allow quantitative determination of CIPC in the 2ml extract. At 500ml/minute at room temperature in the laboratory, evaporation occurred at a rate of ~5ml/hour. Evaporation will increase with air temperature, but since store temperature is assumed to be lower than ambient room

temperature this value represents a worst-case estimate. The redesigned traps hold 25ml methanol, so after 3 hours sampling, at least 10ml will remain. Since the traps were designed to be tall and narrow, air will still bubble through the solvent even when only 10ml is left. During the following study it was recommended that the traps were topped up every 3 hours if longer sampling times were required.

4.5 In-store sampling over a range of temperatures from 2-12°C

The next stage of the study was to examine the vapour phase concentration of CIPC in air over a range of temperatures. This work was again carried out in experimental 12-tonne stores (Stores 33, 34 and 36). The rate of sample collection was increased from 100ml/minute in the previous work to ~500ml/minute. Sample times varied from 300 minutes at the lowest temperatures to 180 minutes at higher set points. Sample collection and changes to set points were carried out in all 3 stores simultaneously to minimise the influence of any external factors.

4.5.1 Store preparation:

An application of CIPC was carried out in each store on Thursday 15th November 2001 as part of another study. After stores were emptied (24 hours post-application), they were sealed with the kickplates in place and set for 2.5°C. None of the stores were expected to reach this by the time sampling began on the following Monday, but they were set in order to achieve the lowest possible temperature.

Store temperature control systems (CornerStone) regulate air temperature (to within ±0.3°C of set-point) based on readings from probes inside the store. Set point can be based on air temperature or on readings from probes inside tubers. In order to bring the crop up to the desired temperature, air temperature must rise way above the set point, and will only begin to come slowly down once the crop is at the correct temperature and the fans come back on. Figure 41 overleaf shows the fluctuations in crop and air temperature while samples were being collected in Store 33 – the other 2 stores followed similar patterns. The fluctuations in air temperature got larger the higher the crop set point. One way of reducing this overshoot in air temperature would be to remove the tubers from the crop probes – this way, store temperature control will be based on air readings alone. In work like this, maintaining a stable air temperature is vital, as the concentration of CIPC in the air will fluctuate depending on it.

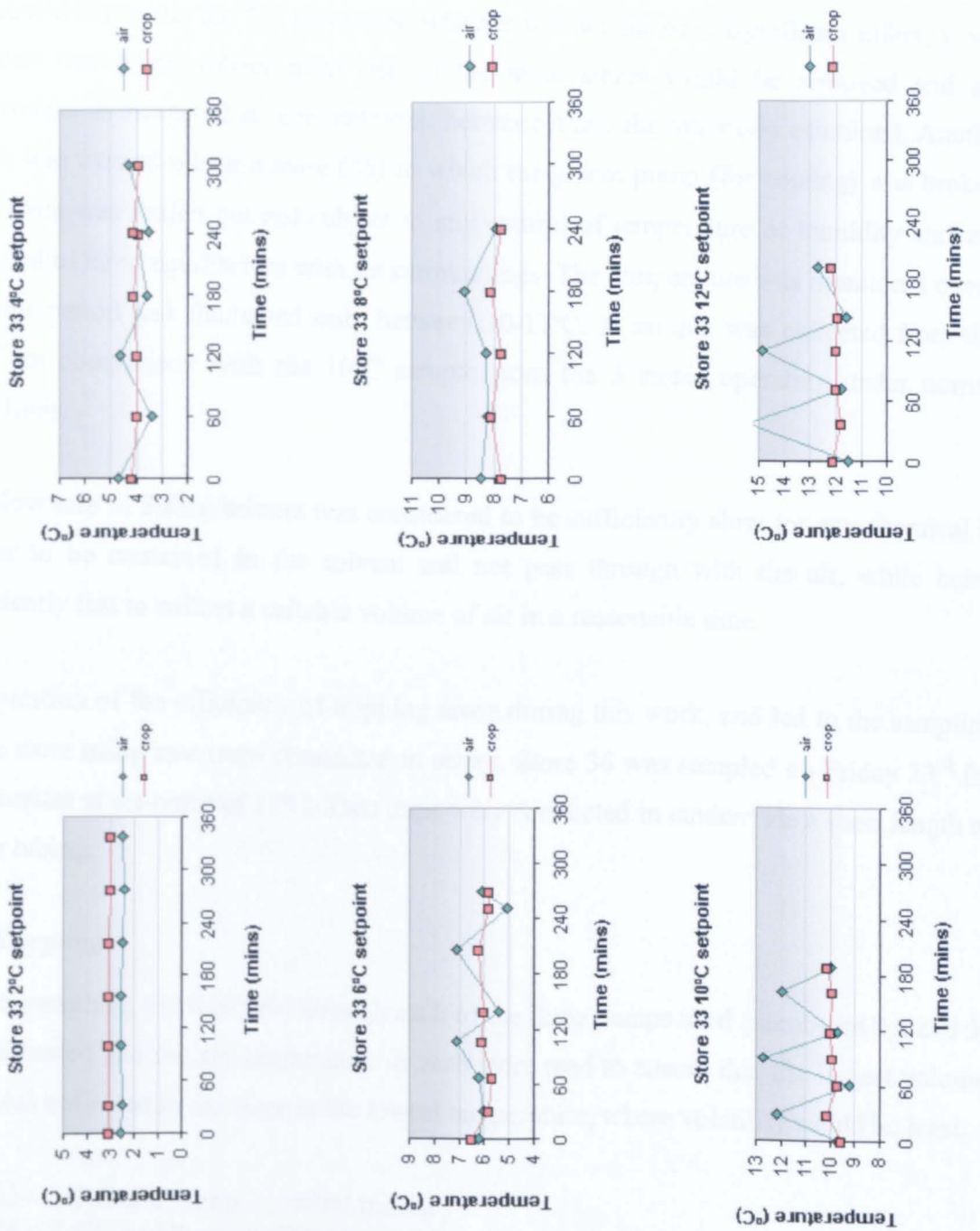


Figure 41 Crop and air temperature fluctuations in Store 33 with tubers attached to crop probes

However, if the tubers are removed from the crop probes, the fans and other store machinery will switch on and off more regularly to maintain temperature since there is no crop to buffer any changes. It is possible that condensation of CIPC may occur onto refrigeration coils that may be up to 2°C cooler than the air, resulting in a reduced vapour concentration in the air. To determine whether this would be a significant effect, it was decided that probe tubers from one of the three stores would be removed and any differences in measured air concentration between it and the other two examined. Another check was carried out in a store (35) in which the glycol pump (for cooling) was broken. This store was sealed but not subject to any control of temperature or humidity and was assumed to be in equilibrium with its surroundings. The temperature was monitored over a 48-hour period and fluctuated only between 10-11°C. A sample was collected from this store for comparison with the 10°C sample from the 3 stores operating under normal conditions.

The flow rate of 500ml/minute was considered to be sufficiently slow for any chemical in the air to be contained in the solvent and not pass through with the air, while being sufficiently fast to collect a suitable volume of air in a reasonable time.

The question of the efficiency of trapping arose during this work, and led to the sampling in one store using two traps connected in series. Store 36 was sampled on Friday 23rd for 121 minutes at set-point of 12°C. Two traps were connected in tandem via a short length of rubber tubing.

4.5.2 Sampling:

Prior to sampling, the flow rate through each of the three pumps used (numbered 2,4 and 5) was calibrated and the air temperature in each store read to ensure that the largest volume of air was collected in the store at the lowest temperature, where volatility would be least.

Store 33 – 2.6°C and Pump 2 (550ml/minute)
Store 34 – 2.8°C and Pump 4 (500ml/minute)
Store 36 – 1.9°C and Pump 5 (600ml/minute)

In each store both air and crop temperature were recorded and checked on a regular basis. In this experiment, the air temperature is much more relevant than crop temperature, although store control is based on crop measurements. Other parameters such as relative humidity are also controlled via the same system. During the experiments, probe tubers

were located in the store and the store control system (Cornerstone Systems Ltd) maintained their temperature to within ± 0.3°C.

At the lower temperatures (2.5°C and 4°C), sampling time was 300 minutes. Collection time was reduced as the temperature increased – a shorter sampling time was thought to be beneficial, as variations in temperature would be lessened. Where sampling took longer than 3 hours, pumps were run for 180 minutes then traps were checked and topped up with methanol if necessary, then left to run for the remainder of the sampling time. The rate of evaporation from traps was significantly less than observed in the laboratory, probably because of the lower air temperature in the store.

Samples were collected between Tuesday 20th November and Friday 23rd November 2001. Table 26 below gives details of the temperature set-point and sampling time for each samples, and the order in which they were collected.

Table 26 Temperature set-points and sampling times for each store, in chronological order

Date/time		Store 33	Store 34	Store 36	Store 35
Tues 20/11	am/pm	2.5°C 300 mins	2.5°C 300 mins	2.5°C 300 mins	
	overnight	4.0°C 240 mins	4.0°C 240 mins	4.0°C 240 mins	
Wed 21/11	am	4.0°C 60 mins	4.0°C 60 mins	4.0°C 60 mins	
	pm	6.0°C 240 mins	6.0°C pump stopped	6.0°C 240 mins	
	overnight	8.0°C 240 mins	6.0°C 240 mins	8.0°C 240 mins	
Thurs 22/11	am	10°C 180 mins	8°C 240 mins	10.0°C 180 mins	
	pm	12.0°C 180 mins		12.0°C 180 mins	
	overnight		10°C pump stopped		10°C 180 mins
Fri 23/11	am			12.0°C series 121 mins	

There were a number of practical problems during sampling. In Store 34, the pump collecting the 6°C sample stopped partway through, so this sample had to be repeated overnight. As a result, the stores were no longer all at the same temperature, so it was decided that probe tubers would not be removed from any store during this study in order to keep conditions as similar as possible.

4.5.3. Analysis:

The sample was prepared as described in Section 4.2.3, then 5µl was injected into a Pye Unicam PU4500 packed column (1.5m length 3mm i.d 3% OV-17 on Gaschrom Q) gas chromatograph equipped with a flame ionisation detector. Under the conditions described in Section 4.2.4, CIPC has a retention time of ~4 minutes on the column. Limits of quantification and detection are significantly better using the packed column gas chromatograph than with the capillary GC and megabore column. The concentration in air was calculated by dividing the weight of CIPC (µg) in the extract by the volume collected in litres.

4.5.4. Results:

Table 27 overleaf gives details of the samples collected at each set point in each store (33, 34, 35 and 36).

Figures 42 – 44 show the results of air sampling in stores 33, 34 and 36 over a range of temperatures from ~2°C to ~12°C. Points are plotted as the concentration (y-axis) vs the mean recorded air temperature (x-axis). Note that all graphs are plotted on the same scale. The mean temperature values are only approximate, and are based on readings taken at regular intervals during the sampling.

Figure 45 shows the data from all stores plotted together on the same graph.

Table 27 Details of air samples collected in stores 33, 34 and 36 (16th-23rd November 2001)

Store and set-point (°C)	Mean temperature (°C)	Flow rate (l/min)	Sampling time (min)	Sample volume (l)	Weight CIPC (µg)	Concentration in air (µg l^{-1})
Store 33 2°C	2.5	0.55	300	165.00	3.94	0.024
Store 34 2°C	2.8	0.60	300	180.00	5.43	0.030
Store 36 2°C	2.8	0.50	300	150.00	4.08	0.027
Store 33 4°C	4.0	0.55	300	165.00	5.80	0.035
Store 36 4°C	3.6	0.50	300	150.00	6.16	0.041
Store 33 6°C	6.1	0.55	240	132.00	9.06	0.069
Store 34 6°C	6.0	0.60	240	144.00	12.92	0.090
Store 36 6°C	6.0	0.50	240	120.00	10.48	0.087
Store 33 8°C	8.4	0.55	240	132.00	10.04	0.076
Store 34 8°C	7.6	0.60	240	144.00	17.10	0.119
Store 36 8°C	7.6	0.50	240	120.00	8.92	0.074
Store 33 10°C	10.8	0.55	180	99.00	10.06	0.102
Store 36 10°C	10.5	0.50	180	90.00	8.08	0.090
Store 33 12°C	13.0	0.55	180	99.00	13.98	0.141
Store 36 12°C	12.6	0.50	180	90.00	10.48	0.116
Store 35 10°C (store off)	10.6	0.50	180	90.00	7.83	0.087
Store 36 12°C (series)	12.1	0.55	121	66.55	4.51	0.068 (<LOD in Trap 2)

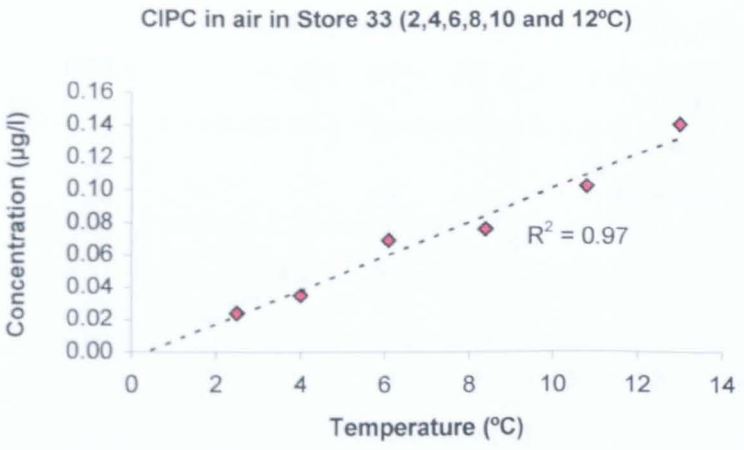


Figure 42 Concentrations of CIPC in samples of air from Store 33

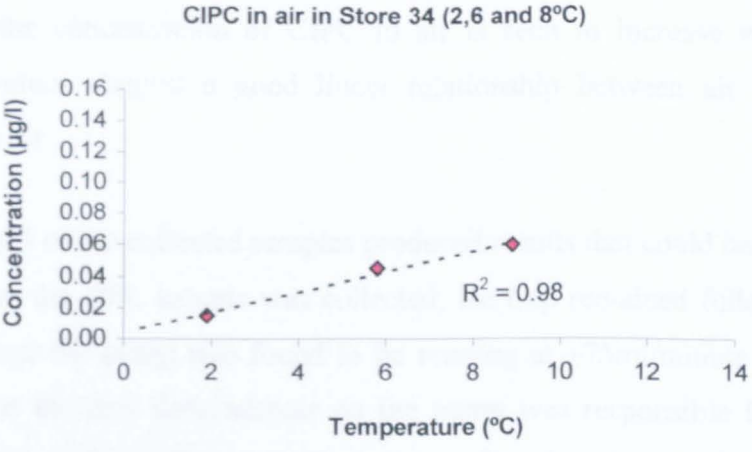


Figure 43 Concentrations of CIPC in samples of air from Store 34

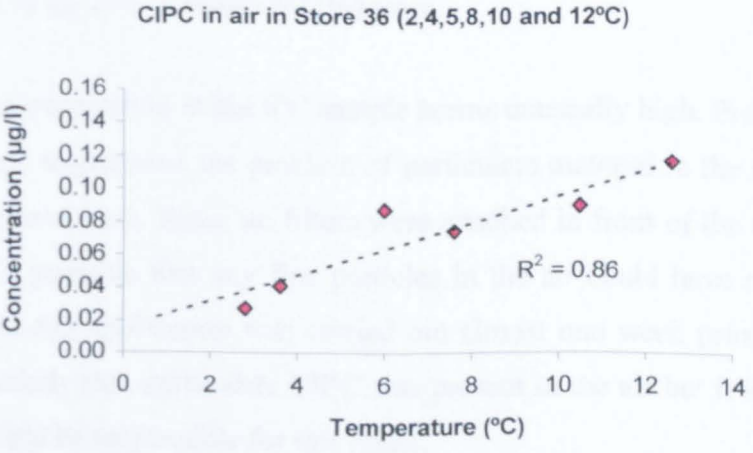


Figure 44 Concentrations of CIPC in samples of air from Store 36

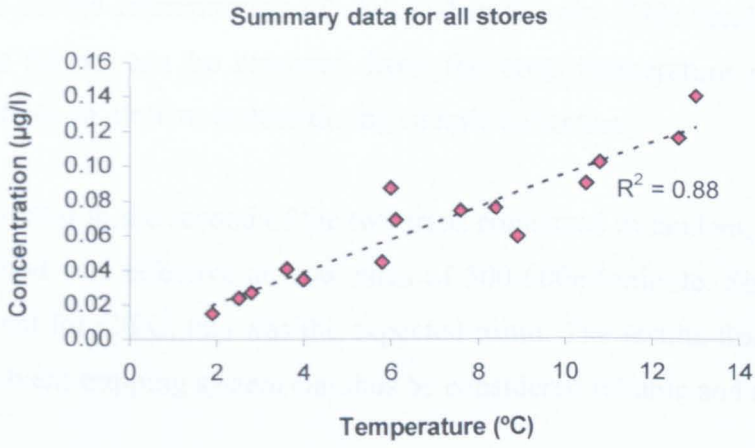


Figure 45 Calculated CIPC concentrations in all air samples from all stores

4.5.5. Discussion:

In each store, the concentration of CIPC in air is seen to increase with temperature. Calculated r^2 values suggest a good linear relationship between air temperature and concentration in air.

In Store 34, only 3 of the collected samples produced results that could be plotted with any confidence. After the 10°C sample was collected, the trap remained fuller than expected, and when checked the pump was found to be running at ~75ml/minute with no load. It seems likely that the low flow adapter on the pump was responsible for the problems experienced in this store. In retrospect, the volume of methanol remaining in the trap after collection at 4°C was more than usual, suggesting a problem during collection of this sample. On analysis, no CIPC was detected in the methanol. Since this store was running at 2°C less than the others (due to the repeat 6°C sample) no 12°C was collected within the time available, leaving only 3 results for this store.

In Store 36, the concentration in the 6°C sample seems unusually high. Previous discussion in this chapter has highlighted the problem of particulate material in the air and its effect on perceived concentration. Since no filters were attached in front of the traps in this part of the study, it is possible that any fine particles in the air could have reached the trap. Since the thermal fog application was carried out almost one week prior to the affected samples, it is unlikely that particulate CIPC was present in the air but it is possible that a single particle could be responsible for this result.

The result from Store 35 at ~10°C was comparable with other stores at similar temperatures, suggesting that the switching on/off of store machinery does not have any

significant effect on the concentration of chemical in the air. This result means that, in future work, the tubers can be removed from the crop temperature probes in order minimise fluctuations in air temperature during sample collection.

No CIPC was detected in the second of the two traps connected in tandem, confirming that the trapping method was effective at flow rates of 500-600ml/minute. Since methanol is such a good solvent for CIPC, this was the expected result. The results from the described studies using a solvent trapping system can thus be considered reliable and accurate.

4.6 Collection of headspace samples on adsorbent resin traps and analysis by thermal desorption – method development

4.6.1 Background

In previous studies carried out in this project, headspace samples have been collected in solvent traps, and concentrated up prior to analysis. This technique requires that a large volume of air is sampled at a reasonably slow flow rate (to ensure efficient trapping), resulting in long sampling times. Although this technique has worked well to date, lower volume trapping techniques are highly desirable to allow better control of variables such as air temperature and associated chemical volatility. In addition, the rate at which CIPC concentration builds up in air at different temperatures is of great interest in this work, so a method in which the samples are collected in a shorter time was devised, based on the method of Boyd (1984).

In this method, thermal desorption is used to flush CIPC off adsorbent resin traps onto a GC column for direct analysis. Air is sampled onto glass precolumns packed with adsorbent resin (Tenax GC) to pre-concentrate the sample. This precolumn is then directly coupled to the top of a GC column, and flash heated to 240°C to volatilise the trapped CIPC, which is then flushed onto the column by the N_2 carrier gas. The major advantage of this technique is that all the collected CIPC is introduced onto the column at the same time, in contrast to collection in solvent or solvent elution from a solid where only a small percentage of the chemical is injected in a small aliquot of sample e.g. for a 2ml extract where 5µl is injected onto the GC, only 0.25% of the chemical is analysed, meaning the concentration needs to be 400 times higher to achieve the same limits of quantification and detection.

Tenax-GC is a porous polymer [poly (p-2,6diphenylphenyleneoxide)] whose properties and characteristics make it suitable for the trapping of headspace volatiles: its high thermal stability [Sakodynskii *et al* (1974)] means it can be conditioned and desorbed at high temperature with no adverse effects. It has no affinity for water [Russell (1975)], the presence of which could complicate the analysis of samples by GC. It can be reconditioned up to 15 times with no significant decrease in trapping efficiency, and stored for up to 3 weeks with no significant loss of adsorbed compounds [Pellizzari *et al* (1976)]. The breakthrough volume and collection efficiency is unaffected by environmental conditions such as humidity [Pellizzari *et al* (1976)].

Boyd (1984) devised the thermal desorption technique on which this method is based, and carried out several studies to determine the optimum conditions. He compared thermal desorption of CIPC with direct injection of the same amount, and concluded there was no significant difference between the two techniques. In his work, 99.8% of CIPC was eluted from the precolumn in the first 4 minutes of heating at 230°C. Although it was originally thought advantageous to couple the end through which the air was drawn onto the top of the GC column, his work showed that the orientation of the precolumn made no difference to the result. His investigation into the storage life of sampled columns concluded that they could be stored for up to 5 days without appreciable loss of chemical.

4.6.2. Preparation of Tenax precolumn traps:

Glass tubes (6mm o.d, 3mm i.d, 105mm length) were rinsed with acetone then toluene, then immersed in a 5% solution of hexamethyldisilazane (HMDS) in toluene for 15 minutes to deactivate any bonding sites on the glass and prevent CIPC sorption onto the glass. On removal from the solution, tubes were rinsed with toluene, then acetone and dried in the oven at 100°C for 15 minutes.

Once cool, a 2cm bed length of Tenax GC resin was packed into each tube between two silanised glass wool plugs. Once packed, tubes were conditioned under a flow of N_2 (~30ml/min) at high temperature (~300°C) in a specially constructed aluminium heating block for a minimum of 2 hours to remove any sorbed volatiles or other impurities. The precolumns were allowed to cool under N_2 once removed from the block, then sealed with PTFE tape and aluminium foil. Boyd (1984) showed that conditioned columns could be stored for up to 7 days at 20°C prior to use with no significant accumulation of background volatiles. After sampling, tubes could be kept for up to 5 days in the fridge with no appreciable loss of sampled volatiles.

In this work, precolumns were stored in the fridge (3-4°C) after conditioning and used within a few days. Samples were desorbed as soon as practicable after sample collection, normally within 3 days, to prevent accumulation of interferences or loss of sampled volatiles.

4.6.3. GC method development:

Thermal desorption of resin traps cannot be carried out via the standard injection system on a gas chromatograph, and can require significant modification to the existing system. Boyd

(1984) employed several mechanisms including a heated switching valve before settling on a high-temperature desorption block directly coupled to the top of the GC column.

In the described work, a Pye Unicam PU4500 packed column GC was used, with an aluminium desorption block attached to the front of the column. To achieve this, modifications had to be carried out to the conventional injector port. Figures 46 and 47 below show schematic representations of both the normal injector system for conventional analysis by sample injection, and the modified injector employed for thermal desorption on the gas chromatograph used in this work.

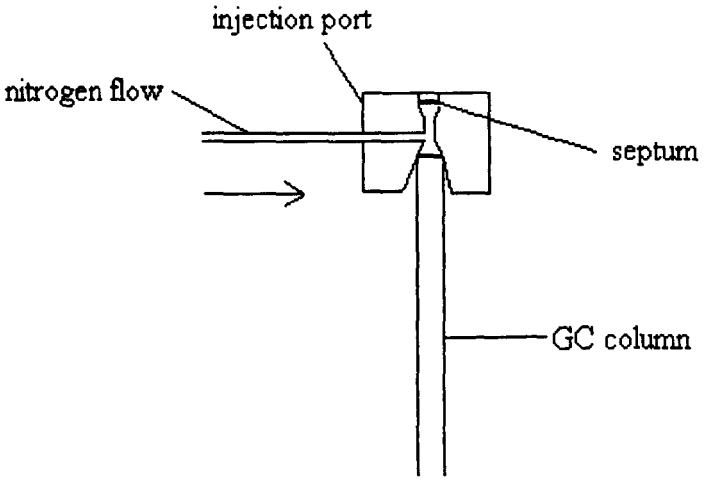


Figure 46 Schematic representation of a conventional injector system for gas chromatography

In the conventional system, the top of the injector fitting is a solid metal disc with a small hole drilled through to allow the introduction of the syringe during sample injection. To prevent leakage of N_2 carrier a Teflon lined septum is fitted on top of the disc to maintain a gas-tight seal.

In order to accommodate the heating block and the Tenax precolumn coupling to the front of the GC, the injector port had to be drilled out.

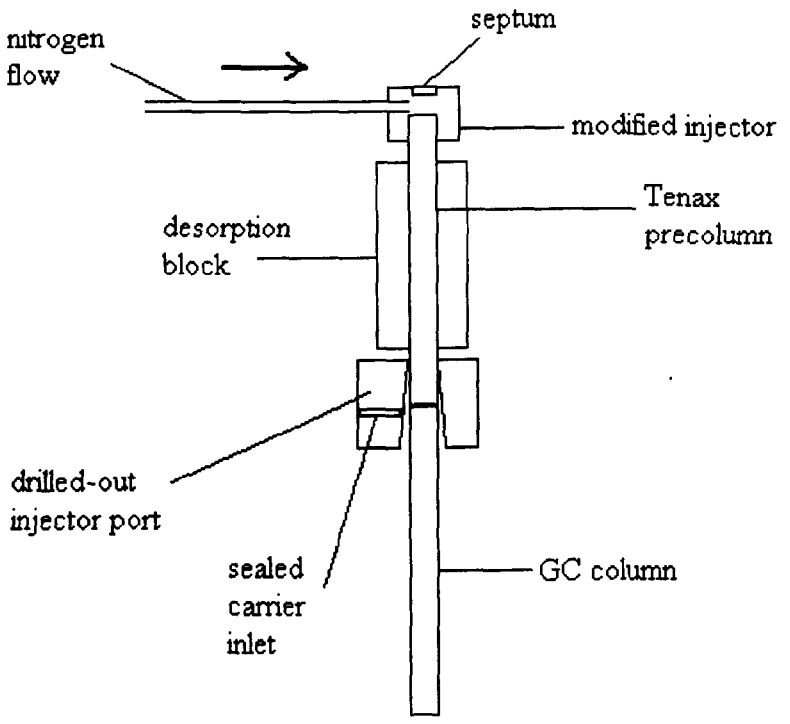


Figure 47 Schematic representation of the modified injector system for thermal desorption

In our modified system, this disc was drilled out to allow the precolumn to butt directly onto the GC column. Both the GC column and the precolumn are held in place with ¼ inch couplings and rubber O-rings. The inlet for N_2 carrier in the original injector fitting was sealed off, and a new gas inlet was attached to the modified injector port connected to the top of the precolumn. Thus the carrier gas is introduced at the top of the sample precolumn and flows through it to reach the GC column.

Sample precolumns are attached directly onto the top of the GC column for desorption, so the N_2 carrier must be switched off to allow change over. This operation must be carried out as quickly as possible (ideally in less than 30 seconds) to prevent damage to the column, as stripping of the column coating will occur at high temperature with no carrier gas flow.

Once the modified injector was installed and the desorption block attached at the front of the GC, it was found that there was not enough length of precolumn at either end of the heating block to allow connection and disconnection of the N_2 flow. Three possible solutions were suggested to get around this problem:

1. The outer lid of the GC could be removed to create more working space near the injection port.

2. Extra length could be added to the front of the GC column so that it would reach further up inside the drilled out fitting, meaning less of the length of the precolumn is inside the fitting and more is left for working with during connection to the gas supply.

3. Longer lengths of 6mm glass could be used for the Tenax traps (current length ~105mm), leaving more length exposed at either end of the desorption block.

Removing the lid was discounted as unsafe since permanently removing the lid would leave electrical connections exposed. Lengthening the traps was also rejected as it was felt the length of the glass tubes was already optimised: any longer and there may problems associated with cold spots on the glass and condensation of chemical.

It was decided that adding a 0.5cm length of precision glass (1/4 inch o.d) to the front of the column was the best way around the problem. However, when this column was tried it did not fit because the injector fitting is slightly tapered to prevent the column being inserted above the N_2 inlet during normal use (see Figure 47). A new column was constructed whose length was increased by adding 0.5cm of 6mm o.d glass to the injector end. This column was packed with 3% Silicone OV-17 on Chromosorb WHP 100-120 mesh and conditioned with N_2 prior to connection to detector. Once installed in the GC, the column was connected to the N_2 gas flow via an empty 6mm glass precolumn.

Once the system was completely installed, aliquots of hexane were injected to evaluate the response when run under normal operating conditions. Routine CIPC analysis is carried out at an oven temperature of 180°C, but in this study the temperature was lowered to 150°C to allow determination of 3-chloroaniline (3CA) as well as CIPC – at 180°C, 3CA co-elutes with the solvent and cannot be quantified. It is possible that 3CA might be present as a result of thermal breakdown of CIPC, so it was considered important to be able to detect it.

Oven temperature:		150°C
Injector temperature:		220°C
Detector temperature:		250°C
Gas flows:	N_2 carrier	30 ml/minute
	Flame H_2	30 ml/minute

Flame air 180 ml/minute

The desorption block was maintained at 230°C, as recommended by Boyd (1984).

The resulting chromatogram showed a very wide, tailing solvent front. When standards of CIPC and 3-chloroaniline (a breakdown product of CIPC) in hexane were injected, they showed the same wide solvent front but no peak for CIPC or 3-chloroaniline. There are a number of possible explanations for this response, so troubleshooting was carried out to eliminate each component of the system in turn:

1. *Detector:* The detector was cleaned – resulted in no improvement in response

2. *Combustion gases:* A blockage was found in the air line and rectified. Still no improvement in response.

3. *Column packing material:* Since the extended column had been packed with OV-17 from a new batch, it was replaced with another from the same GC to determine whether the problem was due to the packing material. Still no improvement in response.

4. *Injector volume:* to determine whether the extra volume of the empty glass precolumn (connecting the gas flow to the column) was allowing the sample to expand into too large a volume, another precolumn was packed with 3% OV-17 to remove most of the empty space. The system still produced a wide solvent front, and no peak for CIPC

5. *Flow rates of carrier and combustion gases:* All couplings were checked for leaks but none were found. The flow rates for all 3 gases were checked – no problems found. H_2 and air flows were increased, and a new peak (assumed to be 3CA) appeared at RT ~3.5 minutes. Peak shape was poor – very small and wide.

6. *Connections at modified injector:* The block and modified injection port were replaced with a conventional injector, all joins tested for leaks and carrier flow measured. No obvious problems were found. Because the modified column is extended by 0.5cm, when the conventional injector is in place it cannot be fitted in the oven and connected to the detector without placing the glass under considerable strain. Flow rates were measured by attaching the flow meter directly to the back end of the column.

7. *Modified injector and/or column packing*: The column was replaced with another standard length column packed with 3% OV-17 and returned to the original injector. The system produced good sharp peaks for 3-CA and CIPC, so the injector was ruled out as the cause of the problems.

8. *Oven temperature programming:* With the modified injector and heating block re-attached, the oven temperature was increased to 180°C with the conventional column in place. The solvent front and 3CA came off much more cleanly giving sharper peaks. A broad hump was seen at retention time (RT) ~5 minutes, which was assumed to be CIPC. The oven was programmed at 180°C for 2 minutes, rising 8°C/min to 210°C for 4 minutes. The 'hump' became a more distinct peak, although still very broad. This peak came off while oven temperature was still increasing, so a better shape might be obtained if the oven was isothermal at high temperature by this point.

   Several attempts were made at programming the oven temperature to try to sharpen up the CIPC peak – it is possible that oven temperature is suitable for 3-CA but too low for CIPC, resulting in it spreading into a wide band rather than sweeping through cleanly.

9. *Temperature of heating block:* The temperature of the heating block was checked and the setting was increased from 120 on the dial (~200°C) to 130 (~220°C) – the result was much cleaner, sharper peaks under the same oven program.

   Prior to all the problems described above, the block had been maintained at 220°C, but during the troubleshooting phase where potential leaks in the system were investigated, it was thought that the CIPC might be broken down in contact with the metal at the high temperature so the temperature was reduced to minimise this risk.

Once the problems were solved using the standard length column and the modified injector, the lengthened column was put back in and run under the new temperature conditions. Once again the 3-CA peak was good and sharp, but the CIPC was not acceptable. The desorption block temperature was increased to >250°C with no improvement. At temperatures any higher than this, it is likely that CIPC would begin to break down during desorption. Altering the combustion gas (H_2:air) ratio caused a slight improvement, although the peaks were still very small in height and very wide. On inspection of the packed mini-column inside the desorption block it was found that the

packing material had come loose and the glass wool from the base of the precolumn had become trapped in the injector. It was repacked and left to condition.

No improvement was seen when the new minicolumn was re-installed, so the lengthened column was replaced with a standard length OV-17 column again, and the system worked well. Desorption of several Tenax precolumns was attempted with limited success – although reasonable CIPC peaks were obtained, the chromatograms were messy. Since the Tenax precolumns had been conditioned about 8 weeks prior to use, such a response was expected.

The temperature run was altered after this set of samples – the CIPC peaks from the last set had large shoulders at the back, suggesting that the final holding temperature needed to be lower. The new program was 130°C for 7 minutes, rising at 12°C/min to 180°C, holding for 4 minutes.

The first modified column (extended with ¼ inch precision glass) was packed with 3% OV-17 on Gaschrom Q, conditioned and installed into the system with the modified injector – the glass was under a little strain due to the extra length, but it could be fitted into the oven. With direct injection, the system worked well although the peaks were generally smaller than with a standard column.

In the course of the analysis, during disconnection of the N_2 supply, back pressure caused the OV-17 packing of the minicolumn to blow out: this column was replaced with an empty 6mm glass column and the system continued to work well. In Boyd's work, direct injection was done through empty glass with no problems.

The following day, a Tenax precolumn became stuck on the top of the column, and the whole system was cooled in order to remove it. Broken glass was found on the glass wool at the top of the GC column, so the column was taken out and the fragments of glass removed. It was also noticed that the OV-17 packing material in the GC column was loose, so the glass wool and top centimetre of packing were removed, the column connected up to vacuum and repacked. After this, the system worked consistently well.

4.6.4 Summary of method development

After troubleshooting the entire system, conditions were found under which both 3-CA and CIPC could be analysed successfully. In retrospect, a number of experimental parameters

were responsible for the problems in the early stages of method development, any/all of which would have caused problems with the analysis.

Correct column temperature programming is essential for effective separation and determination of compounds in air – a great deal of trial and error was required to find the correct program for the particular GC and column used in this study.

The build up of debris on the glass wool (either on the precolumn or the GC column itself) and disturbance of the column packing caused by repeated connection and disconnection of the N_2 gas supply both had detrimental effects on the response.

The temperature of the desorption block is also vital – CIPC must be desorbed off the Tenax column quickly and swept onto the GC in a thin band. The rate at which CIPC is removed from the Tenax is dependent on the temperature of the desorption block, (and with the rate of carrier flow) which needs to be high enough to facilitate effective desorption, but not high enough to result in thermal breakdown of the CIPC molecule. In this study, the block was maintained at 240°C.

Frequent checks of gas flow rates and desorption block temperature, along with inspection of the column and packing material and removal of any debris were carried out routinely to ensure the continued effective running of the system.

4.7. Sampling with resin traps located in store at a range of temperatures (3-18°C)

4.7.1. Store preparation:

Headspace samples were collected from three 12-tonne experimental stores at Sutton Bridge Experimental Unit. In contrast with the previous studies, no thermal fog application was carried out prior to the sampling. It was assumed that within each store (following several applications of chemical that season) there were adequate quantities of CIPC to generate a saturated vapour at the range of temperatures to be investigated.

Stores were set to achieve air temperature of 3°C and fully sealed on Friday 22nd and sampling carried out from 25th-28th March. Samples were transported to Glasgow and analysed on 29th-30th March.

For this part of the work, the tubers were removed from the temperature probes in store in order to maintain the air temperature to within ± 0.3°C (in previous work temperature control was based on the temperature of a small number of tubers in store). All temperature probes were left in the stores, giving twice the number of air readings over the sampling time. Air temperature was far more uniform and was maintained closer to the set-point under these new conditions – with the probe tubers in place, air temperature varied by up to 4°C during sample collection (see Figure 41); with the tubers removed, air temperature held to within 1°C – shown in Figure 48 overleaf.

4.7.2 Sampling

Since Tenax resin traps were used and all the CIPC would be introduced to the GC at once, both the sample collection rate and sampling time could be significantly reduced from the 500ml/min and 300 minutes in the last study with methanol traps. Three air sampling pumps (SKC Aircheck Model 224-PCXR8) were used to collect samples from three 12-tonne experimental stores. Air flow was set at 100ml/minute using the low-flow adapters on the pumps, and sampling times were of the order of 100 minutes for all temperature set-points.

Air samples were collected from 3 stores (Stores 33, 34 and 36) to allow some degree of replication (although air temperature varied among stores so samples cannot be considered true replicates for statistical purposes). Controls on the pumps were set to achieve ~100ml/minute, but flow rates were checked for each individual resin trap, as variations in the packing material can cause differences in air flow rate and hence sample volume. Air temperature set points were increased in 3°C increments between samples, and stores left to equilibrate for ~2 hours at the new set point before the next sample was taken.

4.7.3. Analysis:

Quantification of CIPC was carried out by thermal desorption onto a Pye Unicam PU4500 packed column gas chromatograph equipped with a 1.5m column (3% OV-17), flame ionisation detector and thermal desorption block.

Under the GC conditions described in Section 4.2.3, chlorpropham has a retention time on the column of ~9 minutes.

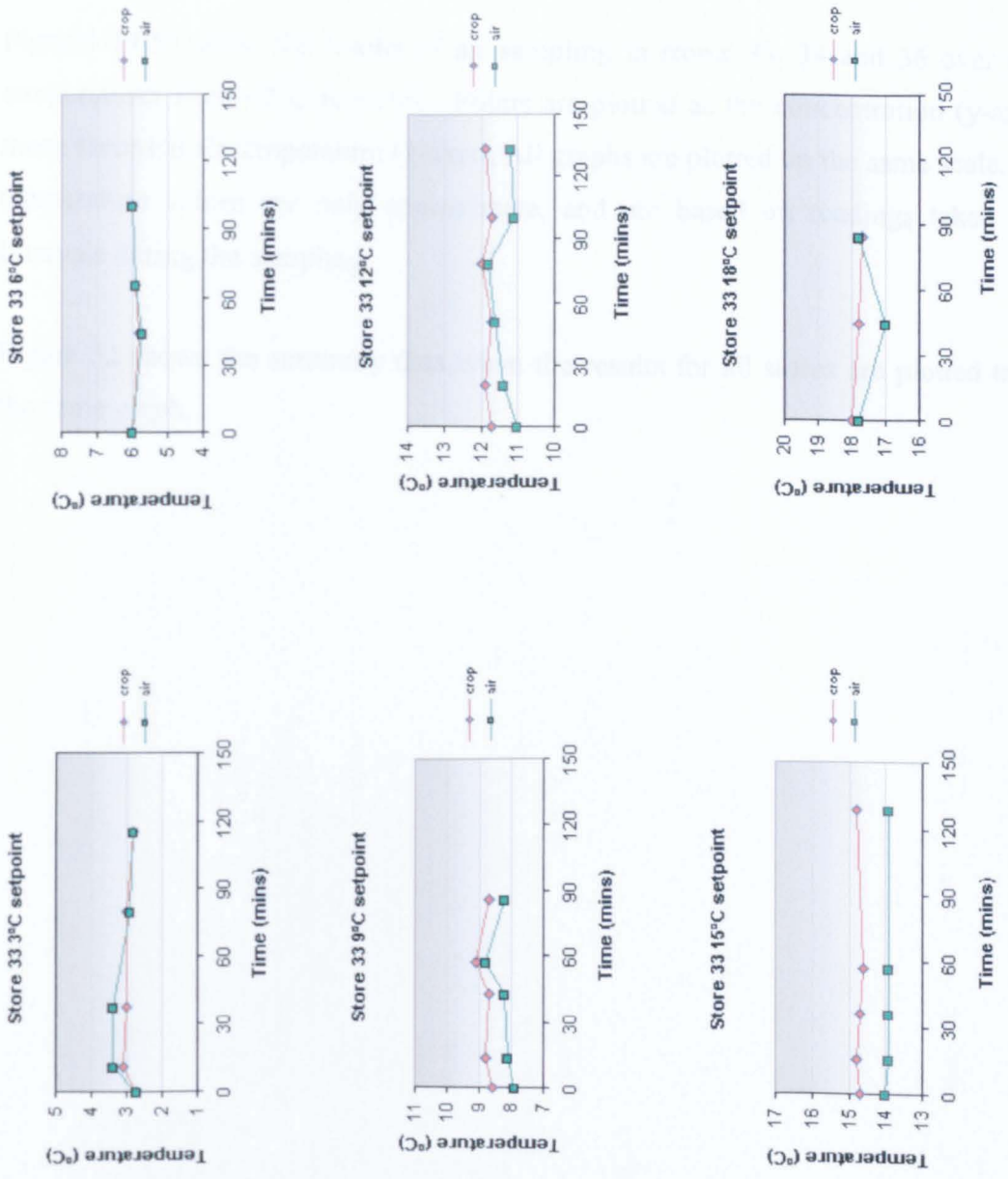


Figure 48 Crop and air temperature fluctuations in Store 33 with no tubers attached to crop probes

4.7.4. Results:

Table 28 overleaf gives details of the samples collected on Tenax-GC resin from experimental stores.

Figures 49-51 show the results of air sampling in stores 33, 34 and 36 over a range of temperatures from ~3°C to ~18°C. Points are plotted as the concentration (y-axis) vs the mean recorded air temperature (x-axis). All graphs are plotted on the same scale. The mean temperature values are only approximate, and are based on readings taken at regular intervals during the sampling.

Figure 52 shows the summary data when the results for all stores are plotted together on the same graph.

Table 28 Details of samples collected 25th-28th March 2002

Store and set-point (°C)	Mean temperature (°C)	Flow rate (l/min)	Sampling time (min)	Sample volume (l)	Weight CIPC (µg)	Concentration in air (µg l^{-1})
Store 33 3°C	3.23	0.135	80	10.80	-	-
Store 34 3°C	2.98	0.150	100	15.00	0.578	0.039
Store 36 3°C	2.97	0.150	100	15.00	0.530	0.035
Store 33 6°C	5.95	0.100	100	10.00	0.446	0.045
Store 34 6°C	5.91	0.125	100	12.50	0.563	0.045
Store 36 6°C	6.00	0.100	100	10.00	0.076	0.008
Store 33 9°C	8.71	0.110	62	6.82	0.498	0.073
Store 34 9°C	8.51	0.132	79	10.43	0.865	0.083
Store 36 9°C	8.75	0.150	82	12.30	1.000	0.081
Store 33 12°C	11.59	0.120	100	12.00	0.395	0.033
Store 34 12°C	11.58	0.110	100	11.00	0.962	0.087
Store 36 12°C	11.68	0.095	100	9.50	1.018	0.107
Store 33 15°C	14.49	0.125	100	12.50	0.955	0.076
Store 34 15°C	14.32	0.105	100	10.50	-	-
Store 36 15°C	14.62	0.100	100	10.00	1.655	0.165
Store 33 18°C	17.48	0.112	100	11.20	3.589	0.320
Store 34 18°C	17.68	0.097	100	9.70	2.267	0.234
Store 36 18°C	17.63	0.117	100	11.70	3.432	0.293

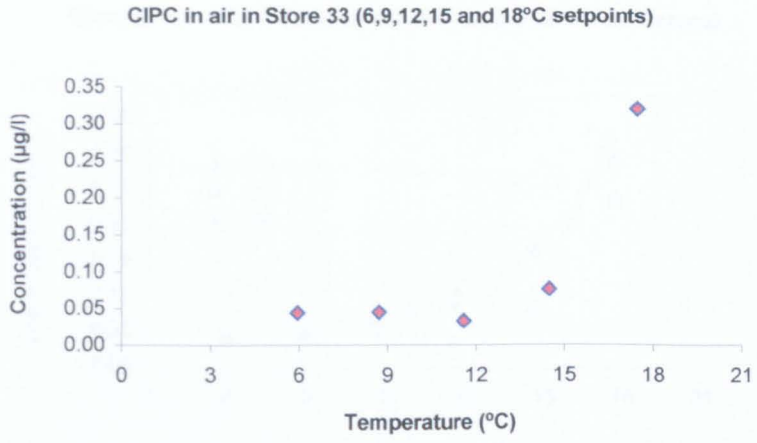


Figure 49 Concentrations of CIPC in air samples from Store 33

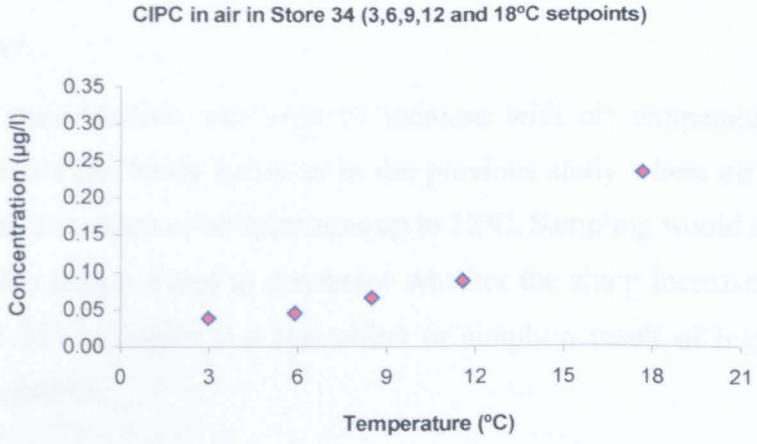


Figure 50 Concentrations of CIPC in air samples from Store 34

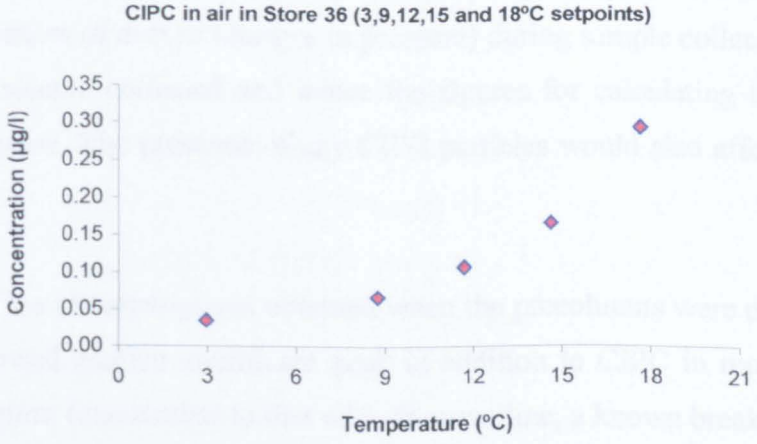


Figure 51 Concentrations of CIPC in air samples from Store 36

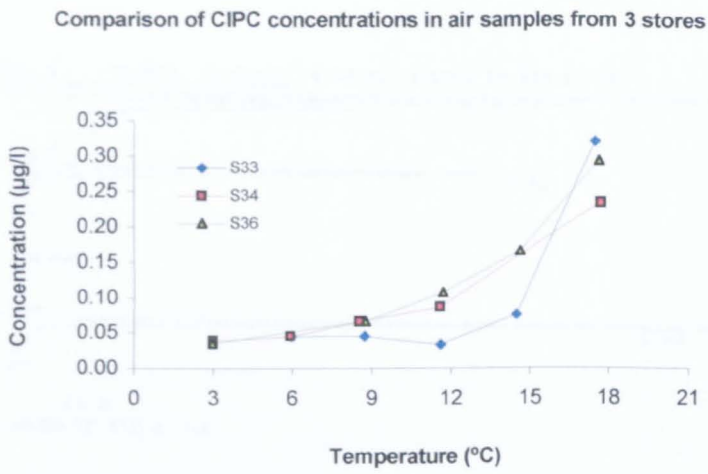


Figure 52 Comparison of calculated CIPC concentrations in samples from 3 experimental stores (3°C to 18°C).

4.7.5. Discussion:

Chlorpropham concentration was seen to increase with air temperature, although the relationship was not as clearly linear as in the previous study where air was collected in methanol traps over a range of temperatures up to 12°C. Sampling would need to be carried out at even higher temperatures to determine whether the sharp increase in concentration observed in the 18°C samples is a real effect or simply a result of higher variability at increased temperatures.

Differences in measured concentration can be explained in several ways. Firstly, sample collection and analysis may cause variability. Due to constraints on equipment, replicate samples were not collected from each store, meaning that the statistical validity of the individual values cannot be assessed. Any variation in pump flow rate (e.g. due to partial blockage by particles of dust or changes in pressure) during sample collection would affect the volume of sample collected and hence the figures for calculating the concentration would be inaccurate. The presence of any CIPC particles would also affect the calculated concentration.

Examination of the chromatograms obtained when the precolumns were desorbed onto the GC column showed another significant peak in addition to CIPC in most samples. This peak had a retention time similar to that of 3-chloroaniline, a known breakdown product of CIPC. Figure 53 overleaf shows a typical chromatogram obtained by thermal desorption of a Tenax precolumn – the example shown was collected from Store 33 at a temperature of 18°C.

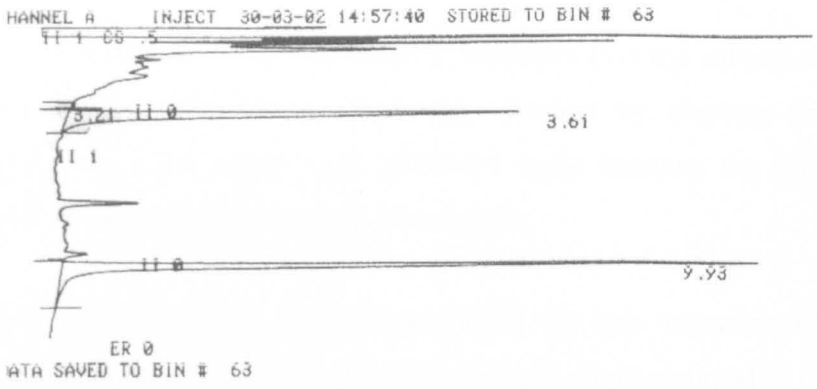


Figure 53 Typical chromatogram obtained by thermal desorption of Tenax resin air sample

Although the retention time of this peak was very similar to that of 3-chloroaniline, its identity could not be confirmed (e.g. by GC-MS) at that time due to the fact that desorption of the Tenax and analysis by GC-FID destroys the sample leaving none for identification purposes. In addition, most GC-MS cannot cope with thermal desorption of analytes, and require that the sample is made up in solvent (e.g. methanol).

Thermal decomposition of chlorpropham at high temperature has often been noted in the literature. The potential presence (unconfirmed at this stage) of 3-chloroaniline in these air samples was believed to be a result of breakdown of the CIPC molecule during the thermal fogging application process, although more work would be required to confirm this hypothesis. Romagnoli and Bailey (1966) reported significant pyrolysis of the CIPC molecule on a GC column at 230°C. Nagayama and Kikugawa (1992) also found significant degradation to 3-chloroaniline following heating for several minutes at temperatures >200°C. The temperature inside the combustion chamber of a commercial fogging machine ranges from 300°C-500°C (most equipment operates nearer the top end of this range) so thermal degradation could be possible. However, the short residence time in the burner chamber (formulation passes through the machine at a flow rate of ~1 litre/minute) is believed to prevent significant breakdown in this way. However, in addition to the burner, several metres of metal ducting pipe can be used to carry fog into store – the temperature of fog at the end of a 7m pipe is known to be in excess of 200°C (measured at SBEU, May 2002). Contact with hot metal surfaces is known to promote breakdown of molecules – indeed, past problems with breakdown of compounds on contact with hot metal led to the development of all-glass flow paths for GC analysis.

4.7.6 Identification of 3-chloroaniline (3-CA) by gas chromatography-mass spectrometry (GC-MS)

An extra sample from Store 34 was collected in methanol (via the solvent trapping system previously described) in November 2002 and analysed by electron impact GC-MS. Solvent trapping was used rather than adsorbent resin because the GC-MS facilities available required a solvent-based sample for analysis.

Once received in the laboratory, the methanol from the trap was concentrated down to ~1ml because of the small amount of chemical expected. Once reduced to this volume, the sample became cloudy in appearance. There was also a significantly higher amount of baseline noise in this sample than in the corresponding standard in hexane (see figures overleaf). Both the cloudiness of the sample and the background noise is thought to be due to the presence of water in the sample: the store was maintained at 95% relative humidity during sample collection, so it is likely that moisture from the air was trapped in the methanol along with the compounds of interest. In contrast to the solvent, Tenax resin has no affinity for water, so no noise attributable to water is present when these samples are analysed.

A standard of 3-CA in hexane was prepared and injected under the same conditions as the sample, to allow comparison of the fragmentation pattern of the unknown peak with that of authentic 3-CA. Figure 54 overleaf shows the GC-MS trace for the first ~2 minutes after injection of the 3-CA standard, and the fragmentation pattern for the peak at 1.39 minutes, identified as 3-CA. The trace also shows an impurity in the standard at RT 1.91 minutes. This peak was not characterised.

Figure 55 shows the GC-MS trace for the first two minutes following injection of the headspace sample in methanol. Although a split peak was produced, both parts (RT 1.41 and 1.46 minutes) were integrated together and generated the cracking pattern shown underneath.

The similarities in the fragmentation patterns confirm the presence of 3-chloroaniline in the air sample. The major ion at m/z = 127 corresponds to the 3-CA molecule itself. The smaller peaks common to both samples relate to various products of the cracking of the 3-CA molecule e.g. the peak at m/z = 92 to aniline, formed by removal of the chlorine atom from 3-CA.

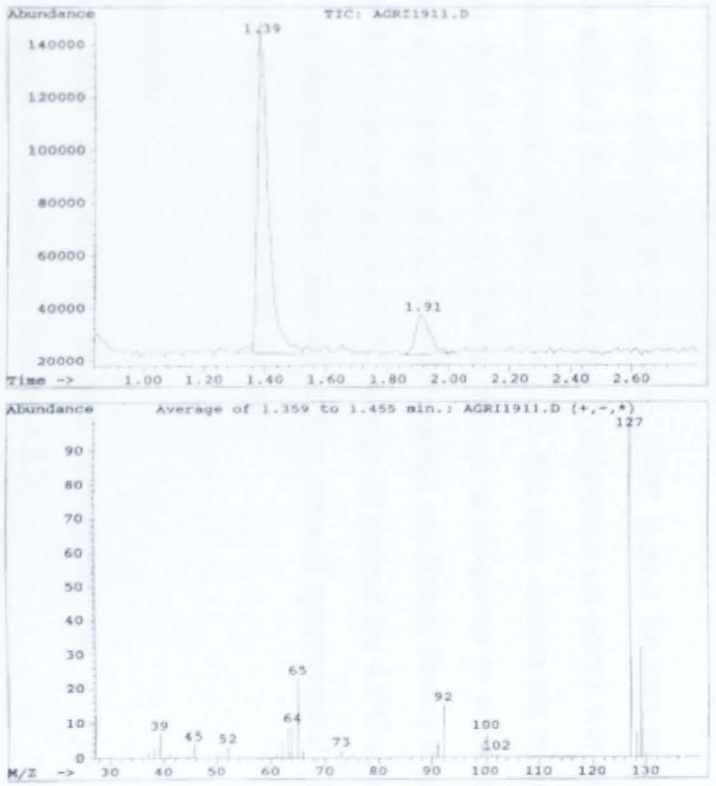


Figure 54 GC-MS trace and fragmentation pattern for 3-chloroaniline standard in hexane

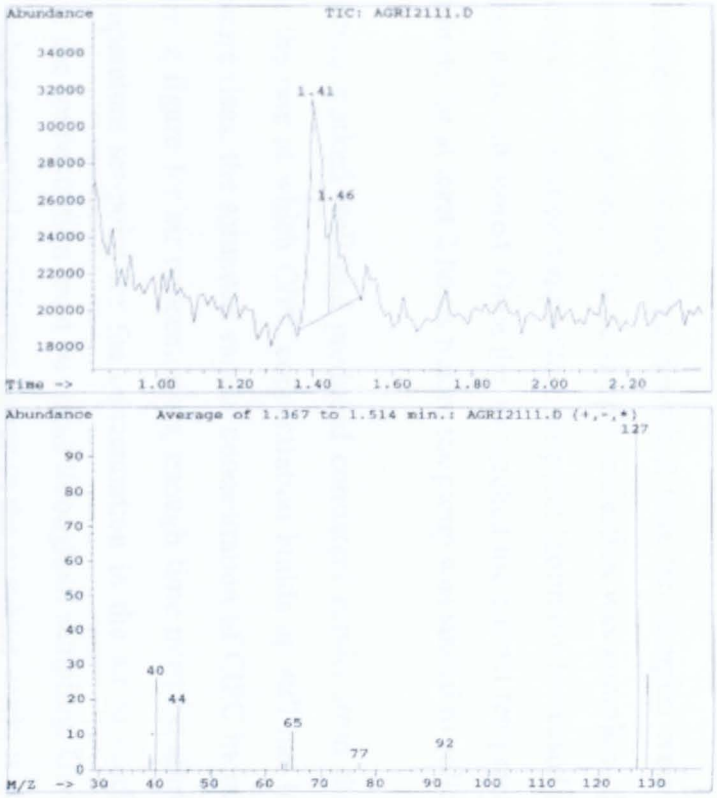


Figure 55 GC-MS trace and fragmentation pattern for Store 24 headspace sample in methanol

4.8 Comparison of 2hr equilibration with 24hr equilibration

4.8.1. Introduction:

In the studies with Tenax traps described thus far, samples were collected in order of increasing air temperature. Once sample collection was complete, the store systems were set to achieve the next air temperature set-point (normally increased in 3°C increments) and air temperature monitored. Once the air reached the correct temperature, the store was left to equilibrate for at least 2 hours before the pump was started to collect the next sample.

This system worked well and produced consistent results from the three stores, but the issue of the rate at which CIPC concentration builds up still has to be addressed. As air temperature rises, the saturated vapour concentration of CIPC increases in line. To obtain an accurate figure for air concentration, enough time must be allowed after reaching the new temperature set-point for the concentration in the air to reach the new equilibrium point i.e. the concentration must be stable throughout sampling. Given the good agreement among values recorded in different stores in the previous work, it was assumed that stores were in equilibrium during sampling. However, a small study was conducted in early April 2002 where stores were left for a full 24 hours following temperature increase before sampling began.

4.8.2. Sampling and store preparation:

Samples were collected by Ajay Jina (BPC Sutton Bridge) and posted to Glasgow for analysis within 3 days of collection. Temperature set-points were as similar as possible to the previous work to allow comparison, but time constraints meant that not all could be repeated. 3,6,9, 15 and 18°C were chosen as set-points to cover the range that might be expected in commercial stores under normal conditions during storage. Store 33 struggled to reach the lowest set-point of 3°C so was set instead for 4.5°C where it held more steadily and easily. Samples were collected at flow rates of approximately 100ml/min (checked for each individual sample) for 100 minutes.

4.8.3. Analysis:

Samples were analysed by thermal desorption on a Pye Unicam PU4500 gas chromatograph as described in Section 4.2.3.

4.8.4. Results:

Table 29 overleaf gives details of the samples collected after 24-hour equilibration. Figure 56 plots the points as concentration ($\mu g\ l^{-1}$) vs recorded temperature (°C) – temperatures were only recorded at the start and end of the sampling so no data is available on the changes during sampling. Results from the last study (2hr equilibration) are also shown in Figure 57 for comparison.

Table 29 Details of air samples collected after 24 hours equilibration time (8th-12th April 2002)

Store and set-point (°C)	Actual temperature (°C)	Flow rate (ml/min)	Sampling time (min)	Sample volume (l)	Weight CIPC (µg)	Concentration in air (µg l^{-1})
Store 33 4.5°C	4.4	122.5	100	12.25	0.009	0.001
Store 34 3.0°C	3.0	87.5	100	8.75	0.219	0.025
Store 36 3.0°C	3.0	110.0	100	11.00	0.324	0.029
Store 33 6.0°C	6.1	117.5	100	11.75	0.837	0.071
Store 34 6.0°C	5.9	127.5	100	12.75	0.542	0.042
Store 36 6.0°C	5.9	100.0	100	10.00	-	-
Store 33 9.0°C	9.1	110.0	100	11.00	1.044	0.095
Store 34 9.0°C	9.1	127.5	100	12.75	0.088	0.069
Store 36 9.0°C	9.1	87.5	100	8.75	0.400	0.039
Store 33 15.0°C	14.9	87.5	100	8.75	1.713	0.196
Store 34 15.0°C	14.7	122.5	100	12.25	1.757	0.143
Store 36 15.0°C	14.6	92.5	100	9.25	1.452	0.157
Store 33 18.0°C	17.9	97.5	100	9.75	2.724	0.279
Store 34 18.0°C	17.4	105.0	100	10.50	2.557	0.243
Store 36 18.0°C	17.4	85.0	100	8.50	2.038	0.240

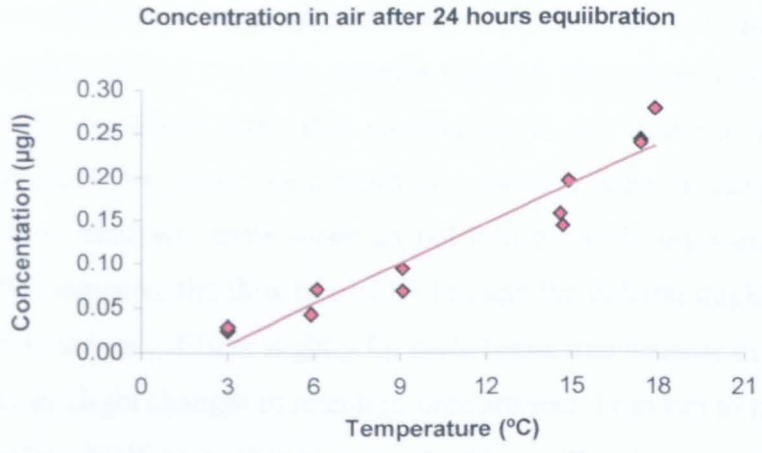


Figure 56 CIPC in air over a range of temperatures (3-18°C) after 24 hours equilibration

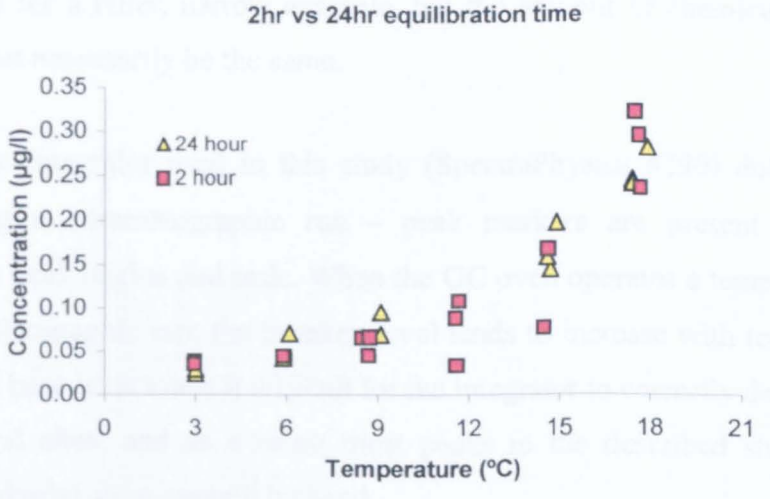


Figure 57 Comparison between samples collected after 2 and 24 hours equilibration time

4.8.5 Discussion:

Figure 56 shows a good linear relationship ($r^2 = 0.92$) between air temperature and CIPC concentration. When compared with the values obtained after 2 hours, there is no significant difference, although the relationship is more clearly linear. Because 'replicate' samples were collected from different stores (rather than three replicates in the same store at the same time), the several uncharacteristically low values found after 2 hours cannot be discounted as outliers. This lower concentration might suggest the store air was not in equilibrium during sampling. If this is the case, we might expect greater discrepancies at higher temperatures. Such an effect is not seen. Both the low values come from the same

store (Store33) but could be due to variations in flow rates during sampling or could be merely atypical low values. It was not practicable to carry out replication in each store for statistical analysis, thus it is impossible to completely discount any unusual results. A repeat of both studies with 3 replicate samples taken in each store would shed light on whether the results genuinely show that equilibrium is not achieved in two hours or whether the occasional low values are a result of variability either at sampling (e.g. pump flow rate) or during analysis: some tubes do not butt perfectly onto the top of the GC column. When this happens, the flow rate of N_2 through the column might be reduced due to leakage. Carrier flow rate differs slightly for each Tenax trap because of variations in the packing material, so slight changes in retention time are seen from run to run. A carrier gas leak might manifest itself as a change in peak shape rather than a noticeable shift in retention time, as the flow of carrier determines whether the CIPC is swept cleanly off the Tenax in a thin band or in a wider front. This might result in a peak that is small and wide, rather than tall and narrow as desired. The area recorded for such a small wide peak might be the same as for a taller, narrow example, but the amount of chemical generating the response will not necessarily be the same.

In addition, the integrator used in this study (SpectraPhysics 4290) does not draw the baseline during a chromatographic run – peak markers are present to show when integration of a peak begins and ends. When the GC oven operates a temperature program during a chromatographic run, the baseline level tends to increase with temperature. Such increases in the base level make it difficult for the integrator to correctly determine where a peak begins and ends, and as a result most peaks in the described studies (including calibration standards) are measured by hand.

4.9 Sampling with resin traps located in store (from 21 to 27°C)

4.9.1. Sampling and store preparation:

Temperature control systems (Cornerstone Systems Ltd) in Stores 34, 35 and 36 were set for 21°C on 8th June 2002. For this part of the study, the fridges in each of the stores were disabled to prevent large temperature fluctuations. Part of the safety mechanism in each store is a high temperature thermostat that automatically switches the fridges on when temperature reaches an unacceptably high level. This mechanism normally activates if the temperature in the store reaches ~20°C, since under normal storage conditions the temperature would rarely exceed 15°C in the store. Temperatures in excess of 21°C, as required in this study, would not be met under normal working conditions and proved difficult to achieve and maintain. It was hoped that by disabling the fridge in each store, temperatures would remain more constant over the 80-minute sampling time, since once the set point is achieved, only the fans will operate. Controls of relative humidity (normally maintained at >90% during normal storage practice) were also switched off to prevent the drawing of moisture through the traps. At these high temperatures, humidity dropped to 50-60%.

4.9.2 Results:

Table 30 below gives details of each of the samples collected. Figure 58 shows the concentrations plotted against the mean recorded temperatures.

Table 30 Details of air samples collected in experimental stores at 21-27°C (12th-14th June 2002)

Store and setpoint (°C)	Mean temperature (°C)	Flow rate (l/min)	Sampling time (min)	Sample volume (l)	CIPC (µg)	Concentration (µg l^{-1})
S34 21°C	20.88	0.105	120	12.60	4.330	0.344
S35 21°C	21.02	0.098	120	11.76	4.690	0.399
S36 21°C	20.87	0.123	120	14.76	8.600	0.583
S34 24°C	24.44	0.112	80	8.96	3.580	0.400
S35 24°C	24.57	0.080	100	8.00	3.960	0.495
S36 24°C	24.45	0.120	80	9.60	7.770	0.809
S34 27°C	27.37	0.113	80	9.04	4.190	0.463
S35 27°C	27.34	0.103	80	8.24	4.680	0.568
S36 27°C	27.65	0.088	80	7.04	6.920	0.983

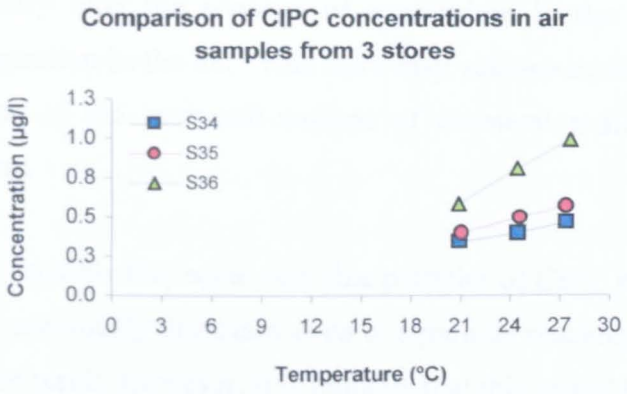


Figure 58 Comparison of calculated CIPC concentrations in samples from 3 experimental stores at temperatures from ~21°C to 27°C.

4.9.3 Discussion:

Differences in concentration among stores at higher temperatures may be explained by differences in gassing history and/or holding temperature of the store throughout the storage season. Each store contains a finite amount of chemical, as both vapour and particles, with some remaining in the air and some sorbed onto solid surfaces. The amount of chemical in the store will vary depending on a number of factors including the number of treatments it has received, the air temperature, the amount of venting and the degree of 'leakiness' in the store. Assuming the store is stable, the CIPC in the air will be in equilibrium with that held on solid surfaces.

Levels of humidity in the air are also suspected of having an impact on vapour concentration in air, although the effect is not well understood. Where humidity is high, lower concentrations of chemical in air are expected [Duncan, personal communication] than under drier conditions. This being the case, the low levels of humidity in store air may play a role in the high concentrations seen at temperatures above 21°C – when store control equipment was switched off, relative humidity dropped from the usual 95% to between 50-60%.

The results from Store 36 at high temperatures (21°C and above) were consistently and significantly higher than in the other two stores sampled at the same set-point at the same time. There are a number of possible explanations for this.

1. More applications were carried out in this store throughout the season than in the others, and as a result there may have been a larger reservoir of CIPC in the store.

This may alter the position of equilibrium in the store, resulting in a higher concentration in the air. This store may achieve equilibrium faster than the others because of the increased amount of chemical available for volatilisation from surfaces.

2. It is possible that some very fine particles of CIPC may have remained in the air, and as previously discussed even one particle reaching the trap could significantly alter the result. However, it is unlikely that this would have happened three times in the same store. There also still appears to be a linear relationship between temperature and concentration, making this explanation unlikely.

4. Drier conditions in Store 36 might account for the higher concentration of CIPC in the air. However, humidity was not routinely monitored during sampling, so any differences between stores are not known.

4.10 Summary

Air samples were collected over a range temperatures from 2 to 30°C from 12-tonne stores at Sutton Bridge Experimental Unit. Stores had received several treatments with CIPC as a thermal fog during the season. They were sealed and airtight both before and during sample collection. After a short time at the desired temperature, the store air was assumed to be in equilibrium. Quantifiable amounts of CIPC were detected in every sample.

The concentration of CIPC in store air was strongly correlated with air temperature.

In terms of efficiency, the two trapping methods are broadly comparable, with both types performing well. The methanol traps were shown to be efficient by the absence of CIPC in a second trap online. Results from Tenax traps agree well with the solvent traps, showing them too to be reliable. Tenax has several advantages over the solvent traps in terms of the lower volume of sample required and reduced sampling times, and also the increased sensitivity of the method. It has no affinity for water (unlike methanol), which can complicate the analysis by GC if present (as shown by the increased baseline noise in Figures 54 and 55). However, solvent trapping is still required for identification purposes as thermal desorption destroys the sample, and most GC-MS systems require a solvent-based sample for analysis.

There was no significant difference in concentration after 2 and 24-hour equilibration times, although the relationship between temperature and concentration was more clearly linear after 24 hours. It is therefore assumed that in these stores, equilibrium is achieved within a few hours. However, these are low volume stores with a large reservoir of available CIPC, which remained sealed during sampling. Under commercial conditions, the situation could be very different (i.e. in high volume, leaky stores receiving fewer applications per season).

3-chloroaniline was detected in samples collected on Tenax and identified by electron impact GC-MS. It was not identified in the original samples collected in methanol, because of the chromatographic conditions under which the samples were run. Confirmation of the unknown peak as 3-CA was carried out using a sample in methanol, showing that 3-CA may have been present in the methanol samples, though not detected.

The presence of 3-chloroaniline in the air suggests that the CIPC molecule may be thermally decomposed during the fogging process. 3-CA is also known to be a product of microbial breakdown of CIPC, although the physical conditions in the store make significant microbial activity unlikely.

Quantification of 3-chloroaniline was not carried out for the majority of samples, but examination of peak size and relative response factors for CIPC and 3-CA show the concentration to be of the same order as CIPC (i.e. $\mu g\ l^{-1}$). Thus it is feasible that the proportion of the applied CIPC lost in this way could be significant. This being the case, the efficiency of thermal fogging as a means of getting CIPC into a store is called into question. Low-temperature application methods should perhaps be considered as an alternative.

In future work, it is recommended that a filter is attached to the front of the trap as a precaution to prevent particulate CIPC reaching the trap: some of the variability in the results may be explained by the presence of particles in the air. Although larger particles settle out within a few hours of application, finer material may remain in suspension for far longer. The amount of CIPC present in the trap can be significantly and unpredictably affected by any particles reaching the trap.

In addition to air temperature, a number of factors can influence the concentration of chemical in the air. Relative humidity, the presence of crop, the degree of leakiness in the store and the number of treatments carried out in the store are some of them, but this list is

by no means exhaustive. Some of these variables were investigated in small-scale experiments in the laboratory, as described in the following chapter.

Chapter 5

HEADSPACE STUDIES ON CIPC ANALOGUES IN A STATIC SYSTEM

5.1 Introduction

5.1.1 Background

The volatilisation of pesticide chemicals is an important process in the environment, for example where chemicals are applied to the soil. In potato stores, the volatilisation of chlorpropham from contaminated materials in treated stores can be responsible for germination and growth problems in non-target crops (e.g. seed and grain), and can result in a detectable chemical residue on organic or non-treated tubers. Thus, the tendency of a chemical to partition into the air under various sets of conditions can be very useful in predicting movement in the environment and potential contamination problems.

Previous workers have investigated the vapour pressure and concentration of a number of pesticides in air using various techniques for trapping and analysis. Determination of either vapour pressure or vapour density (concentration) allows the other to be calculated. Work reported elsewhere in this thesis describes the trapping and analysis of vapour phase CIPC using a solid sorbent trap and analysis by thermal desorption onto a GC column. This technique was used to determine chlorpropham concentrations in samples of air from treated stores.

Direct measurement of the pressure of a vapour in equilibrium with the pure solid or liquid form of the chemical can be achieved, but only when the vapour pressure is 130Pa (~1mm Hg) or more [Taylor and Spencer (1990)]. For most pesticides, elevated temperatures are required to reach this pressure, and extrapolation of the data to environmental temperatures is required. This brings added uncertainty and error to the measurement.

Gas chromatographic retention times can also be used to determine vapour pressure [Bidleman (1984)] by comparison of the retention time of a test substance with that of a compound with known retention time and vapour pressure. Appropriate column materials and reference compounds must be selected for the chemical character (e.g. polarity) of each test substance. Limitations of the method include the assumption that retention time is

dependent only on vapour pressure, and that extrapolation of the data from GC oven conditions to environmental temperatures possible.

Effusion methods have been used to determine the rate of chemical escape from a chamber through an orifice of known diameter into a vacuum. Chemical loss can be measured as a change in weight of the chamber, or the escaping vapour can be trapped in a liquid N_2 cold trap and analysed. Hamaker and Kerlinger (1969) produced a comprehensive review of effusion methods.

The gas saturation method of Spencer and Cliath (1983) has been used to determine the vapour pressure of pesticides as pure chemicals and also as residues in soils. The partitioning of a chemical between soil, water and air, and the volatility of soil-applied herbicides can be predicted using this technique. In the method, a slowly moving stream of inert carrier gas (e.g. N_2) is saturated with chemical and the vapours collected in a trap (e.g. solvent or adsorbent material) suitable for that particular chemical. Analysis of a volumetric sample at a known temperature allows direct measurement of the amount of vapour in a given volume (i.e. vapour density or concentration).

Volatilisation of soil-applied chemicals in the environment was measured by Kearney and Kontson (1976) and Turner and Glotfelty (1977) who collected chemical vapours on polyurethane plugs. Large volumes of air were drawn through the plugs, and chemical was removed from the adsorbent using Soxhlet extraction. This method has interesting implications for the potato industry, where polyurethane spray foam is commonly used as insulation, and is often left exposed (particularly in older buildings).

Of the described techniques for measuring vapour pressure of pesticides, gas chromatographic and gas saturation methods have been shown to provide more consistent results than effusion techniques [Taylor and Spencer (1990)].

5.1.2 Experimental design

A number of experiments were carried out in small airtight jars to investigate the volatility of a range of sprout suppressant chemicals, and the effect of various physical parameters on the amount of chemical in the headspace above a chemical source.

The method was based on a technique used by food chemists to study the flavour of foods [McCarthy *et al* (1963)]. A similar approach was also adopted by O'Hagan (1991) to

investigate the behaviour of substituted naphthalenes in air in a closed system. A small amount of the sample of interest is placed in a closed container. After a period of equilibration, the air in the jar is sampled with a gas-tight syringe and injected directly onto a packed column GC for identification and /or quantification.

Although chlorpropham is the primary chemical of interest in this work (given its status as the only post-harvest sprout suppressant available in the UK), its low volatility made it unsuitable for use in this experiment, where small volumes of air were to be injected directly onto the GC with no pre-concentration step. As a result, certain chemicals with higher volatility were chosen.

5.1.3 Chemicals

Three chemicals were selected for use as CIPC analogues in this experiment, each of which has some relevance to the issue of sprout suppression. All chemicals were technical grade (>95% purity) and were used as received.

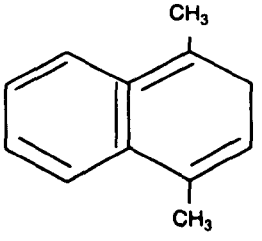
- **3-chloroaniline (3CA):** A metabolite of chlorpropham with higher volatility than the parent compound. Identified in samples of air from experimental potato stores, it is a compound of interest in terms of its environmental fate. Listed in EU Priority Pollutants Circular No 90-55 (1990).

- **Tecnazene (TCNB)**: An organochlorine compound widely used as a sprout suppressant in the past, it is now banned in the EU because of environmental problems arising from its use (tecnazene is toxic to aquatic organisms). GC-FID is very sensitive to this compound (because of its 4 chlorine atoms) allowing very small amounts to be quantified with confidence.

- **1,4-dimethylnaphthalene (DMN)**: A substituted naphthalene used as a sprout suppressant in the US and elsewhere (e.g. New Zealand). The chemical is currently undergoing the EU registration process. Has considerable volatility and is active as a sprout suppressant in vapour form.

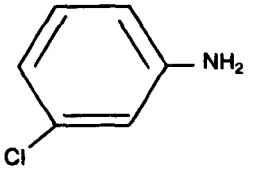
Table 31 below summarises the main chemical properties of the compounds:

Table 31 Structures and chemical properties of sprout suppressant chemicals and analogues*



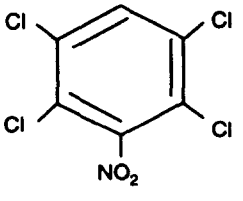
1,4-dimethylnaphthalene

Molecular weight	156.2g
Boiling point	264°C
Solubility	5.1 mg litre^{-1} at 25°C
Vapour pressure	560 mPa at 25°C



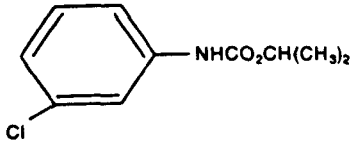
3-chloroaniline

Molecular weight	127.5g
Boiling point	230°C (decomposes)
Solubility	6,000 mg litre^{-1} at 20°C
Vapour pressure	9,000 mPa at 20°C



tecnazene

Molecular weight	260.9g
Boiling point	304°C
Solubility	0.44 mg litre^{-1} at 20°C
Vapour pressure	240 mPa at 15°C



chlorpropham

Molecular weight	213.7g
Boiling point	247°C (decomposes)
Solubility	89 mg litre^{-1} at 25°C
Vapour pressure	1.33 mPa at 25°C

* Data compiled from a number of Internet and literature sources

5.1.4 Relationship between saturated vapour concentration and vapour pressure

Vapour pressure and vapour density are related by Equation 1 below [Taylor and Spencer (1990)]

$$P = (w/v)\,(RT/M) \qquad \text{[Equation 1]}$$

where
p = pressure (mPa)
w = mass (g)
M = molecular weight (g)
T = absolute temperature (K)
R = molecular gas constant
v = volume (litres)

Equation 1 reduces to give $d = 0.12 * pM/T$ [Equation 2]

Where d = vapour density, which replaces (w/v) in Equation 1

The saturated vapour concentration of each chemical can thus be calculated using the temperature and vapour pressure stated in Table 1 and Equation 2 above: Table 32 shows saturated vapour concentrations calculated in this way

Table 32 Estimated saturated vapour concentrations of sprout suppressant chemicals at reference temperatures

Chemical	Reference temperature (K)	Vapour pressure (mPa)	Vapour density or concentration ($\mu g\ l^{-1}$)
DMN	-	560*	-
3-chloroaniline	293	9,000	468
Tecnazene	293	240	25.6
Chlorpropham	298	1.33	0.11

* No reference temperature given for the stated vapour pressure (www.ams.usda.gov/nop/NationalList/TARPReviews/14dimethylnaphthalene.pdf)

The first three compounds were selected for use in the study because their headspace concentrations could be measured directly on a GC equipped with flame ionisation detector, unlike chlorpropham, which would have required the collection of a large volume of air and pre-concentration on a porous polymer (e.g. Tenax). Because of the small volume of the jars (~120cm^3) and the added complications in the analysis of Tenax, chlorpropham itself was considered unsuitable.

5.2 Experimental Methods

Procedures common to a number of experiments are described in this Section. Detail on specific experiments can be found in the following sections.

5.2.1 Headspace jars

Narrow-necked flasks sealed with alloy septum lids were used to create a sealed environment in which to measure headspace concentration. The volume of the flask was ~120cm^3. Figure 59 illustrates the equipment used when chemical was added directly into the empty jar.

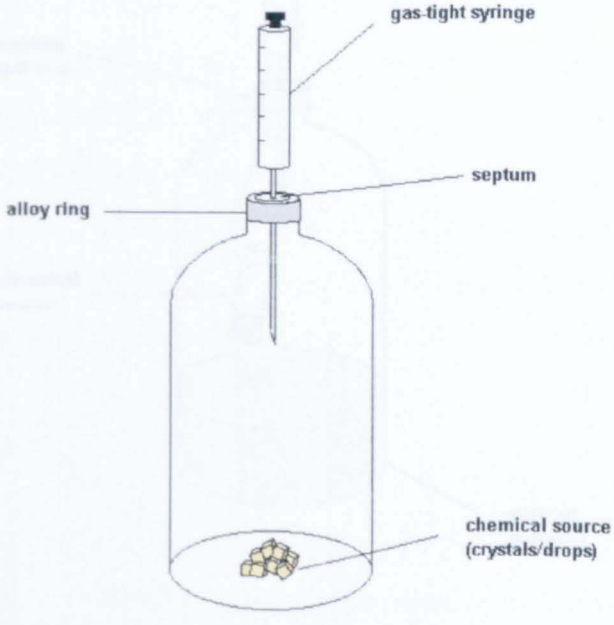


Figure 59 Schematic diagram of set-up for sampling headspace when chemical is added directly to the bottom of the jar

Tecnazene was added to the bottom of the jar as crystals, but both 3-chloroaniline and 1,4-dimethylnaphthalene are liquids at room temperature .

In some cases, DMN was added instead as a 2% alumina dust, particularly in earlier experiments.

5.2.2 Chemical sources

For initial experiments, small quantities (~0.1g) of chemical were weighed directly into the bottom of the empty jar: 3-chloroaniline as a liquid, DMN as 2% dust and tecnazene as crystals. Crystals were ground in a mortar and pestle to create the maximum surface area for volatilisation.

Once initial measurements of headspace had been made in empty jars, any effect caused by the presence of other materials in the jar was investigated. At this stage, chemical was weighed into a 2ml vial, which was suspended on a thin wire from the lid. This acted as a source of headspace concentration and allowed solid materials to be placed in the jar without coming in direct contact with the chemical. DMN was added as a liquid in these jars.

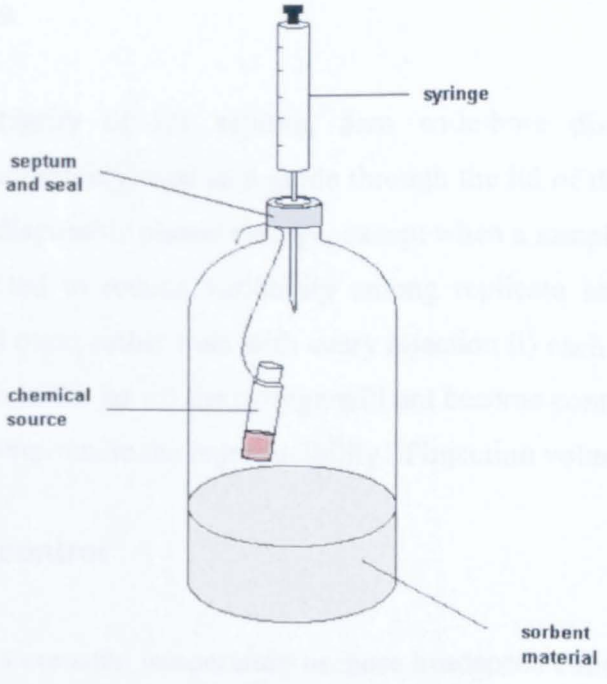


Figure 60 Sampling set-up with chemical suspended above adsorbent materials

In a small number of experiments, the chemical source in the jar was a 'spiked' soil. The spiking process was carried out prior to the soil being added to the jar. A known amount of chemical was applied to the soil dissolved in a solvent and mixed well. The solvent was allowed to evaporate off, and then the soil was added to the jar. Small quantities of solvent may remain on the soil and be found in trace amounts in the air.

5.2.3 Syringes

Initial work (not described in this Chapter) was carried out using a 500µl gas-tight syringe (Hamilton, Switzerland) with Teflon-tipped plunger and plastic barrel. However, carry-over between samples was noted, particularly with 3-chloroaniline, and the gas-tight syringe was eventually replaced with a 3ml disposable luer-lock syringe (Norm-Ject) and disposable needle. This not only eliminated any carry over, but also allowed a greater volume of air to be sampled. The downside is that the accuracy of injection volume is not as good with the disposable syringes – the 3ml syringe is only graduated to 0.1ml, whereas the gas-tight syringe is calibrated in 10µl divisions.

5.2.4 Needle guides

To maintain the integrity of the septum, 5cm wide-bore disposable syringe tips (Microlance 3) were commonly used as a guide through the lid of the jars. The guide was sealed off with a 1ml disposable plastic syringe, except when a sample was being removed. The guide was expected to reduce variability among replicate samples because i) the septum is only pierced once, rather than with every injection ii) each sample will be drawn from the same location in the jar iii) the syringe will not become contaminated with septum debris, which could compromise the reproducibility of injection volume.

5.2.5 Temperature control

Samples were held at a constant temperature because headspace concentration can be very sensitive to fluctuations in temperature. Initially, jars were held in a water bath at 30°C on the bench top. Jars were immersed up to their necks, and were held in place with clamps.

Because of the high level of variability found among replicates from the water bath, later experiments were carried out in an incubator at either 20°C or 30°C. Thus, any effects of draughts or diurnal variation in ambient temperature were minimised.

5.2.6 Sampling

One sample (volume between 500µl – 2ml) was taken from each jar on a daily basis. Between each sample, a period of at least 24 hours was left to allow the headspace concentration to recover, and the jar to reach a state of equilibrium.

The incubator and water bath were in a different room to the GC, so there was a delay of approximately 1 minute between sample collection and injection while the sample was in transit. During transit, syringe handling was kept to a minimum by carrying the syringe on a polystyrene tray to minimise the transfer of body heat to the sample.

While in transit, a Teflon septum was used to plug the end of the syringe tip to maintain sample integrity. In practice, a sample of >500µl was withdrawn from the jar and transported in the syringe. Immediately prior to injection onto the GC, the sample volume was adjusted to 500µl.

5.2.7 Analysis by GC

Air samples were injected directly onto a packed column gas chromatograph. One advantage of a packed column over capillary in this instance is that a larger volume of air can be injected without any problem.

Samples were analysed on a Pye Unicam PU4500 gas chromatograph equipped with flame ionisation detector and a 1.5m column (3% OV-17 on Gaschrom-Q). Conditions were as detailed below:

Oven temperature	150-180°C	
Injector temperature	220°C	
Detector temperature	250°C	
Gas flows	N_2 carrier	30ml/minute
	Flame H_2	30ml/minute
	Flame air	180ml/minute
Injection volume	0.5 – 2ml	

Table 33 overleaf shows the retention times for each compound under these GC conditions. Note that oven temperature was higher for tecnazene than for the other two compounds.

Table 33 GC conditions and retention times for selected compounds

Compound	Oven temperature (°C)	Retention time (min)
3-CA	150	1.90
DMN	150	4.30
TCNB	180	4.60

5.2.8 Statistical handling of data

Each data set consisted of at least six values, although the actual number of samples taken from each jar differed. In most cases, three replicate jars were set up for each 'treatment'. Each of these jars was considered as a separate experiment in the initial stages, although data from the three could be considered as one treatment.

All data sets were highly variable, so prior to data analysis by ANOVA any outliers were identified and discarded. Genuine outliers (to either side of the data set) were identified using the process below:

- Data points were ordered from smallest to largest
- Quartile 1 was determined as the value at position $(n+1)/4$ *
- Quartile 3 was determined as the value at position $3(n+1)/4$
- The inter-quartile range (IQR) was defined as the difference between Q_3 and Q_1
- The equations below were applied to the data and any values outwith the calculated range were discarded as outliers:

$$X_i < Q_1 - (1.5^* \text{ IQR}) \qquad \text{[Equation 1]}$$

$$X_i > Q_3 + (1.5^* \text{ IQR}) \qquad \text{[Equation 2]}$$

* where $(n+1)/4$ did not produce an integer, interpolation was used to determine the value of Q_1

Once outlying data points had been discarded, statistical analysis of the data was carried out using ANOVA techniques (Minitab 13 for Windows).

5.3 Headspace sampling of 3-chloroaniline, tecnazene and 1,4-dimethylnaphthalene in empty jars

5.3.1 Jars held in waterbath at 30°C

5.3.1.1 Experimental methods

Chemical source

In these initial experiments, source chemical was added directly into the bottom of empty jars, rather than suspended in a vial. 0.10g tecnazene was weighed out as crystals; 0.10g 3-chloroaniline as a liquid. DMN was added as a 2% dust on neutral alumina (0.20g dust). Each chemical was added to each of three empty jars, which were sealed with an alloy septum lid.

Needle guides were employed in each case to reduce some of the variability among samples.

Temperature control

Jars were immersed in water at 30°C ± 1°C up to their necks. The water bath was located on the bench top, and as such was subject to the effects of diurnal variation in air temperature, draughts and light in addition to fluctuations in water temperature caused by the tolerance range of the heater. The bath required periodic topping up with water, resulting in changes in temperature of several degrees for a short period of time.

Sampling

One sample was removed from each jar on a daily basis. In preliminary work (not reported here), successive samples were taken from the same jar on the same day. The results showed that the headspace concentration decreased significantly after the first injection and remained variable for the rest of the day. The final protocol included a period of equilibration between samples to allow the headspace to recover, and 24 hours was considered a suitable amount of time.

A sample volume of 500µl was selected as appropriate for direct injection onto the GC column. Because of the problem with carry-over between samples, the gas-tight syringe

was replaced with 3ml disposable syringes in this experiment, which are only graduated to 0.1ml (compared with 10µl for gas-tight syringe). This will doubtless affect the reproducibility of sample injection – a conventional GC syringe (10µl) or gastight syringe (500µl) would deliver a much more accurate sample volume.

5.3.1.2 Results

Headspace concentrations in samples of air withdrawn from jars in a waterbath at 30°C are shown in the table and figures below for tecnazene, 3-chloroaniline and 1,4-dimethylnaphthalene. Table 34 summarises the data, and Figure 61 shows the relative spread of the data for each chemical

Table 34 Mean concentrations (and associated standard deviations) for chemicals in empty jars, held in a waterbath at 30°C

Chemical	Mean concentration (µg l^{-1})	Standard Deviation
3-chloroaniline	356.50	82.4
DMN	7.54	1.2
Tecnazene	20.80	5.0

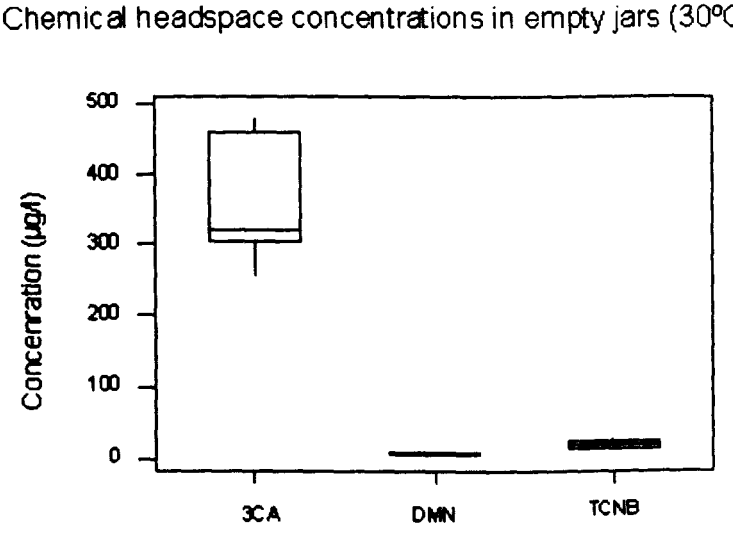


Figure 61 Headspace concentrations of three chemicals in empty jars at 30°C

5.3.1.3 Discussion

Crystals of tecnazene were seen to form on the surface of the glass jar, suggesting that the air concentration had reached saturation at some point, but as temperature fluctuated slightly, crystals began to nucleate on the glass. The variation in concentration could be related to this and the change in surface area of the solid with time.

The data set for each chemical as shown in Figure 61 consists of values from three separate jars, as no note was kept in this initial study of which jar each individual sample was taken from. Overall, 3CA values were much higher than both DMN and tecnazene but no more variable when standard deviation was considered relative to the mean value.

The DMN concentration was less than TCNB, and significantly less than 3CA, which was unexpected considering their relative vapour pressures. This could be either because the amount of DMN added to the jar was not sufficient to generate a saturated vapour, or because of the effect of the chemical being sorbed onto a solid support.

Where 2% dust was used as the chemical source, there was less chemical in the system, as the weight of dust was similar to the weight of 'pure' chemical in other experiments.

When chemical is added neat to the jar, equilibrium will be established between the pure chemical and the air, where diffusion across the surface of the liquid is the only mechanism in action. Where the chemical is held on a solid support (e.g. alumina) volatilisation back off the surface into the air is an additional process that requires energy, and as a result the amount of chemical in the air at equilibrium may be different. Later work showed that volatilisation back off a solid (in spiked soil experiments) resulted in a far lower headspace concentration for the same weight of chemical.

5.3.2 Jars held in incubator at 20°C

5.3.2.1 Experimental set-up

A number of empty jars were set up to measure the headspace concentrations of each chemical under different conditions to those previously described. This time, however, the jars were held in an incubator rather than a waterbath in an attempt to reduce the variability among replicate samples. The temperature was also reduced from 30°C to 20°C. While the effect of a change in temperature is interesting in itself, it was changed in this instance because facilities were limited and another experiment was already underway at 20°C in the only available incubator.

Triplicate jars were set up for each chemical, with needle guides in each. However, an extra jar of DMN was also included where the needle guide was omitted. O'Hagan (1991) found that the presence of the guide could interfere with measured concentrations of substituted naphthalenes, of which DMN is an example.

5.3.2.2 Results

The boxplot below shows the range of data for DMN and tecnazene. 3-chloroaniline is not included on the same graph because of its significantly higher concentration.

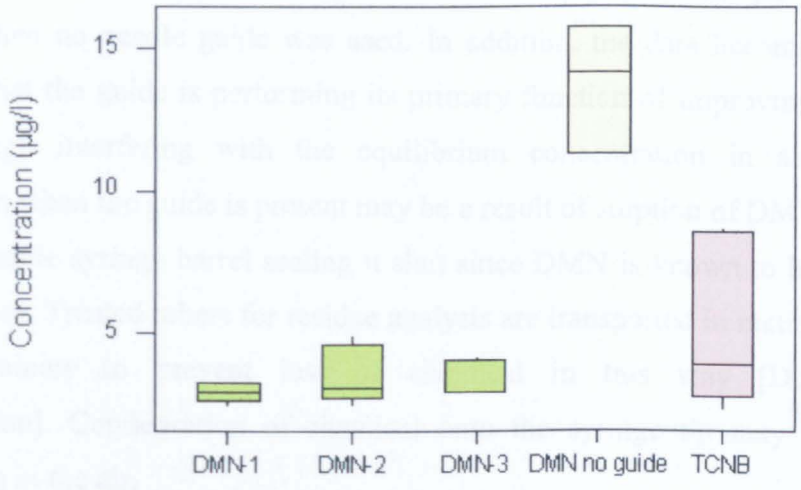


Figure 62 Range of concentrations of DMN and tecnazene in jars at 20°C

Table 35 Mean concentrations (and associated standard deviations) for chemicals in empty jars, held in an incubator at 20°C.

Chemical	Mean concentration ($\mu g\ l^{-1}$)	Standard Deviation
3-chloroaniline	93.30	35.43
DMN with guide	1.65	0.36
DMN no guide	6.89	1.12
Tecnazene	2.73	1.42

5.3.2.3 Discussion

DMN and tecnazene

From the boxplot, it can be seen that there is no difference between the three jars containing DMN with a needle guide (DMN-1 to DMN-3). Statistically, there is no difference between these data and the TCNB data, although the tecnazene concentration was much more variable. Data from all three tecnazene jars are shown as one set in the boxplot because details of which sample came from which jar were lost during the experiment.

The boxplot also shows that the headspace concentration in the DMN jar was significantly increased when no needle guide was used. In addition, the data become more variable, suggesting that the guide is performing its primary function of improving reproducibility well, although interfering with the equilibrium concentration in air. The reduced concentration when the guide is present may be a result of sorption of DMN onto the guide or the disposable syringe barrel sealing it shut since DMN is known to be adsorbed onto certain plastics. Treated tubers for residue analysis are transported in metal tins rather than plastic containers to prevent loss of chemical in this way [Duncan, personal communication]. Condensation of chemical onto the syringe tip may also reduce the concentration in the air.

Although there is significantly more chemical in the air when the guide is removed, the concentration of DMN in the jar is still far lower than was originally expected, given its volatility. The source in these jars was a 2% dust of DMN (0.2g dust), which equates to 0.004g of pure chemical. The nature of the source itself could be responsible for the low concentration in air: in this situation it is important to distinguish between a saturated vapour concentration and the concentration achieved under equilibrium conditions within the jars.

With a saturated vapour, the temperature of the air is limiting rather than the amount of chemical in the system: adding more chemical will make no difference to the concentration. An increase in air temperature would allow more chemical to volatilise and be present in the vapour phase, and a decrease in air temperature would result in a reduction in concentration.

When chemical is added to the jar in pure liquid form, the only process that occurs during equilibration is diffusion of molecules across the surface of the liquid into the air. The

amount of chemical present as vapour is dependent on the vapour pressure of the liquid and the temperature of the air, which may become the limiting factor once a saturated vapour is achieved.

In contrast, if the chemical is held on a solid support, the situation becomes more complicated. To be found in the vapour phase, chemical must actively volatilise off the surface of the impregnated carrier and compete against any affinity it has for the solid. The extent to which the vapour concentration is reduced in this situation depends largely on the nature of the solid and how strongly it retains the chemical. In this experiment, the relatively inert alumina support allows a measurable amount of chemical to volatilise into the air, even though the total amount of chemical in the system is significantly less than in other jars where 3-chloroaniline and tecnazene are added as pure chemical. The absolute reduction in vapour concentration due to the DMN being added on alumina rather than as pure chemical cannot be determined in this case, because in later experiments where liquid DMN was added the weight of chemical was different.

3-chloroaniline

Individual concentrations of 3CA determined in empty jars ranged between 44 and 180μg l^{-1} with an average of 93μg l^{-1}. These levels are considerably lower than those determined in a waterbath at 30°C, and also the calculated saturated vapour concentration of 468 μg l^{-1} at 25°C. However, pesticide vapour pressures can vary significantly for a change in temperature of only a few degrees so it is possible that at 20°C the concentration could be much lower than the textbook value at 25°C.

Summary

When compared with data from empty jars containing equivalent weights of chemical held at 30°C in a waterbath, the mean values for each chemical are lower (with the exception of the 'DMN no guide' data set, which was not included in the 30°C study), illustrating that headspace concentration in empty jars is strongly correlated with air temperature.

The concentration of 3-chloroaniline was significantly higher than DMN and tecnazene. This was the expected result, given its higher volatility.

Tecnazene (TCNB) produced the most variable results, and the concentration in air was very low, thus only 3-chloroaniline and 1,4-dimethylnaphthalene were used in the next set of experiments to examine the effect of various adsorbent materials on headspace

concentration. Although DMN also produced low concentrations, the variability was much less. The small amount of chemical in air is believed to be a consequence of the chemical being added as a dust, rather than as pure liquid. More chemical should be found in the air above a pure source than above an impregnated carrier. TCNB use in the EU is now banned, so it is not necessary to investigate its behaviour too closely. However, it is important to note that residues of tecnazene are still being detected on crop and in stores where it was previously used for many years [R.Barnes, personal communication]. The ease of detection of the compound by GC-FID means that it is relatively easy to detect traces of chemical in crop and stores, which can cause problems in terms of meeting statutory guideline levels.

5.4 3-chloroaniline and DMN headspace in jars containing sorbent materials

When chemical is added to an empty, sealed jar, equilibrium is achieved between the pure chemical (either liquid or solid) and the atmosphere through diffusion across the surface of the chemical. Vapour pressure and air temperature are the most important factors governing the amount of chemical in the air.

In contrast, when other materials are present, the equilibrium concentration in the air will be determined by the partitioning of chemical between the three phases – pure chemical, air and solid/liquid. Partitioning behaviour will be dependent on a number of factors including volatility, solubility, Henry's Law constant, uptake onto organic matter/clays/mineral components of soil and the affinity of the material for the chemical.

In the first set of described experiments, two different soils were added (dry) to the jars. In later trials, a series of adsorbent materials with different properties were also included.

5.4.1 3-chloroaniline headspace in jars containing soil (30°C incubator)

5.4.1.1. Introduction

3-chloroaniline was selected as the most appropriate chemical for use in the following piece of work because it had the highest concentration in air in empty jars (at least an order of magnitude higher than the other two). 3CA is also a good choice because it is known to be a product of microbial degradation of CIPC in soils [Kaufman and Kearney (1965); Burge and Gross (1972)]. It has also been identified in samples of air from experimental

potato stores, as described in Chapter 4 of this thesis, where it is believed to result from the thermal degradation of chlorpropham during application. These experiments were designed to investigate

1. How the presence of soil affects the headspace concentration above the chemical source

2. Whether different types of soil cause significantly different effects under similar conditions

3. Any effect of the way chemical was added to the jar (e.g. spiked onto soil vs. free liquid) on the resultant concentration

The amount of chemical either taken up from the air or released off soil surfaces in these jars will be determined by a number of factors including temperature, humidity, soil characteristics, and the partitioning behaviour of the particular chemical between liquid, air and solid material under experimental conditions.

5.4.1.2. Experimental

Storage and sampling

Jars were held in an incubator at 30°C, with temperature held to within ± 1°C of the set point, except when the door was opened to remove a sample when changes of several degrees were common (to either side of set point: temperature reduced when the door was open, and commonly overshot after it was closed again). Needle guides were used in every case, since 3CA concentrations in previous experiments had approached the saturated vapour concentration and sorption onto plastic was assumed to be negligible. (With tecnazene, the concentration was less than the calculated saturated vapour concentration, so there may have been some sorption onto the plastic. However, this effect was not investigated any further as TCNB was not used in this set of experiments).

Triplicate jars were set up for each treatment, and a 500µl sample was collected in a 3ml disposable luer-lock syringe daily.

Soils

Two different types of soil were used in these experiments to determine whether the characteristics of the soil had a significant effect on partitioning of chemical between the

air, the solid and the pure chemical state. Soil organic matter is strongly correlated with uptake of pesticides, so soils containing very different amounts of organic matter were selected to exaggerate any effect. Table 36 below describes the characteristics of the two soils used in the study.

Table 36 Characteristics of two soil types used in headspace studies

Soil type	Approximate percentage		
	Sand and silt	Clays	Organic matter
Barassie (mineral)	90	4	5
Fen Peaty (organic)	10	48	41

Both soils were air dried and passed through a 2mm sieve. Approximately 10g were weighed out (top pan balance) and added to the bottom of the jar using a plastic funnel.

Chemical source

0.1g of 3-chloroaniline was added to the jar in the form of liquid, which was weighed into a 2ml vial. The vial was suspended on thin wire from the neck of the jar, which was held fast by the alloy lid once crimped into place (as shown in Figure 60). In each jar, the vial was suspended approximately half way between the soil and the lid.

In addition, a set of jars was also included in which the chemical was added in the form of a spiked soil. 10ml of 1000ppm 3CA in hexane were added to 10g Barassie soil and mixed well. The solvent was allowed to evaporate off at room temperature, and then the soil was added to the bottom of a jar using a plastic funnel. The aim was to determine whether enough chemical volatilised back from the surface of the soil to result in a quantifiable concentration in the air. Barassie soil was used in preference to Fen Peaty because the chemical will be less strongly held on mineral surfaces than on organic matter, making desorption from the soil more likely.

5.4.1.3 Results

Chemical suspended in vial above the soil

The table and figure below compare the chemical concentration determined in each jar under each set of circumstances. The boxplot below (Figure 63) shows the full data set for each treatment on the same axes for easy comparison of values and ranges of data.

Table 37 Mean headspace concentrations with 3-chloroaniline source suspended in vial from the neck of the jar (incubator 30°C).

Soil type	Mean concentration (µg l^{-1})		
	Jar 1	Jar 2	Jar 3
Empty jar	470.1	482.7	439.1
Barassie (mineral)	32.4	20.5	38.0
Fen Peaty (organic)	35.1	20.4	8.0

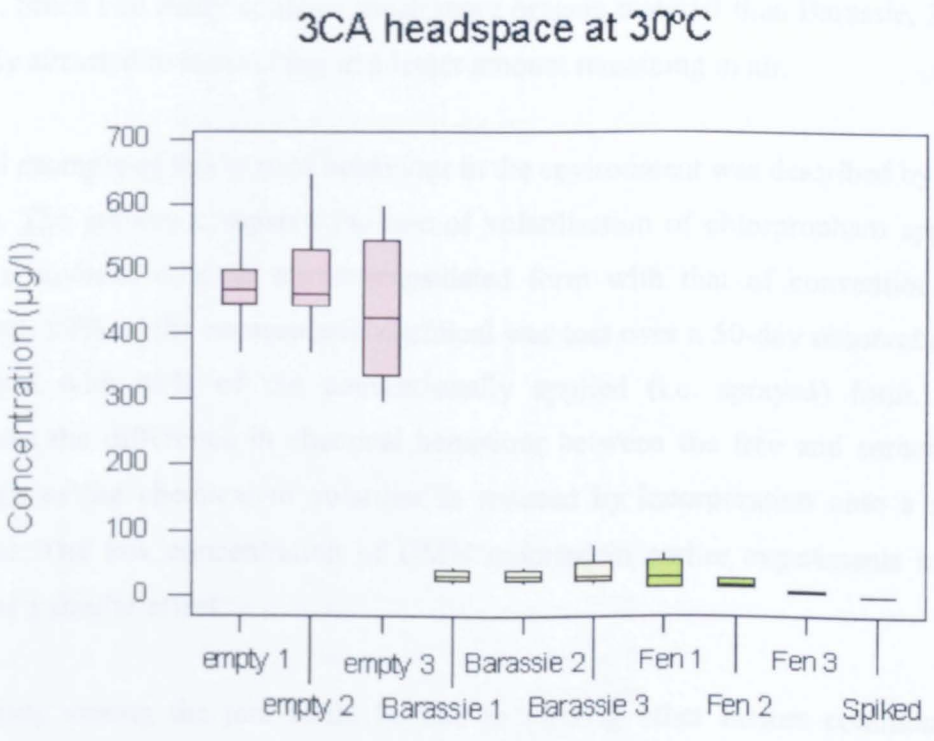


Figure 63 Headspace concentrations in jars where chemical source is either suspended above the soil or spiked onto the soil

5.4.1.4 Discussion

Chemical source suspended above soil

There were no significant differences identified between jars containing the same material, so each set of three replicate jars were taken together and considered as one data set.

With soil in the jar, the concentration is significantly (p=0.000) reduced relative to an empty jar held under the same conditions.

There was found to be a statistically significant difference between the headspace concentrations above the two soil types (p = 0.004), with the air concentration higher above Barassie soil (sandy) than Fen Peaty (organic). Although statistically significant, the difference in terms of concentration is small. It is assumed that the amount of chemical in air at equilibrium is affected by the presence of the dry soil in the jar, since chemical will be partitioned among the three media (i.e. chemical liquid, air and solid surface). The nature of the chemical and the properties of the soil (e.g. organic matter content and texture) will both be important in determining the partitioning behaviour of the chemical in the jar. Since Fen Peaty contains much more organic material than Barassie, 3CA is more strongly attracted to it, resulting in a lesser amount remaining in air.

A good example of this type of behaviour in the environment was described by Turner *et al* (1978). The authors compared the rate of volatilisation of chlorpropham applied to soil under a soybean crop in microencapsulated form with that of conventionally applied chemical. 20% of the encapsulated chemical was lost over a 50-day observation period as compared with 49% of the conventionally applied (i.e. sprayed) form. This effect illustrates the difference in chemical behaviour between the free and sorbed form. The tendency of the chemical to volatilise is reduced by incorporation onto a solid carrier material. The low concentration of DMN reported in earlier experiments might be the result of a similar effect.

Variability among the jars could be due to (among other factors common to all e.g. sampling procedure and temperature control) small differences in the weight of soil present in each (approximately 10g weighed to two decimal places), and variation in the composition of the soil in each jar. By nature, soils are not homogeneous and although the approximate composition of each soil type is known, each 10g as added to the jar may not

contain clay, sand/silt and organic matter in exactly the stated proportions. In addition to its high organic matter content, Fen Peaty soil also contains a lot of clay (although the type of clay is not specified). Significant amounts of pesticide can also be adsorbed onto clay minerals, although for weakly polar or non-ionic pesticides, sorption onto soil organic matter content is the most important uptake process [Spencer and Cliath (1983)].

Chemical added as a spiked soil

When 3-chloroaniline was added to the jar in the form of a spiked soil (Barassie) the resultant headspace concentration is significantly lower than where the same weight of chemical is suspended above the same weight of soil. In this case, a different set of processes is governing the amount released into the air. When chemical is incorporated into the soil the amount diffusing across the soil/air boundary is dependent on not only the factors described above governing the distribution of chemical in each compartment, but also the concentration in the surface layer of the soil, and the rate at which air is transporting across the boundary. In real-world environmental situations (e.g. where a pesticide is applied to the surface of the soil) there will be a significant flux of chemical due to air movement, the evaporation of water from the soil and the 'wick effect' transporting more chemical to soil surfaces to replace that lost through volatilisation. However, in these small jars, there is no incentive for air movement or diffusion of chemical out of the soil, and thus the system becomes static. The small concentration in air is mainly governed by the amount of chemical present on the top surface of the soil, which could be a relatively small proportion of that applied. The larger the exposed surface area, the more chemical may be found in the air.

5.4.2 Effect of a range of sorbent materials on concentrations of DMN and 3CA in air (30°C incubator)

It has previously been shown that the presence of soil in sealed containers can significantly reduce the amount of chemical present in the air. The following experiments were carried out in order to determine whether the type of material in the jars has an effect on the magnitude of the change. Sorbents were selected to represent the type of materials likely to be encountered in a potato store.

The chemical properties of the 2 chemicals are very different e.g. DMN is nonpolar and relatively insoluble in water (5.1ppm) while 3CA is more polar and more water-soluble (6,000ppm). The sorption and partitioning behaviour of the two might therefore vary considerably. It is useful to know whether each chemical has particular affinities for one

material over another (e.g. peel vs soil), as this will allow us to predict how the chemical will behave in a potato store and where it is likely to end up (e.g. remaining in the air, deposited on crop, sorbed onto insulation, concrete etc).

5.4.2.1 Experimental set-up

Chemical sources

Both 3-chloroaniline and 1,4-dimethylnaphthalene were added to the jars in liquid form. 0.1g of liquid was weighed into a 2ml vial, which was then suspended from a thin wire above the sorbent material.

Adsorbents

3-chloroaniline: 3CA liquid was weighed into jars containing:

- empty jar (control) – with and without needle guide
- 20ml water
- 10g dirty potato peel
- 10g washed potato peel
- 0.15g polystyrene packing beads

1,4-dimethylnaphthalene: No needle guides were used because of the significant reduction in headspace noted in earlier experiments. DMN liquid was weighed into vial suspended in jars containing:

- empty jar (control)
- 20ml Water
- 0.15g PS foam
- 10g dirty potato peel
- 10g washed potato peel

- 20g dry Barassie soil

- 20g wet Barassie soil

5.4.2.2 Headspace concentration of 3-chloroaniline in jars containing a range of adsorbent materials.

Results

The figures and tables below show the relative concentrations of 3CA identified in air from airtight jars containing a range of materials when held at 30°C.

Table 38 overleaf shows the measured concentrations in jars with adsorbent materials, and expresses them as the percentage reduction relative to the mean concentration in empty jar after equivalent periods of equilibration. Figure 64 shows the mean values and relative spread of the data for each material.

Discussion

The main points illustrated in this graphical representation of the data are:

- The presence of anything in the jar other than the chemical itself significantly reduces the amount of chemical in the headspace

- Although the mean values are very similar, there is much greater variability in concentration in an empty jar when no needle guide is used (relative to data from a jar with needle guide). In contrast to the DMN situation (where mean value is also reduced) there does not appear to be significant sorption or condensation of 3CA onto the guide.

- No outliers in the data sets – needle guides were used in all jars (except in one empty jar), and appear to perform the function of limiting variability well (as discussed in earlier section).

- No significant difference between washed and dirty peel, so the chemical shows no real affinity for either soil or potato skin over the other. Comparison of these values with those from previous 3CA experiment where soils were included shows the effects to be similar (concentrations above Fen and Barassie soils ~30$\mu g\ l^{-1}$). Slightly more sorbed onto the clean skin surface, with less variable results than for dirty peel.

- Presence of water significantly reduces chemical concentration in air, suggesting that solubility is not a problem. Either that or an effect of increased humidity.

- PS foam appears to have the least effect, but in terms of weight there was significantly less of it in the jar (0.15g as compared with ~10g peel). On a weight per weight basis, the uptake is more, but per unit volume it is less than any of the other materials.

Table 38 Mean 3CA concentrations in jars containing sorbent materials, and reductions relative to an empty jar[1]

Sorbent material	Mean concentration ($\mu g\ l^{-1}$)	% reduction relative to mean value for empty jar
Empty	302.1	-
Polystyrene foam (0.15g)	143.6	52.5
Water (20ml)	70.8	76.6
Dirty potato peel (10g)	44.9	85.1
Washed potato peel (10g)	31.4	89.6

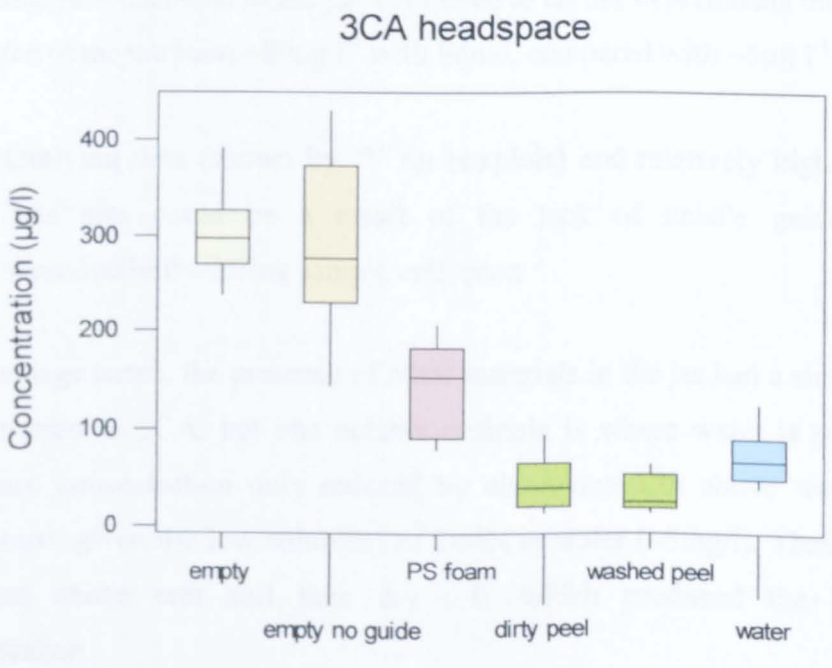


Figure 64 Comparison of range of values for 3CA concentration in air from jars containing a variety of materials

[1] Mean value for comparison taken from the empty jar with needle guide

Overall, potato peel elicited the biggest reduction in chemical concentration (>85% less), followed by water which caused a 75% reduction, while even the small amount of polystyrene resulted in a drop in concentration by half.

5.4.2.3 Headspace concentration of 1,4-dimethylnaphthalene in jars containing a range of adsorbent materials.

Results

Figure 65 and Table 39 below show the concentrations of DMN determined in air from sealed jars containing a range of adsorbent materials. The boxplot (Figure 65) shows the entire data sets, including any outliers, while the means shown in Table 39 were calculated and statistical analysis carried out after the removal of outlying points. The reduction in concentration relative to an empty jar is also shown in Table 39.

Discussion

The main points illustrated in the boxplot overleaf are as follows:

- The presence of any material in the jar resulted in a significant drop in air concentration relative to an empty jar.

- The DMN concentration in air from empty jars has been significantly increased by adding pure chemical to the jar, compared to earlier experiments that used 2% dust as a source (concentration ~80μg l^{-1} with liquid, compared with ~5μg l^{-1} with dust)

    - Outlying data (shown by '*' on boxplots) and relatively high variability in most data sets could be a result of the lack of needle guide leading to poor reproducibility during sample collection

In percentage terms, the presence of other materials in the jar had a similar effect on DMN concentration to 3CA, but one notable example is where water is present. With DMN, headspace concentration only reduced by about one-fifth above water, which was not unexpected, given the low solubility of DMN in water (~5mg/l). There was also less of a reduction above wet soil than dry soil, which produced the biggest change in concentration.

Dry Barassie soil caused a >90% reduction in the concentration of DMN, which is similar to its effect with 3-chloroaniline.

Table 39 Mean DMN concentrations in jars containing sorbent materials, and reductions relative to an empty jar

Sorbent material	Mean concentration (µg l^{-1})	% reduction relative to mean value for empty jar
Empty jar	83.5	-
Water (20ml)	65.4	22
Wet soil (10g + 10ml)	27.6	67
Polystyrene foam (0.15g)	25.9	69
Dirty potato peel (10g)	23.5	72
Washed potato peel (10g)	20.8	75
Dry soil (10g)	6.5	92

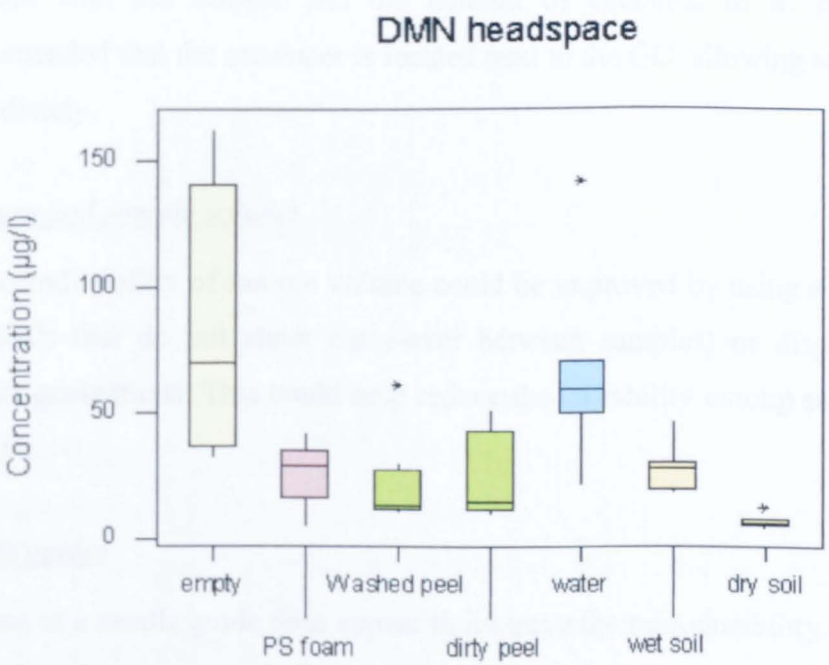


Figure 65 Comparison of the range of DMN headspace concentrations in samples from jars containing a variety of materials at 30°C

5.5 Summary of results and conclusions from direct headspace experiments

5.5.1 Experimental procedure

There was a great deal of variability in the results, attributable at least in part to the way in which the experiment was carried out.

Temperature control

Holding jars in an incubator rather than a waterbath produced more consistent results, although temperature fluctuations when the door was opened could have an impact on samples collected later in the day from jars that had been subject to several cycles of temperature change.

Location of practical work

The incubator and waterbath were located in the laboratory, while the GC was in a separate room. This resulted in a delay of approximately one minute between sample collection and injection onto the GC. During this time, changes in air temperature inside the syringe could interfere with the sample and the amount of chemical in it. In future work, it is recommended that the incubator is located next to the GC, allowing samples to be analysed immediately.

Syringes and sample volume

The reproducibility of sample volume could be improved by using a gas-tight syringe (for chemicals that do not show carry-over between samples) or disposable syringes with smaller graduations. This could help reduce the variability among samples taken from the same jar.

Needle guides

The use of a needle guide does appear to improve the reproducibility of injections from the same jar. However, a material must be selected that does not interfere with the concentration of chemical in the air i.e. by sorption onto plastic. Wide-bore syringe tips were suitable for 3-chloroaniline, but not for DMN. In future work with DMN, perhaps a glass or metal insert would be more suitable. A glass-bodied syringe might also be more appropriate.

5.5.2 Summary of results

- The presence of any material in the jar significantly reduced headspace concentration above a chemical source, relative to an empty jar.

- The magnitude of the change is dependent on the properties of the source chemical and the characteristics of the sorbent material.

- Reproducible results were obtained among and within jars and treatments, so the sampling system is, in principle, a success.

- The use of needle guides reduced the variability among samples taken from the same jar, although they interfered with the DMN concentration (as described in earlier sections) as a result of uptake of chemical onto the plastic.

- Headspace concentration reduced by >90% for DMN and 3CA above a dry soil.

- Significant amounts of chemical were taken up by a small weight (0.15g) of polystyrene packing beads.

- DMN appears to favour dry soil slightly over potato peel (~70% reduction with peel; >90% with soil), while the effect on 3CA concentration is similar for both substances (~90% reduction in headspace concentration).

5.5.3 Implications for the use of chemicals in the potato industry

The significant uptake of both 3-chloroaniline and 1,4-dimethylnaphthalene onto polystyrene packing material means that exposed store insulation may be an important sink for significant amounts of applied sprout suppressants. This may present problems both in terms of efficacy of treatment (if considerable amounts of chemical are lost) and a future crop contamination problem if/when the chemical volatilises back into the air.

3-chloroaniline: Analysis of air samples from commercial and experimental stores have shown that 3CA is present in detectable amounts (of the order of $\mu g\ l^{-1}$ or less) following thermal fog applications of CIPC. Therefore, examining its partition behaviour in these small experiments can help identify where in the store it is likely to be found. The presence of soil or potato material in the jars reduced the amount in air by upwards of 80%, suggesting that any chloroaniline in the store may favour sorption onto crop surfaces over remaining in the air. 3CA is listed on the EU Priority Pollutants Circular No. 90-55,

making it a compound of acute environmental interest. The possibility that it may find its way into human food supplies is bound to raise concerns. Porous polymer material seems to have a strong affinity for the chemical, so sorption onto insulating materials might remove the majority of the chemical from air.

1,4-dimethylnaphthalene: by looking at the percentage reductions in headspace concentration when soil, peel or polystyrene foam is present in the jar relative to an empty jar, it appears that DMN too will favour adsorption onto solids over remaining in the air.

Limitations of the method: It is important to remember that the conditions under which these small experiments were carried out are very different to those experienced in a potato store.

These experiments were carried out in a static system, with no movement or exchange of air, so once equilibrium is attained inside the jar, no significant changes occur. However, potato stores are leaky, and must be ventilated regularly, so movement and replacement of the store atmosphere will be happening on a daily basis. This study does not provide any detail on the volatility of any of the compounds under such conditions. In practice, significant reductions in crop residues of DMN can be achieved using brief periods of airing prior to removal from store [Duncan, personal communication].

In future work, a dynamic system where air or an inert carrier (e.g. N_2) is gently moved through the jars would provide more information on the rates of chemical loss from the system under more 'real-life' conditions.

Chapter 6

STUDIES ON CIPC LEVELS IN POTATO WASHING WATER AND UPTAKE ONTO SOLID SURFACES

6.1 Introduction

6.1.1 Background to the study

Pressure is growing on the potato industry, through its retail markets and government legislation, to improve the efficiency of chlorpropham use. While residues in food are often the most talked about issue, the presence of CIPC in wash-water effluent released into the environment is another important area of concern.

In a recent survey of chlorpropham use and store management practice (described in Chapter 2), 15% of respondents indicated that crop is washed at their stores, and with more and more of the larger processors expecting crop to be washed prior to delivery, this figure is likely to increase. By putting the responsibility for crop washing back onto the supplier, the processors are freed of any accountability for the pollution problems created. The result is a decrease in the small number of identifiable point sources of chlorpropham generated by large washing facilities, and an associated increase in smaller outputs, which are less easily identified and monitored by the Environment Agency (SEPA in Scotland).

The Environmental Quality Standard (EQS) for chlorpropham in surface freshwater is 10μg l^{-1} as an Annual Average (AA), with a Maximum Allowable Concentration (MAC) of 40μg l^{-1} for an individual sample [Martin, 2002]. Minimum Reporting Values (MRV) are set for dangerous substances discharged to surface waters, and are 0.005μg l^{-1} and 0.05μg l^{-1} for chlorpropham and tecnazene respectively. The setting of an MRV aims to provide consistency in reporting as well as some allowance for sample variation.

Large volumes of CIPC contaminated effluent are produced in washing operations, and may receive little or no treatment prior to discharge into watercourses or to drain. In addition to the liquid fraction of the effluent, the solid fraction (e.g. any associated sediment or potato components) must also be dealt with. At present, removal to landfill is the only approved method of disposal, although solids are often spread back onto agricultural land or stored onsite until residue levels decline.

6.1.2 EU Legislation:

Both chlorpropham and its metabolite 3-chloroaniline are classified in the UK by the Joint Agency Groundwater Directive Advisory Group (JAGDAG) as List I substances under the EC Groundwater Directive (80/68/EEC). List I substances are those which "must be prevented from entering groundwater".

The Discharge of Dangerous Substances to Surface Waters Directive (76/464/EEC) has now been integrated into the EU Water Framework Directive (2000/60/EC). Environmental Quality Standards (as annual averages) have been established under these directives for the sprout suppressants chlorpropham and tecnazene in surface waters at $10\mu g\ l^{-1}$ and $1\mu g\ l^{-1}$ respectively. The corresponding Maximum Allowable Concentrations (MAC) are $40\mu g\ l^{-1}$ for chlorpropham and $10\mu g\ l^{-1}$ for tecnazene.

6.1.3 Structure of the reported work

The reported studies were conducted to explore the likely chemical load in chlorpropham contaminated washing water effluent, and to investigate how chemical present in effluent might partition itself in the environment. Three studies were conducted to investigate:

1. Levels in samples of washing water at various points in the treatment process.

2. The potential for cross-contamination and uptake of residues onto untreated crop during the commercial washing process.

3. The sorption and desorption behaviour of CIPC using potato skin and two types of soil in laboratory experiments.

Adsorption studies can be used to examine the transfer of molecules from solution onto solid surfaces such as soil. Desorption studies examine the opposite process, where chemical is released from the surface back into solution. Adsorption can occur onto various components of the soil including clays, organic matter, oxide and hydrous oxides. In the case of chlorpropham, sorption onto organic matter is believed to be the most important process [Spencer and Cliath (1983)]. Studies were conducted in the laboratory to investigate the uptake of CIPC from solution onto two types of soil, and subsequent desorption back into solution. A range of solution concentrations and contact times were

considered, and sorption and desorption isotherms were constructed which relate the amount of chemical on the soil to the amount remaining in solution.

Another important aspect of the washing process is the potential for chemical to be taken up onto the surface of untreated tubers as they pass through the washer barrel. In particular, this is an issue where organic crop is washed in the same water as treated crop, as any detectable residue can lead to rejection of the crop and considerable losses to the supplier. A similar sorption experiment to that described above was carried out in the laboratory to determine the extent of uptake onto potato surfaces.

6.2 Analysis of wash-water samples from commercial stores

6.2.1. Introduction

Large volumes of CIPC contaminated wastewater are produced on sites where treated crop is washed e.g. at pre-pack facilities or where processing crop is washed prior to delivery to the processor. Large washers are often permanently located onsite, although mobile washers are available for hire at smaller operations. When CIPC treated crop is washed, a significant amount of pesticide is removed along with any adhering soil. This may lead to significant chemical residues in washing water, which is often disposed of to drain with no treatment, although solids are commonly collected separately and disposed of to landfill.

The Environmental Quality Standard (EQS) for river water is 10μg l^{-1}, which means that washing waste with a concentration of 1ppm (1mg l^{-1}) would need to be diluted at least 1,000 times in a watercourse to meet the requirements. At the time of this study, very little information was available in the literature on the concentration of chlorpropham present in washing effluent.

A prototype treatment plant at a commercial pre-pack facility was investigated to determine its effectiveness at removing chemical residues. Settlement ponds, filtration and aerobic digestion were all employed to lower residues to within allowable discharge levels. Samples were first collected in winter, and then again in summer to show any seasonal variation due to the increased throughput of crop at that time.

Since the sampling was carried out, a more advanced version of the pilot treatment plant has been permanently installed on site [Anon (2001b); Anon (2001c)]. All effluent from the washing process is now collected in a central sump, from where it is pumped to a

clarifier, where solids are separated out by addition of a flocculant. The solids are then transferred to a press, which squeezes out up to 50% of the residual water, leaving a dry and easily handled 'cake'. The liquid fraction of the effluent progresses to a balancing tank, and then to the aerated treatment unit that provides a treatment to reduce the biological oxygen demand (BOD). This is followed by a second clarifier and two sand filters that remove any remaining solids, plus a carbon filter to remove any remaining chemical residues by adsorption. A final disinfection with chlorine dioxide is carried out as the effluent passes into a storage tank, which acts as a reservoir of clean water – the site has only a limited water supply, so the ability to produce re-usable effluent was built in to the treatment plan. Treated effluent can be used for filling washer barrels, or back-flushing the filters, and any excess can be discharged into the nearby watercourse.

6.2.2 Experimental methods

6.2.2.1 Sampling

Effluent samples were collected in 1-litre plastic bottles from a number of locations on-site in December 1999 before any washing of crop harvested that year had taken place. In January 2000, repeat samples were collected from selected locations shortly after the crop washing operation had begun. Sample locations and dates are detailed in Table 40 overleaf. A further set of samples was collected in May 2000 when throughput of crop at the washing plant was at its highest. Samples were transported to Glasgow and held in a cold room at ~4°C prior to analysis.

6.2.2.2 Sample preparation and extraction

Effluent samples were filtered through GF/C filter paper followed by a 40µm membrane filter to remove all suspended solids. Duplicate 100ml sub-samples (250ml for May samples) were extracted through Varian Bond-Elut C-18 columns at a flow rate of approximately 2ml/minute, on a VacMaster manifold. Prior to the addition of the sample, columns were conditioned with 5ml HPLC grade methanol and 5ml distilled water at a similar flow rate. After the entire sample had been loaded, the cartridge was rinsed with a further 5ml distilled water, then vacuum dried for 1 hour.

CIPC was eluted off the column in ~2ml HPLC grade acetone, and made up to volume in a 2ml volumetric flask.

Table 40 Dates and locations of effluent sampling at pilot treatment plant (1999-2000)

Sample	Location	Date
1	First settlement pond	December 1999
2	Second settlement pond	December 1999
3	Digester effluent	December 1999
4	Water from back-flushing of sand filter	December 1999
5	Discharge to watercourse	December 1999
6	Bucket under pile of peel and sludge	January 2000
7	First settlement pond	January 2000
8	Digester effluent	January 2000
9	Discharge to watercourse	January 2000
10	Bucket under pile of peel and sludge	May 2000
11	Pipe leading into first settlement pond	May 2000
12	First settlement pond	May 2000
13	Second settlement pond	May 2000
14	Digester effluent	May 2000
15	Discharge to watercourse	May 2000

6.2.2.3 Recovery check

The recovery of the method was determined by spiking C-18 columns with a known weight of CIPC, then following the extraction procedure as outlined above. Two different spiking solutions were made up in distilled water, and used to load the columns with weights ranging from 110µg to 1.1µg CIPC. The efficiency of recovery was not found to differ ($p = 0.381$) with spiking level, and the mean recovery of the method was determined to be $97.3 \pm 3.6\%$.

6.2.2.4 Analysis

Quantification of CIPC was carried out on a Pye Unicam PU45400 packed column gas chromatograph, equipped with flame ionisation detector. The GC conditions were as outlined below:

Column packing:	3% OV-17 on Gaschrom Q
Column length:	1.5 m
Injection volume:	5µl
Oven temperature:	180°C isothermal
Injector temperature:	220°C
Detector temperature	250°C
N_2 carrier:	30 ml/min

Flame H_2: 30 ml/min
Flame air: 180 ml/min

Under these conditions, CIPC had a retention time of ~3 minutes on the column.

Certain samples were run under an oven temperature programme, because air samples were being run on the second column in the oven at the same time, as detailed below:

130°C for 7 minutes
12°C/min to 180°C
180°C for 5 minutes

Under these conditions, CIPC had a retention on the column of ~10.5 minutes.

Calibration of the GC was carried out on a daily basis using standards of CIPC in HPLC grade hexane. Standards were prepared by appropriate dilutions of a 1000ppm stock solution. Data collection, integration and storage were carried out on a SP4400 integrator (SpectraPhysics).

The limit of quantification for CIPC in the samples was 0.5mg l^{-1} in the acetone extract, which equated to 0.01 mg l^{-1} for the January samples, and 0.004 mg l^{-1} in the May samples.

6.2.3 Results

The mean CIPC concentrations determined in samples from December and January are shown in Table 41 below. Duplicate 100ml aliquots of each sample were extracted, then injected in triplicate onto the GC. The table shows the concentration determined in each injection of both replicate extracts.

From the table it can be seen that the reproducibility of injections was very good: in general for GC analysis, results within 5% for replicate injections would be considered acceptable. The precision in this case is greater than this, which shows that the analytical procedure itself was not a source of significant variation in the results.

As a result, in later studies (i.e. samples from May) the number of replicate injections was reduced to one because of time constraints on the GC equipment. This could be done without compromising confidence in the results because precision had previously been shown to be very good. In addition, chromatograms were examined routinely to ensure that there was no reduction in GC performance i.e. tall, sharp peaks were consistently obtained with no deterioration in peak shape or significant accumulation of background noise.

Table 41 CIPC concentrations in acetone extracts of water samples collected in December 1999 and January 2000.

Date	Sample	Extract concentration (μg ml^{-1})		
		Injection A	Injection B	Injection C
December 1999	First settlement pond A	6.52	6.73	6.53
	First settlement pond B	9.49	9.37	9.52
	Second settlement pond A	4.68	4.39	4.73
	Second settlement pond B	5.08	5.10	5.17
	Aerobic digester effluent A	-[2]	-	-
	Aerobic digester effluent B	-	-	-
	Backflushing of sand filter A	-	-	-
	Backflushing of sand filter B	-	-	-
	Outlet to watercourse A	-	-	-
	Outlet to watercourse B	-	-	-
January 2000	Bucket under sludge pile A	85.23	88.62	88.70
	Bucket under sludge pile B	94.28	95.28	94.26
	First settlement pond A	15.06	15.14	15.76
	First settlement pond B	15.24	15.64	15.45
	Aerobic digester effluent A	-	-	-
	Aerobic digester effluent B	-	-	-
	Outlet to watercourse A	-	-	-
	Outlet to watercourse B	-	-	-

[2] - CIPC less than limit of quantification (0.5mg l^{-1} in extract)

Table 42 Concentrations in acetone extracts of water samples collected from pilot treatment plant (May 2000)

Sample	Extract concentration (μg ml^{-1})
Pipe supplying effluent to first pond A	1174.47
Pipe supplying effluent to first pond B	1182.19
First settlement pond A	649.36
First settlement pond B	645.75
Second settlement pond A	289.76
Second settlement pond B	291.59
Bucket under sludge pile A	147.24
Bucket under sludge pile B	148.19
Digester effluent A	2.21
Digester effluent B	2.95
Discharge into watercourse A	-[3]
Discharge into watercourse B	-

[3] CIPC less than limit of quantification (0.5mg l^{-1} in extract)

Table 43 Mean CIPC concentrations in samples of effluent collected between December 1999 and May 2000 at a pilot-scale effluent treatment plant.

Date	Sample	Mean effluent CIPC concentration (mg l^{-1})
December 1999	First settlement pond A	0.132
	First settlement pond B	0.190
	Second settlement pond A	0.092
	Second settlement pond B	0.102
	Aerobic digester effluent A	< LOQ[4]
	Aerobic digester effluent B	< LOQ
	Backflush of sand filter A	< LOQ
	Backflush of sand filter B	< LOQ
	Discharge to watercourse A	< LOQ
	Discharge to watercourse B	< LOQ
January 2000	Bucket under sludge pile A	1.750
	Bucket under sludge pile B	1.892
	First settlement pond A	0.306
	First settlement pond B	0.309
	Aerobic digester effluent A	< LOQ
	Aerobic digester effluent B	< LOQ
	Discharge to watercourse A	< LOQ
	Discharge to watercourse B	< LOQ
May 2000	Pipe leading to first settlement pond A	9.396
	Pipe leading to first settlement pond B	9.458
	First settlement pond A	5.195
	First settlement pond B	5.166
	Second settlement pond A	2.318
	Second settlement pond B	2.333
	Bucket under sludge pile A	1.178
	Bucket under sludge pile B	1.186
	Aerobic digester effluent A	0.018
	Aerobic digester effluent B	0.024
	Discharge to watercourse A	< LOQ
	Discharge to watercourse B	< LOQ

6.2.4 Discussion

6.2.4.1 Winter samples (December 99 – January 00)

December 1999 samples were collected before any washing of crop harvested in 1999 had been carried out. As a result, any chlorpropham present in the samples is residual chemical left over from the last season. The absence of a sample from the sludge pile is also explained by the fact that no washing had yet been carried out that season.

By January, a small amount of crop washing had been carried out, and a sludge pile was present on the site. Residue levels in the settlement ponds were already beginning to increase (0.3mg l^{-1} as compared to 0.1mg l^{-1} in December), although no sample was collected from the second settlement pond because it was inaccessible on the day of the site visit due to very muddy conditions.

The only locations where quantifiable amounts of CIPC were found in winter were the two settlement ponds, and a bucket collecting run-off from a pile of sludge. At this time of year, the concentration in the ponds is fairly low (<0.5ppm) but significantly higher than the EQS (MAC = 40µg l^{-1}). The concentration in water in the first pond reduces by about half by the time the effluent reaches the second pond, suggesting that settlement of particles can significantly reduce the load of chemical.

The digestion and filtering processes reduced the chlorpropham concentration in the effluent to below the limit of quantification (LOQ) of the GC method. In a GC method like this, the LOQ of the method is largely a function of the volume of the sample extracted, although the sensitivity of the detector is also an important consideration. Because the concentrations in most of the January samples were less than the limit of quantification, in May the extracted volume was increased to 250ml in an attempt to quantitatively identify chlorpropham in samples from the digester and the outlet to the watercourse.

Duplicate samples generally had very similar concentrations (with the exception of the samples collected from the first settlement pond in December), and can be assumed to be representative of the effluent in the respective parts of the treatment process.

[4] CIPC less than limit of quantification. December-January 0.01mg l^{-1} and May 0.004mg l^{-1} in water sample

6.2.4.2 Summer samples (May 2000)

The sampling points are mainly the same in both January and May, although an extra sample was taken in May from a pipe laid underground bringing 'raw' untreated washing effluent from the pack-house into the first settlement pond in the treatment plant. The liquid coming out of the pipe was still cloudy after filtering through GF/C filter paper. This effect may be due to the presence of potato components present in the solution (a similar effect was noted when potato flesh was shaken with CIPC solutions in the lab: they initially filtered clear, but developed cloudiness over time). No potato processing was carried out onsite; therefore only small amounts of starchy material, released as a result of tuber damage during the washing process, will be present. This raw effluent contained around 10ppm chlorpropham, which is a similar level to that found in samples from other washers [Park, unpublished results].

Figure 66 below illustrates the reduction in chemical residue at each stage of the treatment process

Residue levels in the second pond are approximately half those in the first pond, showing that settlement can have a significant effect on the chemical load. The concentration in the first pond is approximately half of that in the raw effluent. It would be interesting to know the residence time of the effluent in the pond, but no information on this was available at the time of sampling. As a result, we cannot determine the rate at which the residues decline in the pond.

By the time the effluent leaves the digester, the chemical concentration has reduced by >95% to 0.02mg l^{-1}. This concentration is twice the EQS of 10µg l^{-1} for surface water – however, a maximum allowable concentration (MAC) of 40µg l^{-1} exists for individual samples.

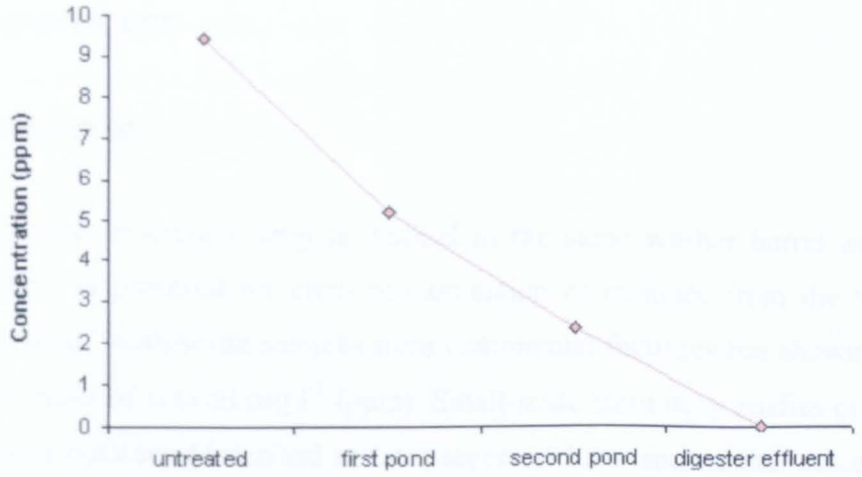


Figure 66 Decrease in chlorpropham residue levels in effluent following various stages in the treatment process

At the point where the effluent enters the watercourse, the concentration had reduced to < 0.004 mg l^{-1} (4µg l^{-1}), which is well within the EQS guidelines and would not create any problem in terms of consented discharges.

Residue levels in the effluent at various stages in the treatment process are consistently higher in May than in January, showing a clear seasonal variation in levels related to the throughput of crop, and the increased number of treatments received by crop stored for longer periods of time. Figures from a survey on chlorpropham use (reported in Chapter 2) show that the major movement out of stores occurs after 6-7 months of storage, which would mean that washing is at its most intense in May-June. Any raw effluent would require significant dilution in order to meet EQS requirements, which might present a particular problem in summer when residue levels are high, but the watercourses are at their lowest.

Figures on the volume of effluent produced and the tonnage and treatment history of the crop washed would have provided useful background to this study, but no information of this type was gathered as a part of this study. In all future studies relating to crop washing, it was included as standard.

6.3 Study on potential for cross-contamination of crop during the washing process

6.3.1 Introduction

Where untreated or organic crop is washed in the same washer barrel as CIPC-treated material, there is potential for cross-contamination of residues from the water onto the crop. Analysis of wash-water samples from commercial facilities has shown residue levels to be of the order of several mg l^{-1} (ppm). Small-scale laboratory studies on the uptake of chemical onto potatoes (described in later sections) have shown that detectable residues can be found on untreated crop after a relatively short time (1hr) in contact with solutions with concentrations as low as 1ppm.

This small study was carried out in March 2002 and investigated the likelihood of detectable residues being picked up onto set-skin maincrop potatoes (free of CIPC) as a result of washing in water previously used for washing CIPC treated material.

Samples were collected from commercial washing facilities at GeestQV (Holbeach Hurn, Lincs) and sent to Glasgow for analysis. Washing samples, in particular, were analysed within a couple of days of being received at Glasgow, as sample quality deteriorated rapidly. Septicity was a particular problem, since starch and other organic components had not been removed from the solution prior to transport.

6.3.2 Sampling

6.3.2.1 Water sampling

Samples of washing water were collected directly from the washer barrel in 2-litre plastic bottles three times throughout the day:

1. First thing in the morning, once the barrel had been filled with mains water, but before any crop had gone through the system.

2. After 26 tonnes of CIPC treated potatoes (*cv.* King Edward) had passed through.

3. After a further 26 tonnes of untreated material (*cv.* Maris Piper) had been washed.

6.3.2.2 Treatment history of crop and crop sampling

During the day, tuber samples were also taken from the two loads of potatoes going through the washer. The first load (*cv* King Edward) had received two treatments with MSS CIPC 50M and was sampled both prior to and post-washing. The second load (*cv* Maris Piper) had received no CIPC treatment in store at all. They were washed in the barrel after the CIPC treated crop, and again were sampled pre- and post-washing.

Each load took approximately 10 minutes to pass through the washer barrel, which had a capacity of 2,500 litres.

6.3.3 Extraction and analysis

6.3.3.1 Preparation and extraction of water samples

500ml of unfiltered solution was measured into a volumetric flask, then filtered through Whatman GF/C filter paper. Celite filter aid was added to the solution prior to filtration to prevent clogging of the filter paper with solid material. Solutions were extracted on Varian Bond-Elut C-18 SPE columns as detailed in Section 6.1.2.2.

6.3.3.2 Extraction of tubers

Individual tubers (or peel only in some cases) were diced finely ($0.5cm^3$) and Soxhlet extracted with *n*-hexane in the presence of anhydrous sodium sulphate following the method of Khan (1999).

6.3.3.3 Extraction of sediment

The filter paper and associated solid material was left to air-dry overnight, then Soxhlet extracted with acetone (or in later studies, dichloromethane) for CIPC determination.

6.3.3.4 Analysis by GC

5µl aliquots of each hexane or acetone extract were injected onto a Pye Unicam PU4500 packed column gas chromatograph under conditions described in Section 6.2.2.4. Injections were performed in triplicate for each extract and a mean concentration calculated.

6.3.4 Results

Table 44 Chlorpropham concentrations (mg kg^{-1}) in individual treated tubers (*cv.* King Edward) before and after passing through the washer.

Tuber	CIPC concentration (mg kg^{-1})	
	Pre-washing	Post-washing
1	2.36	1.09
2	4.63	1.00
3	3.05	1.27
4	1.72	1.69
5	3.63	2.40
6	2.10	1.57
Mean	2.92	1.50
St Dev	1.08	0.51

Table 45 Chlorpropham concentrations (mg l^{-1}) in samples of washing water collected at various times during the washing run.

Sample	Concentration (mg l^{-1})	
	Chlorpropham	3-chloroaniline
Clean water	0.13	-
Recycled water	0.02	-
After 26 tonnes of CIPC treated crop	2.35	0.25
After 26 tonnes untreated crop	1.26	0.10

Table 46 Amounts (ug) of chlorpropham and 3-chloroaniline in sediment

Water sample with which sediment associated	Weight of chemical in sample (µg)	
	Chlorpropham	3-chloroaniline
After 26 tonnes of treated crop	711.78	2.29
After 26 tonnes of untreated crop	325.44	1.19

6.3.5 Discussion

6.3.5.1 Tubers

When chlorpropham-treated crop was washed in the barrel, the concentration present on the crop reduced by around half, suggesting significant transfer of chemical residues into the aqueous phase.

When a single untreated, washed tuber (*cv.* Maris Piper) was extracted following the procedure detailed in Section 6.2.2.2 and analysed as in Section 6.2.2.4, the only significant peak obtained in the chromatogram did not appear at the confirmed retention time for CIPC (10.5 minutes). This was assumed to be another potato component co-extracted in the solvent.

To verify that the peak was not CIPC, an internal standard of CIPC was added to the sample and the analysis run again. On the resultant chromatogram, CIPC could be seen clearly at its usual retention time (10.5 minutes) with the other significant peak appearing at 12 minutes. It was concluded that if any CIPC was present in the sample, there was too little to be quantified by this method.

A second extraction was carried out on a second tuber, with only the peel selected for extraction. CIPC has been shown to remain largely on the peel and not penetrate the flesh of the tuber to any significant degree, due to its non-systemic nature [Coxon and Filmer, 1985; Lewis et al, 1986; Lentza-Rizos and Balokas, 2001]. A very small amount of chlorpropham was found in this extract, equivalent to a concentration of ~0.1ppm on a whole tuber basis (1.17ppm in the peel). The extraction of peel alone was carried out on a third tuber and again resulted in a concentration of ~0.09ppm in the whole tuber. However, when working at these very low levels, it becomes difficult to maintain a steady baseline and to differentiate between genuine peaks and baseline noise, and such concentrations would be considered below the limit of quantification for the method, although within the limit of detection. There is, however, an indication that a small amount of CIPC has indeed been taken up onto the surface of the potato, as this small response was not noted in the extracts of untreated, unwashed potatoes extracted in a similar manner.

6.3.5.2 Water samples

At the start of the day, once the washer barrel had been filled with mains water, only trace amounts of chemical were present (0.13 mg l^{-1}), likely as a result of residual chemical in the barrel from previous days rather than contamination of the mains supply.

On-site, rinsing water is treated and recycled and may be used to fill the washer on some occasions when fresh supply is limited. A sample from the source of the recycled water contained only 0.02 mg l^{-1}, which would be suitable for re-use in the washer when one considers that residual contamination from the barrel itself is more than five times as high. This recycled water has passed through the treatment system as studied and described in Section 6.1, and the residue level determined here is very similar to that in the effluent coming from the aerobic digester during periods of high activity.

Chemical residues were significantly higher in samples taken directly from the washer barrel during operation. After 26 tonnes of chlorpropham-treated crop had passed through, levels of ~2.5ppm were present in the barrel. This figure reduced by approximately half after a further 26 tonnes of untreated material had passed through.

In addition to chlorpropham, very small amounts of a compound with a retention time equal to that of 3-chloroaniline were found in extracts of the barrel water once CIPC treated crop had been washed. While it is likely that 3-chloroaniline could be present (a metabolite of CIPC, it has previously been identified in samples of air from treated stores) positive identification by a method such as GC-MS would be necessary to confirm this suggestion.

6.3.5.3 Sediment samples

The solids removed in the filtration process were air-dried and analysed for CIPC (along with the filter paper) by extraction with acetone. This process yielded a cloudy yellow extract that was considered unsuitable for injection onto the GC column. Further extractions were carried out in a range of solvents. Hexane has been used to extract CIPC from soil by other workers [Tirmazi (1998)] but has been found to give fairly poor recoveries (<80%) in this work. Methanol extraction produced an even more unacceptable extract, so it was concluded that polar soil component(s) co-extracted in the polar solvents acetone and methanol were causing the problem. Burge and Gross (1972) reported similar problems following ethanol extraction of soils, and attributed them to the presence of microbial lipids in the extracts. A final extraction in dichloromethane gave more

satisfactory results (~94% recovery from a spiked sample), with no cloudiness to the extract. The dichloromethane was evaporated to almost dryness, and the residue re-dissolved in *n*-hexane for injection into the GC.

Because Celite had been added to the solution to aid filtration and the weight of sediment in the original solution was unknown, no concentration of CIPC on the solids can be calculated. However, the results can be expressed in terms of the weight of chemical associated with the sediment present in 500ml of effluent.

After 26 tonnes of treated crop had passed through the barrel, the suspended sediment in 500ml of effluent contained 711.3µg CIPC and 2.3µg 3CA. After a further 26 tonnes of non-treated material had been washed, the figures reduced to 325.4µg CIPC and 1.19µg 3CA.

Only the suspended solids present in 500ml samples of barrel water were analysed – no samples of the solid waste from the washer itself were collected. Most of the sediment washed off the crop would be separated from the liquid effluent (either settling out under gravity, or by addition of a flocculant) and would accumulate at the bottom of the washer. The CIPC content of this material is expected to be high, and analysis of a representative sample of it would have been helpful in terms of constructing a mass balance for chemical in the washer barrel.

6.3.6 Estimation of crop uptake by mass balance

An approximation for the amount of chemical taken up onto the unwashed crop can be determined using the volume of the washer, and the concentrations and weights of chlorpropham determined in the liquid and suspended fractions of our one-litre samples. Any such estimate will be based on the assumption that the contents of the barrel were fully mixed at the time of sampling (i.e. our samples are truly representative), and will not include any contribution to the chemical flux from the settled solids at the bottom of the washer.

6.3.6.1 Chlorpropham present in barrel after washing of 26 tonnes of treated crop

The weight of CIPC present in the liquid phase can be calculated by multiplication of the sample concentration by the volume of the washer i.e.

$$2.35\text{mg l}^{-1} * 2{,}500 \text{ litres} = 5{,}875 \text{ mg (or } 5.875\text{g)}$$

The weight of chlorpropham present in the suspended solid fraction can also be estimated, although the weight of suspended solids per litre of sample is not known. From Table 46, it is estimated that the sediment associated with 500ml of sample contains 0.712 mg CIPC, so the 2,500 litres of effluent in the washer will contain in total 0.712 * (2,500/0.5) = 3,560 mg (or 3.560g)

In total, then, the washing water in the barrel is assumed to contain **9.435g** of CIPC.

This would appear to equate to a wash-off rate of 0.363g per tonne. However, most chlorpropham removed during the washing process will remain associated with the sediment, most of which settles out at the bottom of the barrel and is not included in these figures.

6.3.6.2 Chlorpropham present in barrel after washing of 26 tonnes of untreated crop

The weight of chlorpropham present in the aqueous phase following the washing of 26 tonnes of untreated crop can be estimated as

$1.26 \text{ mg } l^{-1} * 2{,}500 \text{ litres} = 3{,}150 \text{ mg (or } 3.150\text{g)}$

The CIPC present on suspended solids can be estimated (as described above) to be

$(0.325 \text{ mg} * 2) * 2{,}500 \text{ litres} = 1{,}625\text{mg (or } 1.625\text{g)}$

In total, the washing water in the barrel is estimated to contain **4.775g** CIPC

6.3.6.3 Estimates of removal of chemical from the barrel and rate of uptake onto crop

The amount of chlorpropham removed from the barrel as a result of the washing of untreated crop can be estimated as the difference between the two figures above i.e.

9.435g present after washing treated crop; **4.775g** present after washing untreated crop therefore **4.66g** has been taken out of the barrel.

An approximation of the uptake onto the crop could then be made by dividing the weight removed from the barrel by the weight of crop washed i.e. 4.66g ÷ 26 tonnes = 0.179g/tonne, or 0.179ppm on a whole tuber basis

6.3.6.4 Comparison between estimated and observed crop contamination

Although the concentration in extracts of potato peel were lower than the limit of quantification for the GC method, they seemed to suggest uptake rates onto untreated crop of ~0.1 mg kg^{-1} on a whole tuber basis.

This agrees fairly well with the estimated uptake of 0.179 mg kg^{-1}, estimated using the concentrations and weights determined in 500ml samples. In the barrel, CIPC may also be taken up onto the untreated soil washed off the untreated crop, which will remain in the barrel and settle out with the solids at the bottom. Depending on the nature of the soil, significant quantities of chemical may be removed from solution in this way.

6.3.7 Summary and conclusions

Samples were collected early in the day, during the washing of one load of CIPC treated material and a subsequent load of untreated material at a commercial washing facility.

A small amount of uptake onto the surface of previously untreated tubers was shown to occur following ~10 minutes in contact with a solution of concentration ~2ppm. Although too small to be quantified with any confidence (because of limitations of the GC method) this response could be enough to result in rejection of crop being supplied as organic or untreated, where any detectable residue is unacceptable.

After 26 tonnes of treated material had passed through, the concentration in the washing water remained fairly low (~2.5ppm). However, concentrations of up to 10ppm have been determined in raw washing effluent collected at the end of the working day at other locations [Park, unpublished results].

Had the untreated crop been washed in the late afternoon after a whole day's worth of treated material, the situation could have been very different. As more treated crop is washed, the concentration in the water is expected to increase. As the concentration increases, so will the likelihood of cross-contamination onto crop.

The likelihood of crop uptake may be increased where tuber skin is loose or not fully set, for example where freshly harvested crop is hydrocooled prior to delivery to retailers. There have been instances where such crop has been found to contain traces of chlorpropham, despite not having been treated or held with chlorpropham-treated crop at any point [B. Coulson, personal communication]. In such instances, the use of recycled

water on a site where treated crop is washed is thought to be responsible for the picking up of traces of chemical. Wherever possible, it is recommended that fresh mains water only is used to fill hydrocooling equipment.

6.4 Studies on transfer of CIPC from aqueous solution onto potato skin

6.4.1 Introduction

Cross-contamination of untreated tubers as a result of washing in CIPC-contaminated water is a particular concern in the pre-pack industry, in particular where organic or untreated crop is washed. The tendency for chemical to be taken up onto the crop is dependent on a number of factors including solution concentration, contact time and surface area of the tuber.

The influence of such factors was investigated in a series of small experiments involving shaking tubers in CIPC solutions of varying concentration for various time periods.

6.4.2 Experimental methods

6.4.2.1 Materials and solutions

Chlorpropham (>98% purity) was used as received, and ground in an agate mortar and pestle to improve solubility.

Organic, washed tubers (*cv.* Charlotte) were purchased from Safeway in 2.5kg bags, and used as received. Small, whole tubers were selected for use in the sorption experiment, as extraction of previous solutions containing only peel proved difficult due to the presence of starchy material in the solution.

6.4.2.2 Preparation of solutions

A series of solutions of CIPC were made up in distilled water, ranging in concentration from 1ppm to 40ppm. Prior to the addition of CIPC, 2-litre volumetric flasks were filled with ~1.75 litres of distilled water and heated in waterbath to ~50°C to improve the solubility of the chemical. Ground crystals were added to glass weighing bottles and weighed on an analytical balance (4 decimal places). The crystals were added to the 2-litre flask, with washings, and the solution shaken vigorously for several minutes. The flask was stoppered with a plastic lid, then returned to the waterbath at 50°C and shaken periodically until all chemical had dissolved (for the high concentration solutions, this was often overnight). The solution was then allowed to cool, before being filtered through Whatman GF/C filter paper and made up to volume with distilled water.

6.4.2.3 Shaking procedure

Single, whole tubers were weighed and added to 400ml beakers with 100ml of CIPC solution (enough to fully immerse the tuber). The beakers were placed in an orbital incubator/shaker at 25°C and 80 rpm for 1, 5 and 48 hours. Each series of experiments consisted of 7 jars, one for each concentration of solution (1, 2, 5, 10, 20, 30 and 40ppm). After shaking was complete, the tubers were removed and rinsed with deionised water (washings added to the solution) and set aside for analysis.

6.4.2.4 Extraction procedure

The solution in the beaker was extracted onto Varian Bond-Elut C-18 solid-phase extraction columns, as detailed in Section 6.2.2.2 and eluted in 2ml acetone.

Tubers were peeled, and each individual peel was diced and Soxhlet extracted with hexane, following the method of Khan (1999).

6.4.2.5 Analysis by GC

Hexane extracts of peel, and acetone extracts of solutions, were analysed on a Pye Unicam PU4500 packed column gas chromatograph equipped with flame ionisation detector under the isothermal conditions described in Section 6.2.2.4.

6.4.3 Correlation of tuber and peel weight with surface area

In contact studies like these, the surface area of the tuber is a very important factor in determining how much chemical is taken up. However, because of the irregular shape of a tuber, surface area can be difficult to determine, and there is no easy way to estimate or model it.

As a result, a small study was carried out to show that surface area is proportional to peel weight, and also total tuber weight, in order that the weight of tuber could be used for later calculations.

6.4.3.1 Measurement of peel samples

20 tubers of cultivar Charlotte were weighed and peeled and the weight of peel recorded. The peel was then trimmed and laid out on a grid of one-centimetre squares, and the area recorded to the nearest cm^2.

The uniformity of thickness of 100 sections of peel (10 strips from each of 10 tubers) was checked with callipers and found to be 1.05 ± 0.08 mm. The ability to produce peelings of reproducible thickness is crucial if weight of peel is to be used to estimate surface area.

6.4.3.2 Results

Figure 67 overleaf shows the relationships between tuber weight and peel weight, tuber weight and surface area and peel weight and surface area for tubers of the cultivar Charlotte.

6.4.3.3 Discussion

Figure 67 overleaf shows that for the cultivar Charlotte there is a good correlation between tuber weight and surface area, tuber weight and peel weight and peel weight and surface area. The best correlation is between peel weight and surface area ($r^2 = 0.989$).

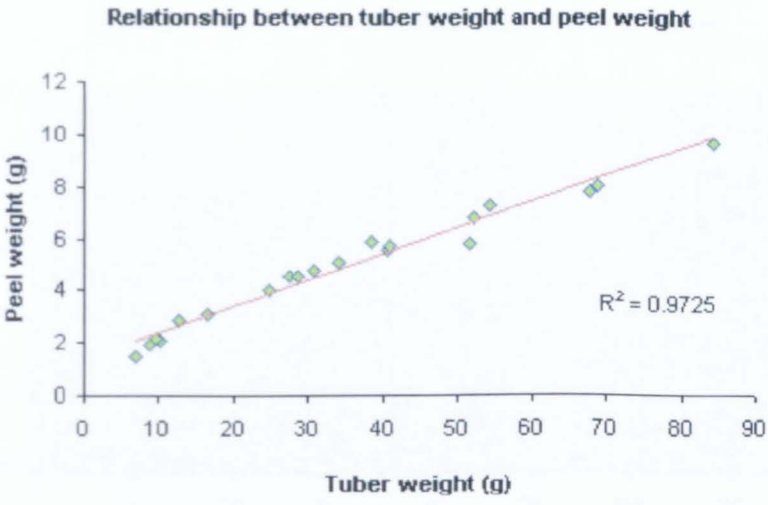
Although these relationships are very convincing for this cultivar, it may not hold so well for different varieties, depending on tuber shape (e.g. Charlotte tubers are fairly spherical, while others may be more elongated or have very rough surfaces). In this work, it can be assumed that weight gives a good indication of surface area. Because surface area is very difficult to measure directly, it is convenient to be able to make an estimate of it based on some more easily determined factor e.g. weight.

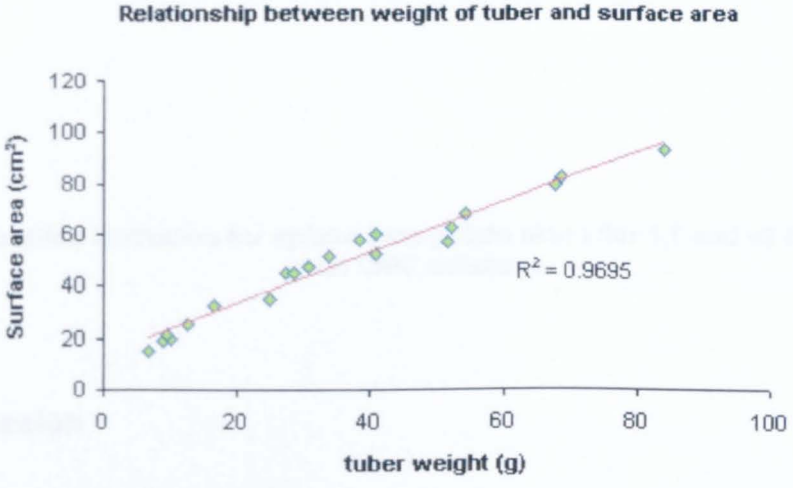
6.4.4 Results for contact times 1, 5 and 48 hours

Table 47 below shows the concentrations, on a whole tuber basis, determined on tubers in contact with solutions of various concentrations for 1, 5 and 48 hours.

Table 47 Chlorpropham residues (mg kg^{-1}) on tubers after 1, 5 and 48-hour contact with solutions ranging in concentration from 1 to 40 ppm.

Starting solution concentration (mg l^{-1})	CIPC uptake (mg kg^{-1} whole tuber)		
	1 hour	5 hours	48 hours
1	0.17	0.42	1.56
2	0.04	0.36	1.88
5	0.50	2.35	5.92
10	0.84	1.80	13.50
20	2.68	4.21	24.90
30	1.96	6.09	31.16
40	7.42	11.65	49.01





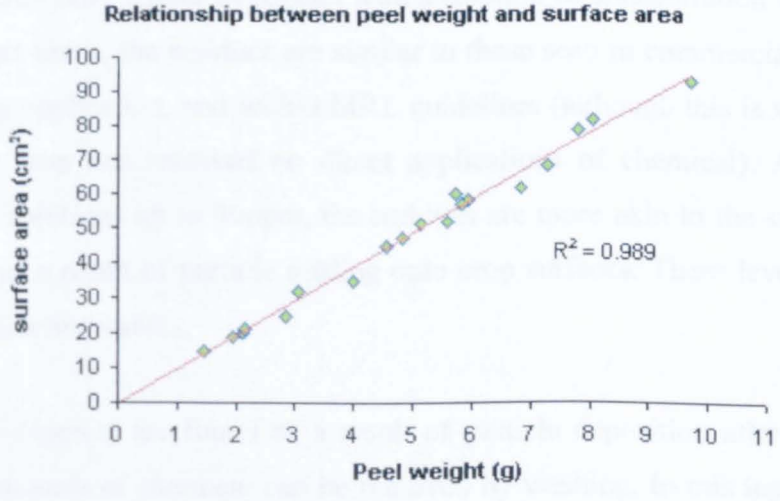


Figure 67 Correlations between tuber weight, peel weight and tuber surface area for tubers of the cultivar Charlotte

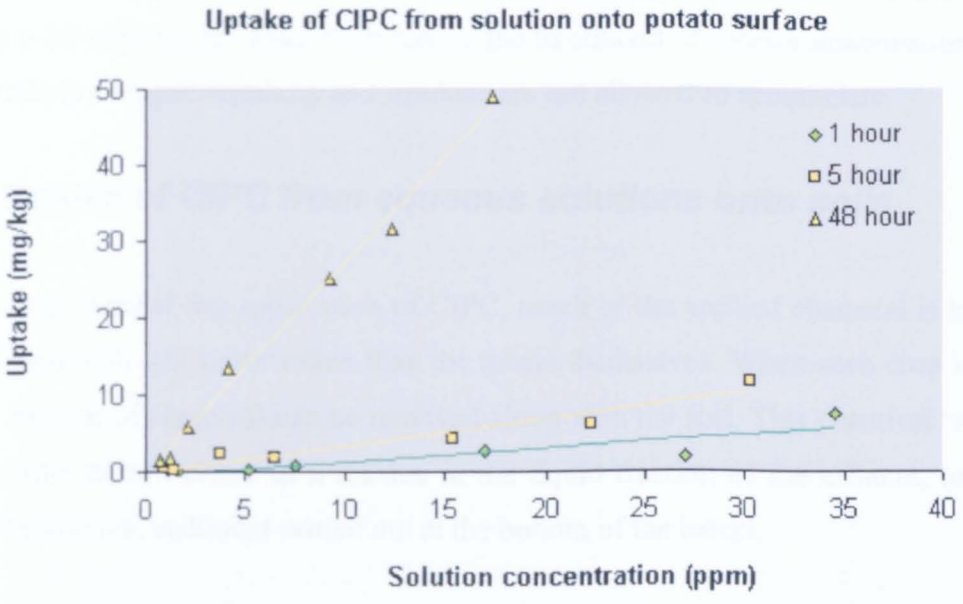


Figure 68 Sorption isotherms for uptake onto potato skin after 1,5 and 48 hours in contact with CIPC solutions

6.4.5 Discussion

From Table 47 and Figure 68, it can be seen that measurable residues can be found on potato peel after only 1 hour in contact with a solution of concentration 1ppm. After 1 and 5 hour contact times, the residues are similar to those seen in commercial stores following a thermal fog application, and within MRL guidelines (although this is still a lot when we consider the crop has received no direct applications of chemical). After 48 hours in contact with solutions up to 40ppm, the residues are more akin to the very large deposits often found as a result of particle settling onto crop surfaces. These levels are well above any 'safe' guideline values.

Where large deposits are found as a result of particle deposition after thermal fogging, significant amounts of chemical can be removed by washing. In this instance, chemical is often only sitting on the crop or any associated soil, rather than being held on the surface. Where chemical is taken up from solution, it may be adsorbed onto the waxes of the periderm, and may be much more difficult to remove. Large residues accumulated as a result of washing in contaminated wash water might therefore be more difficult to reduce.

However, the large volume of the washer and the relatively short residence time in the barrel (~10 minutes per load) both reduce the likelihood of cross-contamination, providing the water is changed regularly and residues are not allowed to accumulate.

6.5 Uptake of CIPC from aqueous solutions onto soils

Following thermal fog application of CIPC, much of the applied chemical is known to be associated with soil cover rather than the tubers themselves. When such crop is washed, a large amount of chemical can be removed along with the soil. This chemical will reside in the washer barrel, either as a residue in the liquid fraction of the effluent, or associated with the soil and sediment settled out at the bottom of the barrel.

CIPC contaminated soils and sediment can play an important role when considering the transfer of chemical from different compartments in the environment. For instance, in a commercial washing situation, CIPC contaminated sediment can contribute to the accumulation of residues in the barrel water, if it is released off the soil surfaces back into solution. Conversely, soil could be an important sink for chemical and may help prevent the accumulation of residues in the water and reduce the likelihood of transfer of residues to crop.

These sorption studies aimed to investigate the behaviour of CIPC in a commercial washing situation. Such knowledge will allow the industry to put in place effective strategies for effluent clean-up and prevent environmental pollution. Owing to the applied nature of the research as a whole (funded as it was by the British Potato Council and the Potato Processors' Association), the way in which the work progressed was driven by input from industry in terms of its concern regarding the behaviour of CIPC post-application. The following studies are an attempt to answer some of these points, namely

- How much CIPC is associated with soil?
- How easily does CIPC move from the aqueous phase to the sorbed phase and vice versa?
- What factors influence the degree of uptake and release of chemical from soil?
- What can we determine about the likely behaviour of CIPC under conditions typical of a commercial washing facility?
- What practical recommendations can we give store managers wishing to minimise pollution of both the environment and their crop?

6.5.1 Structure of the studies

The uptake and holding capacity of a particular soil is dependent on its chemical and structural characteristics, in particular of its organic matter and clay components. As a result, two different soils were used in the described experiments: one predominantly sand and silt, and the other with high clay and organic content.

Sorption isotherms were constructed for each soil by shaking soil with a range of CIPC solutions in water for various lengths of time, and determining uptake onto soil from equilibrium solution concentrations. Traditionally, sorption studies involve the fitting of data to one of various mathematical models (e.g. Langmuir and Freundlich isotherms) in order to describe the uptake processes involved. However, a more pragmatic approach was adopted in the described studies because of the very applied nature of the work. No emphasis was placed on describing the mechanisms (e.g. partition, physical sorption) involved in the sorption process.

Similarly, where desorption from the surfaces was investigated, the traditional approach of desorption isotherm construction by sequential replacement of the supernatant [Celis *et al* (1999); Zhu and Selim (2000)] was not adopted, in favour of a more 'real-life' approach, where an additional volume of fresh water was added to the system following a period of equilibration. Solution concentration was determined following an additional period of shaking, and the amount desorbed from the soil calculated by difference. Such an approach was considered appropriate as a model for the commercial washing situation, where introduction of fresh water during operation is commonplace.

6.5.2 Experimental methods

Procedures common to a range of experiments are described in this section. Details on methods specific to individual studies are presented in the relevant sections that follow.

6.5.2.1 Preparation of solutions

CIPC (>95% purity) was obtained from Sigma Aldrich, and used as received.

1-litre solutions were prepared at concentrations of 1ppm, 2ppm, 5ppm, 10ppm, 20ppm, 30ppm and 40ppm following the procedure detailed in Section 6.4.2.2.

6.5.2.2 Shaking procedure

Soils and solutions were weighed/pipetted into 4oz glass screw-cap jars, which were shaken on an end-over-end shaker for the prescribed time (described in appropriate sections for sorption and desorption studies).

6.5.2.3 Soil types

Two different soils were used in the studies, and their properties are shown in Table 48 below.

Table 48 Characteristics of the two soils used in the sorption and desorption studies.

Soil Type	Approximate percentage of each component		
	Sand and silt	Clays	Organic matter
Barassie (mineral)	90	4	5
Fen Peaty (organic)	10	48	41

6.5.2.4 Extraction procedure

C-18 solid phase extraction cartridges (Varian Bond-Elut) were conditioned with 5ml methanol and 5ml distilled water prior to the addition of the water sample. The sample was then passed through at a rate of ~2ml/minute. Once the sample had been loaded, the cartridge was rinsed with 5ml distilled water to remove any weakly held interfering compounds. The cartridge was vacuum dried for one hour, then CIPC was eluted off in ~2ml HPLC grade acetone and made up to volume in a 2ml volumetric flask. 5µl aliquots of this solution were injected onto the GC to determine the amount of CIPC remaining in solution following the shaking procedure.

6.5.2.5 Control solutions

50ml of each stock CIPC solution was extracted as described above to act as a control. The amount of CIPC taken up onto the soil was calculated as the difference between the amount of CIPC in the control solution and the amount remaining in the solution containing soil following the period of shaking. Adsorption of CIPC onto the walls of the glass jars was assumed to be negligible, but will in any case be accounted for by control solutions, which were analysed both unshaken and following 24hrs on an end-over-end shaker. The concentrations in shaken solutions ranged from 92-110% of the corresponding

unshaken solution, indicating that sorption onto the glass was indeed negligible under experimental conditions.

6.5.2.6 Analysis by GC-FID

Acetone extracts were analysed on a Pye Unicam PU4500 packed column gas chromatograph, equipped with flame ionisation detector. Analyses were carried out under isothermal conditions (180°C) as detailed in Section 6.2.2.4.

Data collection and integration was carried out on a SP4400 integrator (Spectra Physics). The GC was calibrated daily with standards of CIPC in HPLC grade acetone.

6.5.2.7 Construction of sorption isotherms

Sorption onto a surface will continue until a state of equilibrium is reached between the chemical in solution and that held on the solid surface. Equilibrium data for a number of solutions with different starting concentrations can be plotted to give a graphic representation of the sorption process.

When uptake (in $\mu g\ g^{-1}$) is plotted on the y-axis and the amount remaining in solution (μg) or solution concentration ($\mu g\ ml^{-1}$) on the x-axis, the gradient of the line through the plotted points illustrates the rate of chemical removal from the solution (on $\mu g\ g^{-1}$ soil basis). A steep line indicates a high rate of chemical uptake onto the soil, while a shallower slope indicates a lesser amount or slower rate of removal from solution.

6.5.2.8 Desorption data

Desorption studies were not carried out following standard methods, so conventional isotherm construction was not possible. This data was presented in a slightly different way to the usual format for desorption work: in essence, a 'net' isotherm for the combined processes of uptake and removal from soil is shown, for comparison with the sorption isotherm obtained under the same conditions.

6.5.3 Sorption studies

Experiments were carried out at soil-to-solution ratios of 1:50 (1g soil in 50ml solution) and 1:5 (10g soil in 50ml solution).

Several sets of jars were set up for each soil-to-solution ratio to allow different shaking times to be included in the study: 1, 5 and 24 hours were selected as suitable for the mineral soil, with an additional time of 48 hours included for the organic soil.

6.5.3.1 Adsorption procedure

Soil (1g or 10g) was weighed out on a top pan balance into a 4oz glass screw-cap jar, and then 50ml of CIPC solution (ranging in concentration from 1ppm to 40ppm) was added with a bulb pipette. Jars were then placed on an end-over-end shaker for 1, 5, 24 or 48 hours as appropriate. Once removed from the shaker, the solution was filtered, with washings, through Whatman GF/C filter paper prior to extraction as detailed in Section 6.2.2.2. 5µl aliquots were analysed by GC as detailed in Section 6.2.2.4.

6.5.3.2 Results

Uptake data for each soil type (Barassie and Fen Peaty) at soil-to-solution ratios of 1 to 50 and 1 to 5 are presented in the tables and figures on the following pages.

With Barassie soil, contact times of 1, 5 and 24 hours are shown for both 1g and 10g soil in 50ml. For Fen Peaty, an extra contact time of 48 hours was added in to the study of 1g in 50ml as it progressed. Because of time constraints, with 10g in 50ml, only 1 and 5 hours were included.

Results are presented in a number of formats – uptake for each soil is expressed on a microgram CIPC per gram soil (ppm) basis in the initial tables and sorption isotherm figures.

In addition, the proportion (%) of the starting weight of CIPC remaining in solution after shaking is shown for each shaking time. Although seven different concentrations of solution were used the proportion of chemical taken up onto the soil was found to be fairly constant and independent of starting concentration.

Finally, uptake rates for both Barassie and Fen Peaty are expressed as micrograms CIPC taken up per gram of organic matter, as calculated from the approximate soil compositions shown in Table 48. In this instance, the Fen (1g in 50ml) and Barassie (10g in 50ml) are plotted on the same graph because the OM-to-solution ratio was most similar, allowing the fairest comparison between the two.

Table 49 Uptake of CIPC onto 1g of Barassie soil suspended in 50ml solution

Starting concentration (ppm)	Uptake (µg CIPC/g soil) and contact time (hr)		
	1 hour	5 hour	24 hour
1	20.12	19.00	18.29
2	33.06	44.51	32.63
5	61.12	96.01	84.29
10	151.32	169.77	153.87
20	432.54	324.36	293.27
30	527.05	462.77	430.80
40	591.44	654.79	657.81

Table 50 CIPC uptake onto 1g Fen Peaty soil suspended in 50ml solution

Starting concentration (ppm)	Uptake (µg CIPC per g soil) and contact time (hr)			
	1 hour	5 hour	24 hour	48 hour
1	33.91	33.05	41.19	34.41
2	67.99	72.06	77.65	60.19
5	150.98	172.68	195.64	188.74
10	287.31	321.73	341.33	394.34
20	540.41	614.77	665.07	602.96
30	800.48	940.80	919.67	972.45
40	1060.26	1206.43	1334.36	1223.52

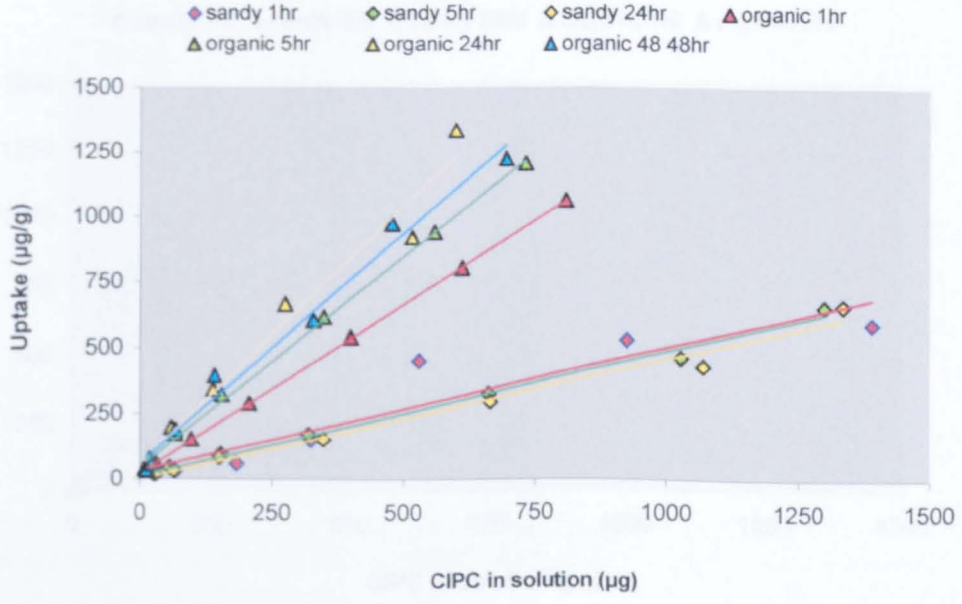


Figure 69 Sorption isotherms for Barassie and Fen Peaty soil at 1:50 soil to solution ratio

Table 51 CIPC uptake onto 10g Barassie soil suspended in 50ml solution

Starting concentration (ppm)	Uptake (µg CIPC per g soil) and contact time		
	1 hour	5 hour	24 hour
1	3.65	-0.12	4.54
2	7.88	9.09	9.54
5	20.68	22.23	22.83
10	42.07	43.01	43.17
20	84.93	84.99	83.45
30	122.51	125.03	124.84
40	160.02	167.85	164.61

Table 52 CIPC uptake onto 10g Fen Peaty soil suspended in 50ml solution

Starting concentration (ppm)	Uptake (µg CIPC per g soil) and contact time	
	1 hour	5 hour
1	4.57	4.38
2	8.67	8.39
5	24.93	24.10
10	53.42	51.27
20	87.03	88.87
30	138.02	139.29
40	177.84	181.16

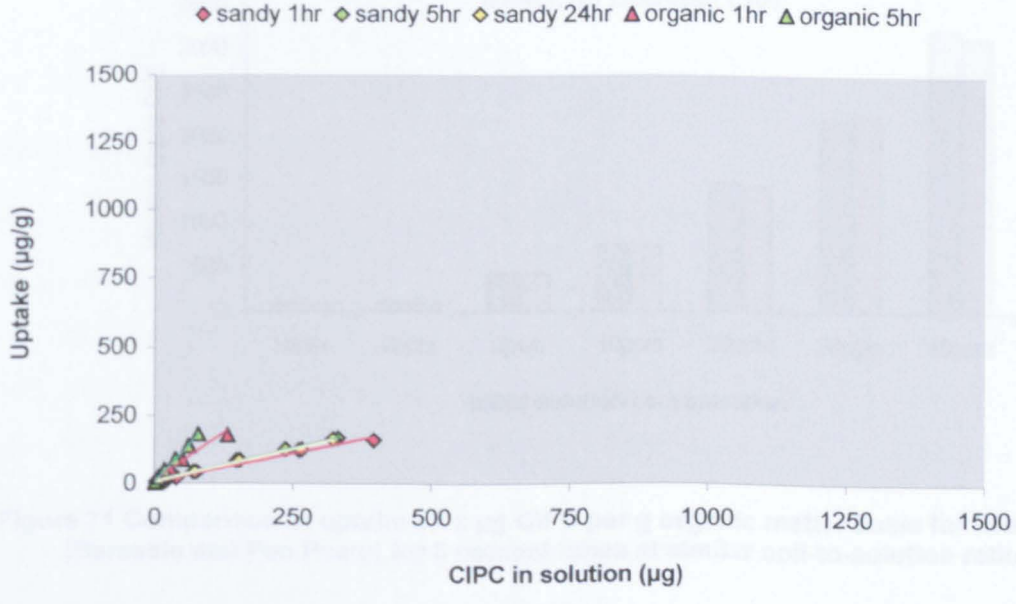


Figure 70 Sorption isotherms for Barassie and Fen Peaty soils at 1:5 soil to solution ratio

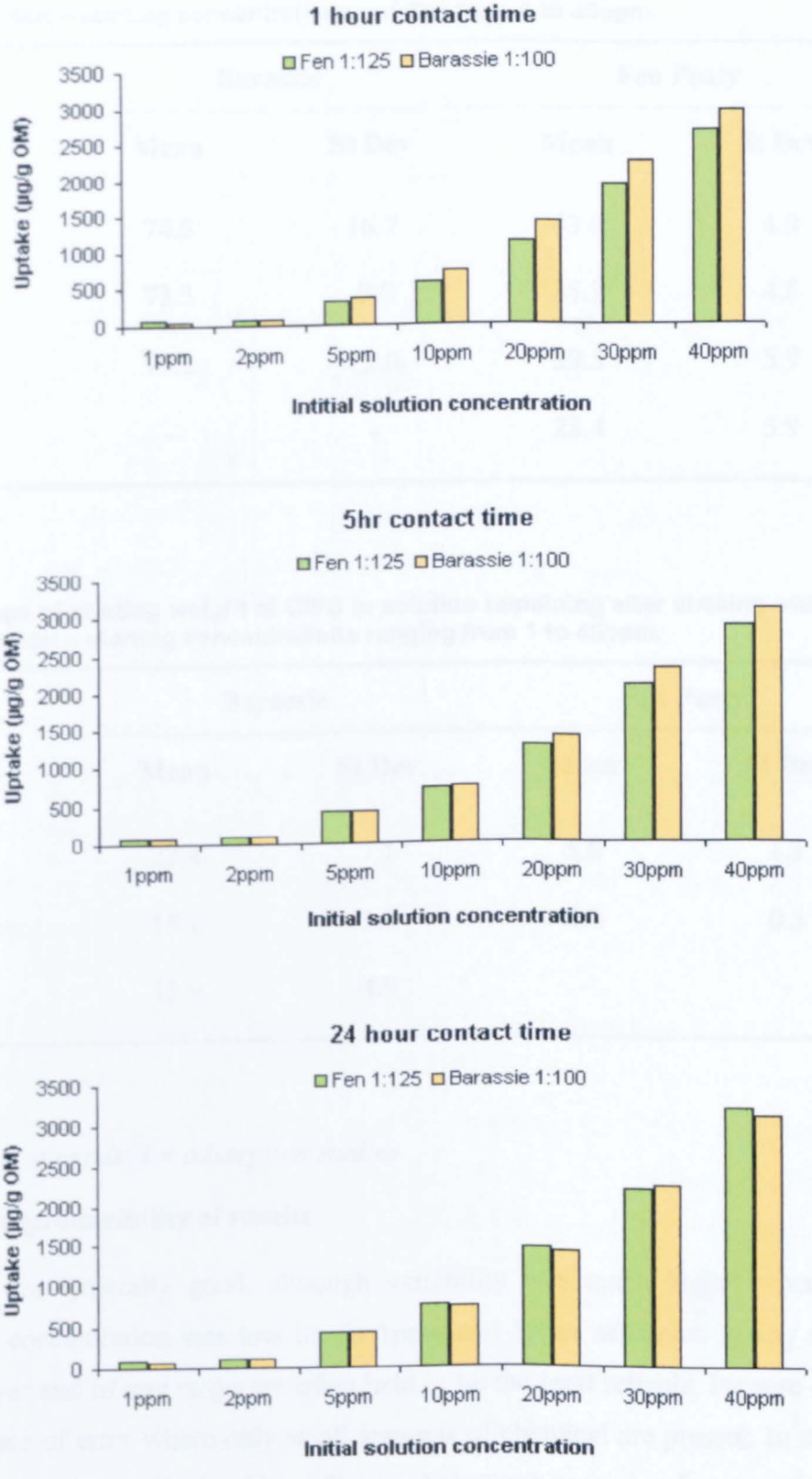


Figure 71 Comparison of uptake on a µg CIPC per g organic matter basis for two soils (Barassie and Fen Peaty) for 3 contact times at similar soil-to-solution ratio

Table 53 Percentage of starting weight of CIPC in solution remaining after shaking with 1g of soil in 50ml solution – starting concentrations ranging from 1 to 40ppm.

Contact time	Barassie		Fen Peaty	
	Mean	St Dev	Mean	St Dev
1hour	74.8	16.7	43.6	4.0
5 hour	73.5	9.0	35.3	4.8
24 hour	77.2	13.0	29.5	5.9
48 hour	-	-	28.4	5.9

Table 54 Percentage of starting weight of CIPC in solution remaining after shaking with 10g of soil in 50ml solution – starting concentrations ranging from 1 to 40ppm.

Contact time	Barassie		Fen Peaty	
	Mean	St Dev	Mean	St Dev
1hour	22.4	7.1	5.8	1.3
5 hour	15.1	2.8	4.0	0.5
24 hour	13.9	4.9	-	-

6.5.3.3 Discussion of results for adsorption studies

Variability and reproducibility of results

Reproducibility was generally good, although variability was much higher where the starting solution concentration was low i.e. in 1ppm and 2ppm solutions. In any study, results at the lower end of any range are often held to be the least reliable, because of the increased influence of error where only small amounts of chemical are present. In studies like these, where values are calculated by difference between a control and an experimental sample, the reliability of the whole data set can depend on the accuracy of the starting, or blank, value. Error in its determination will lead to bias in the whole data set.

In this instance, when the 2ppm control solution (extracted after solution preparation and prior to any shaking) was analysed, its concentration was determined to be 1.2ppm, which

is further from the intended value than expected as a result of error during solution preparation. It is likely that error crept in at some other stage of the extraction and analysis procedure, skewing the results for this particular data set. In the data tables in the Results section, 1ppm and 2ppm values are shown in red: often these were discounted before any statistical analysis of the data was carried out.

Table 53 shows that the proportion of chemical taken up from any solution is fairly constant and independent of starting concentration: the standard deviation value is low relative to the mean, even when the 1ppm and 2ppm values are included in the data set.

When comparing the percentage of the starting weight left in solution after shaking, small differences in the weight of soil added to the jar will contribute in part to the variability: these figures take no account of the uptake on a weight per weight basis.

Statistical handling of the data

For each combination of concentration, shaking time and soil-to-solution ratio, only one jar was analysed because of constraints on time: a very large number of samples were necessary to investigate all the factors considered relevant and interesting. Although no true replication was carried out as part of the study, it was considered appropriate to carry out some simple statistical analysis on some sections of the data.

However, for each combination of shaking time and soil-to-solution ratio, there were seven solutions of different concentration. It became clear when looking at the results that the proportion of chemical taken up from solution was fairly constant for any one contact time, and was independent of starting concentration. As a result, the seven individual solutions were considered to be replicates for the purposes of determining whether contact time has a significant effect on the extent of chemical uptake.

Pairs of treatments were analysed using ANOVA techniques and Tukey's pairwise comparison.

Extent of uptake on $\mu g\ g^{-1}$ soil basis

Fen Peaty takes up more CIPC from solution than Barassie on a gram for gram basis. The vastly different organic matter contents of the two soils are the most likely explanation for this difference. However, the amount of uptake is also influenced by the soil to solution ratio and starting concentration: these factors are responsible for differences seen within

the data from one soil, while organic content is the dominant factor when considering the differences between the two soils.

Extent of uptake on μg g^{-1} organic matter basis

From the approximate soil compositions given in Table 48, 10g of Barassie (5% OM) soil contains approximately an equal amount of organics as 1g of Fen Peaty (40% OM). The graphs in Figure 71 show the uptake of CIPC onto both soils expressed on a μg CIPC per g OM basis at similar OM-to-solution ratio. On this basis, both soils take up very similar amounts of CIPC. This finding confirms the organic fraction of the soil to be the most important in terms of CIPC uptake, rather than clays or other mineral components. Uptake onto clay will be dependent on the nature of the clays (e.g. expanding vs non-expanding) and the chemical nature of the pesticide (e.g. surface charge, acidity). No information was provided on the types of clay present in these soils (sometimes clay is defined purely on the basis of particle size rather than chemical composition), but it can be said that sorption of CIPC onto them was negligible compared to the organic matter.

Effect of soil to solution ratio

The amount of soil relative to the solution has a significant effect on how much chemical is taken up onto soil, on a weight per weight basis. For example, Barassie soil added to 50ml of a 40ppm CIPC solution will take up 160μg g^{-1} when 10g is added, and 600μg g^{-1} when only 1g is present. A similar effect was noted with Fen Peaty, which takes up ~180μg g^{-1} when 10g is present, and ~1000μg g^{-1} when only 1g is added to the jar. In the environment, sorption is known to occur on two timescales: initially, a state of 'equilibrium' will be reached in a matter of hours or days, although more slow reactions will continue to take place for weeks and months [Pignatello and Xing (1996)]. Perhaps on the relatively short timescale of this experiment CIPC is taken up onto the most easily accessible and energetically favourable sites on the surface of the soil. Where more soil is present this will result in a lesser amount of uptake per unit weight of soil, assuming chemical is evenly distributed over the surface of the soil.

The sorption isotherm graphs (Figures 69 and 70) show that the difference between the two soils is greater when only 1g is added to 50ml of solution; when 10g is added the uptake onto the two is more similar.

Effect of contact time

For Barassie soil, the amount of time for which the soil is in contact with the solution does not significantly affect the uptake of CIPC. This is clear when the 1g in 50ml data are examined, but with 10g in 50ml there appears to be a small increase in uptake over time. This difference is statistically significant when the full data set is included, but when the values from the 1 and 2ppm solutions are excluded, there is no difference. Table 8 below shows the p-values for comparisons between different shaking times: this value should be ≤ 0.05 for the difference between any pair of treatments to be significant at a 95% confidence level.

Table 55 Uptake onto Barassie: p-values for comparisons between different shaking times.

Comparison	p value for data set	
	1 – 40 ppm	5 – 40 ppm
1g in 50ml		
1 hour vs 5 hour	0.862	0.831
1 hour vs 24 hour	0.768	0.493
5 hour vs 24 hour	0.549	0.540
10g in 50ml		
1 hour vs 5 hour	0.026	0.140
1 hour vs 24 hour	0.023	0.248
5 hour vs 24 hour	0.565	0.979

Table 56 Uptake onto Fen Peaty – p values for comparisons between different shaking times.

Comparison	p value for data set	
	1 – 40 ppm	5 – 40 ppm
1g in 50ml		
1 hour vs 5 hour	0.004	0.013
1 hour vs 24 hour	0.000	0.000
1 hour vs 48 hour	0.000	0.000
5 hour vs 24 hour	0.063	0.109
5 hour vs 48 hour	0.032	0.088
24 hour vs 48 hour	0.743	1.000
10g in 50ml		
1 hour vs 5 hour	0.006	0.065

Significant differences exist in the data whether 1ppm and 2ppm values are included or not. Differences are in fact less significant when these values are excluded.

The effect of contact time on the amount of chemical taken up onto soil is illustrated in the graphs in Figure 71. The data shown is taken from the 1g Fen and 10g Barassie experiments, to keep organic matter weights and OM-to-solution ratios as similar as possible. After 1 hour, the Barassie has taken up more CIPC than the Fen Peaty; after 4 hours the difference between the two soils is less and after 24 hours, the Fen has taken up more chemical from solution.

A simple model of the soils could be considered where the organic fraction of the Barassie soil exists as a thin coating on the mineral grains, while the Fen organics are more complicated 3-dimensional structures (e.g. humic and fulvic acids). In this model, the organic molecules in the Barassie soil are freely accessible on the soil surface, and any interactions between the pesticide molecule and soil solution and/or organics take place relatively quickly: increasing the contact time makes little difference to the process. Where more complicated structures are involved (e.g. the organics in Fen Peaty soil) although there will be more potential binding sites and a larger surface area, they may be less accessible due to small pore size or the convoluted shape of the molecule. The pesticide may also have to compete with other sorbed molecules or molecules of water. As a result, it may take longer for the process to occur, and a notable increase in the amount of chemical held on the soil may arise from extending the contact time.

Implications for commercial washing process

These small-scale laboratory experiments can be used to provide general information and recommendations for the potato industry with regard to minimising pollution risks from potato washing facilities. In addition to environmental pollution, the risk of contamination of untreated crop by washing in CIPC-contaminated water is also a concern: untreated crop has been found to contain detectable residues of CIPC after washing in the same water as treated material [B.Coulson, personal communication].

These experiments show that, at concentrations similar to those previously determined in potato washing water, CIPC will be taken up onto the surface of soils. The amount of chemical removed from the water in this way will be difficult to quantify, and will depend on a number of factors including the soil-to-solution ratio, the soil type, the contact time,

the treatment history of the soil (re-release into solution is also a possibility) and how frequently the water is refreshed.

It is possible that untreated soil could be useful for preventing the accumulation of residues in washing water, extending the life of the water and reducing the likelihood of contamination of i) untreated crop and ii) watercourses by effluent. At present simple low-cost methods of reducing CIPC residues in liquid effluent are required by the industry in order that discharges to the environment meet EU guidelines (e.g. Environmental Quality Standards) and Environment Agency consents. With the cost of maintaining a clean supply of water constantly on the increase, recycling of water around the site is becoming a more attractive option. Before water can be re-used, any chemical residue must be minimised.

Although crop has a residence time of only minutes in the water, sediment and soil built up at the bottom of the barrel tends to be removed only when the washer is emptied and cleaned. At times of full operation, this may only happen once every few days, when the water gets too dirty to use any more. The decision to change barrel water is dependent on a combination of factors including the amount of crop soil cover, disease levels and extent of foaming [S.Alexander, personal communication]. Often only a proportion of the water is refreshed, meaning that soil can remain in the barrel for days at a time. During this time it may take up CIPC from the solution. Conversely, CIPC contaminated soil could release chemical back into solution. This process is examined more closely in the following sections on desorption studies.

6.5.4 Desorption studies

As previously discussed, the conventional approach to studying desorption of chemicals from soil was not followed in this work, because of the very specific nature of the situation being modelled.

Conventionally, desorption studies are carried out using only one chemical solution and one weight of soil (i.e. a single starting concentration and soil:solution ratio). After the sorption stage, the soil suspension is centrifuged and the supernatant removed for analysis and replaced with fresh solution. This cycle is repeated several times to obtain the data points for construction of a desorption isotherm. Such studies are generally aimed at describing the transport of a chemical in the environment e.g. for soil-applied agrochemicals in a profile, or in river sediments following wash-off. Studies are often carried out in a weak electrolyte solution (e.g. 0.05M $CaCl_2$) to maintain the cation status of the soils.

There are several notable differences between this conventional approach and that adopted in this study:

- Rather than examining sorption and desorption in a single solution, a range of concentrations were investigated. These were selected to represent the range of chemical levels found in washing water to date (up to 10ppm), with higher levels (up to 40ppm) also included to exaggerate any effect.

- The supernatant was not decanted and replaced with fresh solution after the sorption stage. Instead, it was left in the jar and diluted with a further volume of fresh water. After the shaking procedure was repeated to allow desorption to occur, the entire solution was removed for analysis. There was no replacement of the supernatant i.e. only one desorption cycle was carried out.

- Experiments were carried out in tap water rather than synthetic electrolyte solutions to better model the conditions in a commercial washer, where mains water (or recycled water from elsewhere on-site) is used to fill the barrel.

In the desorption stage of the study, both soils (Barassie and Fen Peaty) were used, although the experimental conditions for each soil were different e.g. 10g of Barassie were

used but only 1g of Fen, because of the degree of uptake seen in the sorption studies. Details of the experimental methods will therefore be provided separately for each soil.

6.5.4.1 Desorption method for Barassie soil

10g soil was weighed into a 4oz glass jar, and 50ml of CIPC solution was added by pipette. Jars were then sealed and shaken for 24 hours on an end-over-end shaker to allow sorption to occur.

After 24 hours shaking, an additional volume of fresh water was added to each jar, which was then returned to the shaker for a further period of time.

The experiments with Barassie soil were the first to be carried out, so both the shaking time and the volume of fresh water added were thought to influence the extent of chemical removal. As a result, three sets of conditions were investigated:

- 25ml fresh water added, shaken for a further 1 hour
- 50ml fresh water added, shaken for a further 1 hour
- 25ml fresh water added, shaken for a further 24 hours.

After the second shaking period was complete, the entire solution was filtered through Whatman GF/C filter paper into a Buchner flask. The washings from the soil pad were also added to the flask. The entire volume in the flask was then extracted on a C-18 column as detailed in section 6.2.2.2, and 5µl aliquots were injected onto the GC and quantified under conditions detailed in Section 6.2.2.4.

6.5.4.2 Results for desorption from Barassie soil

The tables and figures below show the amount of CIPC taken up onto the surface of Barassie soil and the subsequent amount released following the addition of fresh water. Three different sets of experimental conditions were maintained – combinations of two additional volumes of water (25 and 50ml) and two desorption shaking times (1 hour and 24 hours).

Figure 72 shows the sorption and desorption data plotted in the style of sorption isotherms, i.e. the amount of chemical in solution after shaking vs. the amount removed from solution.

However, the desorption figures cannot be considered a 'desorption isotherm' proper because of the way in which the experiment was carried out (see earlier discussion).

Table 57 CIPC desorbed from 10g Barassie soil. Effect of varying contact times (1hr vs 24hr) and volumes of water added (25 vs 50ml)

Starting concentration and contact time	Equilibrium CIPC in solution (µg)	Uptake (µg)	Percentage desorbed
24 hour adsorption			
1ppm	4.62	37.76	-
2ppm	4.16	56.26	-
5ppm	20.57	213.10	-
10ppm	73.46	370.96	-
20ppm	153.79	709.30	-
30ppm	266.57	1125.86	-
40ppm	322.61	1558.12	-
1 hour desorption, 25ml added			
1ppm	17.56	24.82	34.3
2ppm	18.45	41.97	25.4
5ppm	42.96	190.71	10.5
10ppm	95.92	348.50	6.1
20ppm	233.81	629.27	11.3
30ppm	246.62	1045.81	7.1
40ppm	478.03	1402.69	10.0
1 hour desorption, 50ml added			
1ppm	14.88	27.50	27.2
2ppm	21.55	38.87	30.9
5ppm	57.44	176.23	17.3
10ppm	121.61	322.81	13.0
20ppm	288.85	574.23	19.0
30ppm	432.47	959.97	14.7
40ppm	591.55	1289.17	17.3
24 hour desorption, 25ml added			
1ppm	7.89	34.49	8.7
2ppm	17.34	43.08	23.4
5ppm	39.03	194.64	8.7
10ppm	-	-	-
20ppm	223.25	639.83	9.8
30ppm	353.22	1039.21	7.7
40ppm	484.70	1396.02	10.4

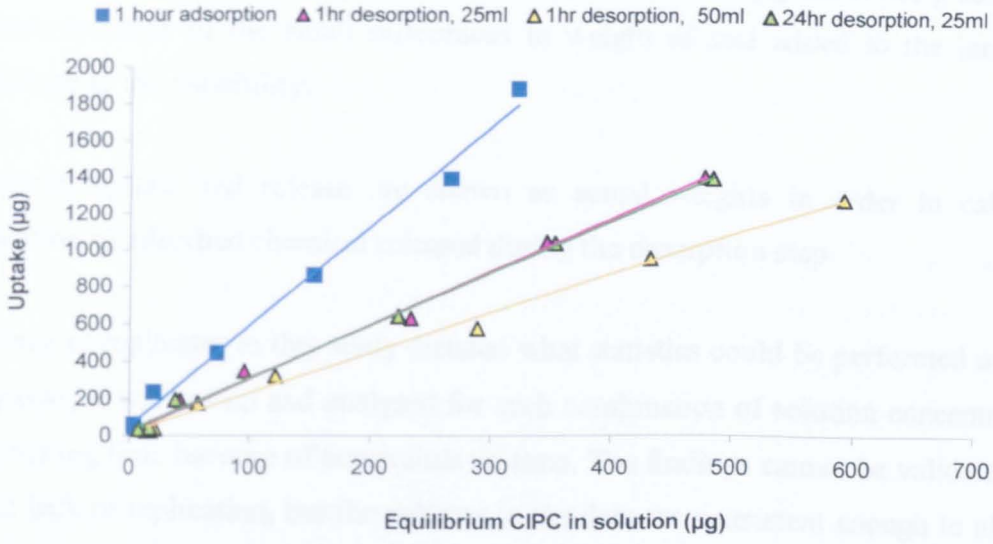


Figure 72 Uptake of CIPC onto 10g Barassie soil following 24 hour equilibration and subsequent addition of fresh water

Table 58 ANOVA p-values for comparisons between treatments

Comparison	p value for data set	
	1 – 40 ppm	5 – 40 ppm
1hr 25ml vs 1hr 50ml	0.316	0.001
1hr 25ml vs 24hr 25ml	0.490	0.909

6.5.4.3 Discussion of Barassie desorption results

When the full data set (solution concentrations from 1 to 40ppm) is included, neither increasing the dilution factor (the volume of water added) or the contact time has any statistically significant effect on the amount of CIPC released from the soil back into solution.

However, low solution concentrations are known to be prone to increased error due to a number of factors including error in i) the extraction process ii) the analysis method iii) the reliability of the original blank value. It was therefore considered appropriate to repeat the statistical procedure without these values i.e. using solutions from 5 to 40ppm only. Patterns in the data are more easily identified once these questionable values are discarded.

Table 57 presents the data as µg CIPC taken up, rather than µg CIPC per g soil. Thus, no account is taken of the small differences in weight of soil added to the jar. This will contribute to the variability.

However, uptake and release are shown as actual weights in order to calculate the proportion of adsorbed chemical released during the desorption step.

The lack of replicates in this study dictated what statistics could be performed on the data. Only one jar was set up and analysed for each combination of solution concentration, soil and shaking time because of constraints on time. The findings cannot be validated because of the lack of replication, but the patterns in the data are consistent enough to allow some confidence in the findings. Where more time is available, the use of at least three replicates per treatment is recommended for statistical validity.

The Barassie results indicated that

- The volume of water added has the most significant effect on the extent of chemical removal from the soil surface: this affects the equilibrium in the jar, and thus the extent of dilution of the supernatant will govern the degree of removal.

- Contact time has little effect: one hour is sufficient for equilibrium to be re-established. This finding is in agreement with sorption data and supports the suggestion that the organic matter on the soil could be represented as a thin coating on the mineral grains, which is easily accessible to the CIPC molecule.

Modifications to the experimental procedure were made for the Fen Peaty experiments, based on the findings from the Barassie study.

6.5.4.4 Desorption method for Fen Peaty soil

Because of the large amount of chemical uptake (and resulting low solution concentration) when 10g Fen Peaty was used in sorption studies, 1g was selected as the most appropriate weight for the desorption experiments.

1g soil was weighed into a 4oz glass jar, and 50ml of CIPC solution was added by pipette. Jars were then sealed and shaken for 24 hours on an end-over-end shaker to allow sorption to occur (sorption studies showed no difference in uptake after 24 and 48 hours).

After 24 hours shaking, 50ml of additional water was added to the jars (solution volume having been shown to have the most significant effect in experiments with Barassie) which were then returned to the shaker for either 1, 4 or 24 hours to determine the influence of contact time.

After the shaking period for desorption was complete, the entire solution was filtered through Whatman GF/C filter paper into a Buchner flask. The washings from the soil pad were also added to the flask. The entire volume in the flask was then extracted on a C-18 column as detailed in section 6.2.2.2, and 5µl aliquots were injected onto the GC and quantified under conditions detailed in Section 6.2.2.4.

6.5.4.5 Results for desorption from Fen Peaty soil

The figure and tables below describe the process of desorption of CIPC from Fen Peaty soil at a soil-to-solution ratio of 1:50, after a 24 hour sorption period followed by the addition of fresh water.

Desorption isotherms are generally constructed following sequential decanting and replacing of the supernatant from one solution. This process generally produces a desorption isotherm with a lesser gradient than the sorption isotherm due to the irreversibility of some types of sorption (hysteresis effect).

In this case, the isotherm is really a representation for the combined processes of uptake and removal of chemical on addition of fresh water i.e. it shows the net uptake onto soil following two separate stages. Because the physical conditions under which the experiments were carried out (solution volume in particular) change during the course of the experiment, solution data must be presented as actual weights rather than concentration.

Table 59 CIPC desorbed from 1g Fen Peaty soil. Effect of varying contact times (1hr vs 4hr vs 24hr)

Starting concentration and contact time	Equilibrium CIPC in solution (µg)	Uptake (µg)	Percentage desorbed
24 hour adsorption			
1ppm	12.02	29.07	-
2ppm	34.40	41.10	-
5ppm	80.71	209.32	-
10ppm	126.59	256.49	-
20ppm	288.83	538.87	-
30ppm	571.88	997.23	-
40ppm	745.47	1265.11	-
1 hour desorption			
1ppm	23.91	17.18	40.9
2ppm	44.53	30.97	24.7
5ppm	96.62	193.41	7.6
10ppm	148.59	234.49	8.6
20ppm	423.23	404.47	24.9
30ppm	742.42	826.69	17.1
40ppm	881.53	1129.05	10.8
4 hour desorption			
1ppm	38.92	2.17	92.5
2ppm	35.00	40.50	1.5
5ppm	95.27	194.76	7.0
10ppm	170.90	212.18	17.3
20ppm	398.03	429.67	20.3
30ppm	726.29	842.82	15.5
40ppm	986.69	1023.89	19.1
24 hour desorption			
1ppm	18.90	22.19	23.7
2ppm	31.56	43.94	-6.9
5ppm	129.32	160.71	23.2
10ppm	180.57	202.51	21.0
20ppm	455.04	372.66	30.8
30ppm	790.51	778.60	21.9
40ppm	1000.95	1009.63	20.2

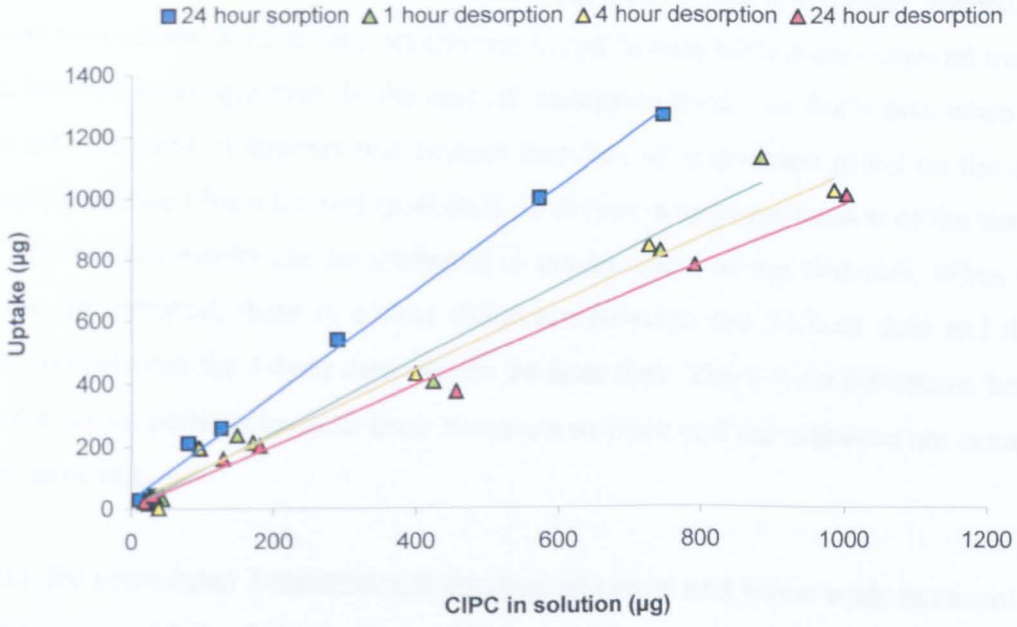


Figure 73 Uptake of CIPC onto 1g Fen Peaty soil following 24 hour equilibration and subsequent addition of fresh water

Table 60 ANOVA p-values for comparisons between treatments designed to determine the effect of contact time on the amount of chemical desorbed from 1g Fen Peaty soil

Comparison	p value for data set	
	1 – 40 ppm	5 – 40 ppm
1 hour vs 4 hour	0.666	0.628
1 hour vs 24 hour	0.991	0.033
4 hour vs 24 hour	0.662	0.036

6.5.4.6 Discussion of results from Fen Peaty desorption

Again, values obtained at low starting concentrations (1 and 2ppm) are the least reliable, as illustrated by some negative values for desorption. At low concentrations, relative errors from a number of sources are greater (e.g. any spillage during the extraction procedure; inaccurate transfer of weighed CIPC crystals to the solution; reading off concentrations on the GC). In this particular case, the starting concentration of the 2ppm solution was determined to be only 1.2ppm – if this reading was in error all subsequent values will be

biased. There is a reasonable case for discarding these values completely. Indeed, when the lowest two values in each data set (shown in red in data tables) are removed trends in the data become more apparent. In the case of desorption from Fen Peaty soil, when the entire data sets are used, it appears that contact time has no significant effect on the amount of chemical released from the soil ($p>0.662$). However, a large proportion of the variability in the set of seven results can be attributed to the inclusion of the first two. When these two values are removed, there is a clear difference between the 24-hour data and the 1-hour data; and between the 4-hour data and the 24-hour data. There is no difference, however, at 1 and 4 hours, perhaps because these times are so close and the reactions are occurring at a fairly slow rate.

Again, the convoluted 3-dimensional structure of humic and fulvic acids in the soil organic matter may make it relatively inaccessible, requiring a longer time for either pesticide to reach the active sites. In contrast, when Barassie soil is used, no difference is seen at 1 and 24 hours after the addition of fresh water. As previously discussed, the organic components of Barassie soil may exist as a thin coating on the surface of the mineral grains, which is readily accessible, allowing molecular interactions to occur swiftly.

Over the 24-hour desorption period, the biggest removal of chemical occurs within the first hour, perhaps as a result of chemical removal from the freely available organic components on the soil surface. After this time, desorption continues to occur at a much slower rate, as pesticide molecules held more deeply within the 3-dimensional structure of the organics are returned to solution.

6.5.5 Conclusions from sorption and desorption experiments and implications for potato washing situation

- CIPC will be taken up onto soils from solution, so untreated soil may be a useful way of mopping up chemical residues from washing effluent. This will still present the problem of dealing with contaminated solid wastes, but storing solids on-site is likely to result in breakdown of residues through microbial action. In the previously described cross-contamination study, the concentration of chemical in the liquid phase did indeed reduce once untreated crop had passed through. Whether this is a result of uptake onto the crop or onto the associated soil is not clear.

- Chemical may also be released back into solution when any additional water is added to the barrel, but the addition of a volume of fresh water will not necessarily

reduce the chemical concentration as would be expected as a result of dilution. At least, there may not be a direct relationship between the increase in volume and the actual reduction in chemical level.

- Observed differences in the amount of chemical taken up by different soil types become greater the more soil is present. In a commercial situation, the weight of soil in the washer will depend on the degree of crop cover, the type of soil in which the crop is grown and the tonnage of crop washed in the barrel since it was last emptied and cleaned.

- It is recommended, in crop terms, that untreated tubers are not washed in the same barrel as treated crop. This will minimise the risk of organic/untreated crop picking up detectable residues, but it will also reduce the potential for chemical residues in the water to be mopped up by the clean soil. Where practical, the most benefit might be gained by washing untreated crop immediately after the washer is filled, and following it with the treated crop. That way, there will be a reservoir of clean soil available to take up chemical from solution and help keep effluent discharges within guideline levels.

- In terms of residue reduction, it is prudent to remove the settled solids from the bottom of the barrel each time the washer is refilled. Also, effective separation of the solid and liquid phases of the effluent (e.g. by addition of flocculating agents or filtration) will minimise the amount of chemical reaching watercourses. Effective treatment of solids to reduce chemical content could be as simple as leaving it outside to age: microbial action (and the action of UV light) will reduce the levels within a period of weeks, at which point the solids could potentially be spread back on land. However, the on-site disposal of chemically contaminated material should only be carried out in consultation with the Environment Agency (SEPA in Scotland) to ensure that pollution of surface and groundwater resources does not ensue and no discharge consents or statutory guidelines are violated.

CHAPTER 7

REMOVAL OF CIPC RESIDUES FROM WATER USING HYDROGEN PEROXIDE

7.1 Introduction

Where CIPC treated crop is washed prior to delivery to processors or retailers, large volumes of CIPC contaminated wastewater are produced. Washers are often located on-site at large facilities, although mobile washers are available for hire for smaller operations. A significant amount of chemical is removed from the crop into the washing water along with any adhering soil. This may lead to significant CIPC residues in the effluent, which is often disposed of to drain with no treatment, although solids can be removed to landfill or stored onsite until residues have reduced. A simple method for removing residues from contaminated wash-water is needed in order for farmers and growers to meet the demands of incoming EU legislation and Environment Agency tolerances. The series of experiments described in the following sections aimed to meet this need by breaking down residual chemical using a small quantity of oxidising agent.

The Environmental Quality Standard (EQS) for CIPC in river water is 10μg l^{-1}, which means that untreated effluent discharged directly into watercourses will require significant dilution in order to meet the requirements. Samples from the barrels of commercial washers have been found to contain up to 10ppm CIPC by the end of the working day, as reported elsewhere in this thesis.

In commercial situations, several methods are used to remove pesticide residues from water including settlement, filtration, digestion and sorption onto solids e.g. activated charcoal. Where permanent washing facilities exist on-site, treatment plants utilising some or all of these methods can be installed to deal with the effluent [Anon (2001b); Anon (2001c)] UV light treatment and sorption onto charcoal can be used as final 'polishing' stages to remove traces of chemical from drinking water, but it can be very expensive to treat large volumes of effluent. In the treatment of drinking water, Foster *et al* (1991) found that with a contact time of 15-30 minutes, activated carbon will remove pesticide residues from surface waters to less than 0.1μg l^{-1} for 6-24 months (depending on the concentration and volume of the effluent) before regeneration of the carbon is required.

Several methods for destroying pesticide residues in the laboratory are reported in the literature. Some of the more complicated methods described, although very successful, were discounted in this study because the aim was to develop a straightforward method for destroying pesticide residues.

Guzik (1978) studied the photolysis of CIPC in distilled water and in 2% aqueous acetone using simulated noonday sunlight (280-1400nm). Although CIPC has negligible adsorption above 280nm, a half-life for disappearance from a 4ppm solution in distilled water at 25°C of 130 hours was calculated. The only photoproduct in distilled water was identified as isopropyl 3-hydroxycarbanilate (3-HOIPC). No 3-chloroaniline was observed during the photolysis of CIPC in distilled water, suggesting a different breakdown pathway to microbial degradation. Microbial breakdown results in production of 3-chloroaniline through hydrolysis of the carbamate function [Kaufman and Kearney (1965)].

Acetone can be used to mimic the effect of dissolved materials found in natural waters. Sensitised reactions may follow different pathways, at different rates and with different products to unsensitised reactions. Ross and Crosby (1973) reported that ethylenethiourea in water photodegraded in the presence of acetone or riboflavin and sunlight, but not in distilled water alone. In Guzik's study, the addition of 2% acetone to the CIPC solution increased the rate of reaction 30-fold and resulted in a second photoproduct, IBQ (2-isopropoxycarbonylamino-1,4-benzoquinone).

Draper and Crosby (1984) investigated the effect of dilute hydrogen peroxide on the rate of breakdown of a number of classes of pesticide in water (thiocarbamate, organophosphorus and N-methylcarbamate amongst others) in sunlight and near-UV light. At very low H_2O_2 concentration (100μM) the rate of breakdown was increased by factors of between 1.5 to 25 for different classes of pesticide, with the greatest enhancement seen with compounds with low direct photolysis rates and weak UV absorption. They concluded that in natural waters, low concentrations of hydrogen peroxide can initiate the oxidation of chemicals that might otherwise be resistant to photolysis and hydrolysis and persist in the aqueous environment. Although successful in distilled water, their system is not necessarily an accurate model for natural waters, where other substances such as bicarbonate ions, carbonate ions and humic materials may be efficient scavengers of the hydroxyl radical, HO· [Mabury and Crosby (1996)].

Concentrated hydrogen peroxide has been used in conjunction with UV light as a treatment for removing pesticide residues from water: in many cases, the addition of a small volume

of peroxide to the solution prior to irradiation has resulted in an increase in reaction rate. Benitez and co-workers (1995) described the photo-oxidation of carbofuran (a carbamate insecticide) using UV light with and without hydrogen peroxide. Peroxide was found to enhance the rate of carbofuran breakdown when used in conjunction with UV irradiation, but had no effect on the breakdown rate when used alone.

Sawata (1998) used UV light with and without hydrogen peroxide in the laboratory to destroy tecnazene residues in water. While UV light alone was effective in lowering residues, the rate of reaction increased when dilute hydrogen peroxide was also added. The half-life of the chemical in water under experimental conditions was a matter of minutes. In this instance, the hydrogen peroxide acted as a photosensitiser: hydroxyl radicals formed on the breakdown of the H_2O_2 molecule reacted with the tecnazene molecules to break them down. This effect was in addition to direct photolysis by UV light. A dark control showed no breakdown of tecnazene, suggesting no chemical hydrolysis of the molecule by H_2O_2.

Tirmazi (1998) studied the use of UV light (254nm) for photodecomposition of CIPC in distilled water and in suspensions of soil. H_2O_2 was not used in this study. Solutions were irradiated for 3 hours, and samples withdrawn at intervals (10, 20, 30, 45, 60, 90, 120 150 and 180 minutes) to follow the progress of the reaction. The rate of phototransformation was found to be dependent on solution concentration, with the fastest rate at low concentrations. Three different soil suspensions were used (arable, peat and acid washed sand), and soil type was also shown to affect the rate of chemical removal. Half-life in 10ppm solution ranged from 0.08hr in distilled water, to 0.11hr in acid washed sand suspension, to ~1.2 hours in the presence of arable and peat soils. The inhibition of the reaction in the presence of arable or peat soil was attributed to a combination of i) soil particles shielding the chemical from incident light and ii) sorption onto soil particles. The photoproducts were identified using GC-MS, and indicated that CIPC undergoes a number of reactions including dechlorination, hydroxylation, alkoxylation and rearrangement reactions when exposed to UV light in aqueous solution.

Advanced oxidation processes (eg UV/O_3, Photo-Fenton) can also be used to break down pesticides in water. Chiron *et al* (2000) produced a review of the most recent methods, including TiO_2 catalysis, ozonation and photo-Fenton reactions. Burrows *et al* (2002) also reviewed the reactions involved in the photodegradation of pesticides, and evaluated the potential use of photochemical processes in advanced oxidation processes for water treatment. Huston and Pignatello (1999) investigated the potential of photo-assisted Fenton

reactions for destroying pesticides and their formulations in water, and noted complete loss of active ingredient in <30 minutes under experimental conditions. Fallman *et al* (1999) also employed the photo-Fenton process to destroy persistent pesticide residues in the wastewater from a recycling plant for pesticide containers. They found that degradation was considerably faster than in their previously published work with TiO_2/UV and $TiO_2/Na_2S_2O_8$/UV photocatalysis.

The hydroxyl radical (OH·) plays an important role in the degradation of pesticides in water. It will react with organics by hydrogen abstraction or electrophilic addition to double bonds. It may also attack aromatic rings at positions occupied by halogens [Chiron *et al* (2000)]. Draper and Crosby (1981) observed that the rate of photodecomposition of thiobencarb was significantly increased by the addition of small amounts of H_2O_2, tryptophan, methylene blue and aqueous acetone, and produced results similar to those of the photo-Fenton system of breakdown. Their results suggest that hydroxyl radicals are active in each system. The authors concluded that much of the photo-oxidation in water traditionally attributed to singlet oxygen might be due, in fact, to the hydroxyl radical since singlet oxygen is known to be relatively selective.

The presence of suspended or dissolved components in the solution can complicate matters. Miller and Zepp (1979) investigated the photoreactivity of pollutants in aqueous solution and when sorbed onto suspended sediments. In all experiments, the disappearance of chemical followed first-order kinetics (i.e. plots of ln concentration vs. time were linear) although differences in behaviour were noted between sorbed and dissolved forms. However, their results differed from others reported in the literature, and they concluded that the way in which the chemicals were introduced to the solutions might have influenced the results. It is common practice to 'spike' solids with pesticides dissolved in organic solvents, which are then evaporated off to give an even spread of chemical over the surface of the solid. Miller and Zepp, however, coated the chemical onto the sides of a glass vessel, then added the solution and solids, allowing the chemical to slowly dissolve and be taken up onto the surface of the soil. Non-polar organics may then be sorbed selectively onto the organic matter of the soil, which provides a different micro-environment in which the photochemical reactions will occur.

Bachman and Patterson (1999) investigated the rate constants for photochemical breakdown of carbofuran in distilled water alone, and in the presence of various samples of dissolved organic matter (DOM). Photodecomposition was seen to follow first-order kinetics, although the presence of dissolved organics inhibited the photolysis reaction,

reducing reaction rate. They suggested two mechanisms by which the DOM might inhibit chemical breakdown: one, competition between the DOM and the pesticide for the available photons; and two, binding of the pesticide by the DOM. When the relationship between the amount of bound chemical (determined by fluorescence quenching) and photolysis rate was investigated, the reaction rate was shown to be inversely proportional to the degree of binding through hydrophobic partitioning.

Wolfe *et al* (1978) explored the hydrolysis, biolysis and photolysis of three carbamate pesticides (carbaryl, propham and chlorpropham) and determined the significance of each as degradation pathways in the environment. Hydrolysis half-lives (at pH 5,7 and 9) of $>1*10^4$ days were determined for IPC and CIPC, illustrating that hydrolysis is not a significant pathway for removal of these chemicals from the aquatic environment. Direct photolysis half-lives of 254 days and 121 days were determined in clear, near-surface water for IPC and CIPC respectively. Biolysis half-lives for CIPC were 120 and 2.9 days for fungi and bacteria respectively. In general, rate constants for bacterial cultures were two orders of magnitude higher than for fungal cultures. In the environment, biolysis will be the most competitive and effective process for removing these chemicals.

David *et al* (1998) used photolysis and sonolysis to investigate the breakdown of chlorpropham and 3-chloroaniline in water. Two mechanisms are involved in ultrasonic degradation: direct reaction of the pesticide molecule with hydroxyl radicals formed on the sonolysis of water, and thermal degradation due to local increases in temperature caused by the implosion of cavitation microbubbles. Sonolysis was more efficient at higher frequencies (at 482 than 20 kHz), and CIPC was completely degraded after 45 minutes at 482kHz. Ultrasonic transformation of 3CA was 85% inhibited by isopropanol, suggesting hydroxyl radicals play a more important role in the degradation of 3CA than pyrolysis by thermal degradation. Irradiation at 254nm was also shown to be effective at degrading both CIPC and 3CA. The first step in the phototransformation of CIPC and 3CA was photohydrolysis of the C-Cl bond, generating hydroxylated products that were easily broken down and did not accumulate. All aromatic and quinonic compounds were completely degraded within a few hours.

In this work, a similar approach to that of Sawata (1998) for destroying tecnazene in water was adopted and modified for CIPC. The use of H_2O_2 as the oxidant for removing residual pesticide from commercial wastewater is attractive for many reasons, not least because it breaks down easily to H_2O and O_2, leaving no further chemical residues to be dealt with. It can also have activity against bacteria, and is currently permitted as an additive in potato

washing effluent for prevention of the spread of brown rot [J.Waltham, personal communication]. It is also effective against other potato pathogens such as silver scurf. [Ufek *et al* (2001)] and is used in 6% solution as a general store disinfectant (e.g. Certis' Jet 5 solution). It is unlikely to encounter any problems in terms of environmental legislation.

7.2 Experimental methods

Experimental procedures common to a number of experiments are described in this section, with additional details of individual experiments following in later sections.

7.2.1. Theory

The aim of these experiments was to determine whether the addition of a small volume of 30% H_2O_2 to a solution of CIPC in water will result in the breakdown of the CIPC molecule, either in the dark or in the presence of UV radiation. Oxidation of pesticide molecules by peroxide would be an attractive method for removing residues from washing-water, and so initial experiments were carried out in the dark to determine the effect of peroxide in isolation.

The concentration of peroxide remaining over time will be determined by reaction with acidified potassium permanganate:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5O_2 + 8H_2O$$

The simplified net ionic equation is

$$5H_2O_2 + 2MnO_4^- + 6H^+ = 2Mn^{2+} + 5O_2 + 8H_2O$$

The hydrolysis reaction in samples for CIPC determination was stopped by the addition of a small volume of 1M $Na_2S_2O_5$ to reduce any residual H_2O_2. Once extracted onto octadecyl-bonded silica (C-18) columns, samples can be stored for several weeks prior to elution into acetone with no significant degradation of the CIPC [Liška and Bílková, (1998)]. Wherever practicable, samples were extracted and analysed within a few days.

7.2.2.Materials

Isopropyl-N-(3-chlorophenyl carbamate) was supplied by Aldrich Chemical Co. and was used as received (purity>95%). All organic solvents used were HPLC grade. Analytical grade sodium metabisulphite (Fisher Scientific), potassium permanganate (Koch Light Laboratories Ltd), sulphuric acid (Fisher Scientific) and 30% hydrogen peroxide (Fisher Scientific) were all used as received. Initial experiments were carried out in distilled water.

7.2.3. Preparation of solutions

2ppm/5ppm CIPC: 0.004/0.010g of CIPC was added to ~1750ml water in a 2-litre volumetric flask. The solution was heated to 40°C, shaken regularly and left overnight. It was then made up to volume, filtered through Whatman No.1 filter paper and stored at 3°C in the dark until use.

50mM potassium permanganate: 7.0915g $KMnO_4$ crystals were dissolved in ~800ml distilled water in a beaker and stirred with magnetic stirrer. The solution was transferred quantitatively to a 1 litre volumetric flask and made up to volume with distilled water.

1M sodium metabisulphite: 47.53g $Na_2S_2O_5$ crystals were weighed into a beaker and ~200ml distilled water added. The solution was stirred for 20 minutes, transferred quantitatively to a 250ml volumetric flask and made up to volume.

Dilute sulphuric acid: 50ml concentrated H_2SO_4 was added slowly by pipette to ~180ml distilled water in a beaker, while the solution was stirred with a magnetic stirrer. The solution was allowed to cool to room temperature then transferred to a 250ml volumetric flask and made up to volume with distilled water. Acid was stored in a glass screw-cap bottle in the acid cupboard until required.

GC standards: A stock 1000ppm CIPC standard was made up in HPLC grade acetone by weighing 0.1g CIPC into a weighing bottle, dissolving in a small volume of acetone and adding to a 100ml volumetric flask. The bottle was rinsed several times with acetone and the washings added to the volumetric flask. The solution was made up to volume with acetone and stored at 3°C until required. Standards of lower concentration were prepared by appropriate dilutions of the stock solution in acetone.

7.2.4. Extraction

Samples for CIPC determination were extracted using solid phase extraction (SPE). The solution was passed through 500mg octadecyl silica bonded (C18) extraction cartridges (Alltech Chromatography) at a flow rate of ~2ml per minute on a VacMaster manifold (IST). Columns were conditioned with 5ml distilled water followed by 5ml methanol prior to the addition of the water sample. Once the sample had passed through the column, 5ml distilled water were added to remove any weakly-held interfering compounds. Columns were vacuum dried for 1 hour to remove any remaining water. CIPC retained on the column was eluted off in ~2ml HPLC grade acetone, and made up to volume in a 2ml volumetric flask. Samples were stored at ~3°C until analysis.

Samples for peroxide determination were added to a conical flask with 5ml dilute H_2SO_4. The resulting solution was titrated with 50mM $KMnO_4$ to the first permanent faint pink colour. The concentration of peroxide remaining was calculated using Equation 2 from Section 7.2.1.

7.2.5. Gas chromatography

Determination of CIPC was carried out on a Pye Unicam PU4500 chromatograph equipped with a flame ionization detector.

GC conditions:

Column:	Length 1m, i.d 4mm	
Packing:	3% OV-17 on GasChrom Q	
Gases:	N_2 carrier	30ml/minute
	H_2 for flame	30ml/minute
	Air for flame	180ml/minute
Temperatures:	Injector	220°C
	Detector	250°C
	Oven	180°C isothermal
Injection volume:	5µl	

Under these conditions, CIPC had a retention time on the column of ~3 minutes. The system was calibrated on a daily basis using standards described in Section 2.2.3. Data collection, integration and storage were carried out on an SP4400 Integrator (SpectraPhysics).

7.2.6 Graphical representation of data

Disappearance data for CIPC and peroxide were normalised and plotted as the percentage of the original amount in solution vs. time. This enabled replicate runs to be plotted on the same graph, even when starting concentrations varied slightly. By plotting CIPC and H_2O_2 data for individual runs on the same figure, the disappearance of each chemical over time can easily be followed. All graphs were plotted on the same scale to allow straightforward visual comparison of data from different experiments.

When plotting the data, points where <5% of the starting amount remained were not included because of the increased error when reading off small concentrations on the GC. Remaining percentages were calculated using the values at time zero, although T_0 data was also omitted from the graphs (see Discussion section 7.3.1.3). Experimental data appear in full in the tables of results in each section.

7.3. Decomposition of CIPC by peroxide in distilled water in the dark

A small volume of 30% hydrogen peroxide was added to solutions of CIPC in distilled water in the dark to determine whether there is any chemical oxidation of the CIPC molecule by H_2O_2. In previous studies, the addition of a small amount of peroxide has been shown to enhance the rate of pesticide degradation by UV light (Sawata, 1998). The author demonstrated that the H_2O_2 contributed to the indirect photolysis of tecnazene, but did not initiate hydrolysis in solution in the absence of UV.

In the described work, the effect of different amounts of peroxide on a 2ppm solution of CIPC in distilled water was investigated at 20°C and 30°C in the dark.

7.3.1 2ppm CIPC and 10mM H_2O_2 at 30°C

7.3.1.1 Experimental methods

Procedure

2 litres of 2ppm CIPC solution were transferred to a 2 litre conical flask wrapped in aluminium foil (to prevent photolysis by sunlight). The flask was placed in an incubator at

30°C overnight and stirred continuously. 2ml 30% H_2O_2 were added to give a starting concentration of approximately 10mM. 100ml samples were withdrawn at intervals for CIPC analysis. Samples were stored in 4oz screw-cap glass jars with 1ml 1M sodium metabisulphite prior to extraction. 100ml samples for peroxide analysis were withdrawn at the same time.

Extraction and analysis:

The sample for CIPC analysis was solid-phase extracted on a 500mg C-18 column as described in Section 7.2.4, and analysed by GC under conditions described in Section 7.2.5. Peroxide samples were acidified and titrated with potassium permanganate following the procedure described in Section 7.2.4.

7.3.1.2. Results

The tables and figures on the following page describe disappearance of CIPC and H_2O_2 in aqueous solution at 30°C at concentrations of 2ppm and 10mM respectively. The figures show the normalised data plotted as the percentage of the starting concentration remaining over time. CIPC and H_2O_2 data for each run are shown on the same figure.

7.3.1.3 Discussion

From Figure 74, it can be seen that CIPC is quickly removed from the solution, and relatively little of the H_2O_2 is consumed during the reaction. Starting concentrations of both CIPC and H_2O_2 varied slightly between runs, and as a result the absolute values may be different, although the overall pattern of decomposition is the same in each.

CIPC: The data as shown in Figure 74 fits a straight line, indicating that the disappearance of CIPC is constant over time. Peroxide was added to the solution in the morning to allow the longest time for collecting samples throughout the day, but few samples were collected between 9 and 24 hours. The samples at 24 hours contained no CIPC at all.

The disappearance of CIPC was expected to follow first-order kinetics, where the relationship between concentration and time is described by $\ln (C_t/C_0) = -kt$ where C_t and C_0 are the concentration at time t hrs and time zero respectively, t is time (hrs) and k is the reaction rate constant. For a first order reaction, plotting $\ln (C_t/C_0)$ against time produces a straight line, the gradient of which is $-k$, the rate constant. The half-life for the disappearance of the chemical can then be calculated thus: $t_{1/2} = \ln 2/k = 0.693/k$

Table 61 CIPC data from 3 replicate runs of 2ppm CIPC, 10mM H_2O_2 at 30°C

Time (hr)	CIPC in extract (μg)	% remaining
0.00	130.60	100.00
1.50	131.70	100.84
3.00	99.90	76.49
6.00	54.10	41.42
0.00	85.48	100.00
1.25	79.45	92.96
3.67	56.81	66.46
23.25	2.97	3.47
0.00	88.63	100.00
2.08	79.20	89.36
4.08	64.97	73.30
6.08	43.02	48.55
7.67	30.35	34.24

Table 62 H_2O_2 data from 3 replicate runs of 2ppm CIPC, 10mM H_2O_2 at 30°C

Time (hr)	Titre (ml)	mmoles $KMnO_4$	mmoles H_2O_2	H_2O_2 conc (mM)	% remaining
0.00	6.10	0.305	0.763	7.625	100.00
1.50	7.50	0.375	0.938	9.375	122.95
3.00	7.25	0.363	0.906	9.063	118.85
6.00	7.00	0.350	0.875	8.750	114.75
22.00	6.80	0.340	0.850	8.500	111.48
25.75	6.70	0.335	0.838	8.375	109.84
48.00	6.50	0.325	0.813	8.125	106.56
53.00	6.45	0.323	0.806	8.063	105.74
0.00	7.85	0.393	0.981	9.813	100.00
1.33	7.80	0.390	0.975	9.750	99.36
3.83	7.65	0.383	0.956	9.563	97.45
23.50	7.20	0.360	0.900	9.000	91.72
29.42	6.80	0.340	0.850	8.500	86.62
47.50	6.80	0.340	0.850	8.500	86.62
53.25	6.70	0.335	0.838	8.375	85.35
70.00	6.50	0.325	0.813	8.125	82.80
94.42	6.10	0.305	0.763	7.625	77.71
0.00	7.95	0.398	0.994	9.938	100.00
2.08	7.70	0.385	0.963	9.625	96.86
6.08	7.30	0.365	0.913	9.125	91.82
8.16	7.50	0.375	0.938	9.375	94.34
9.75	7.20	0.360	0.900	9.000	90.57
23.66	7.35	0.368	0.919	9.188	92.45
48.25	6.60	0.330	0.825	8.250	85.71
55.25	6.65	0.333	0.831	8.313	91.10
71.83	6.60	0.330	0.825	8.250	88.00

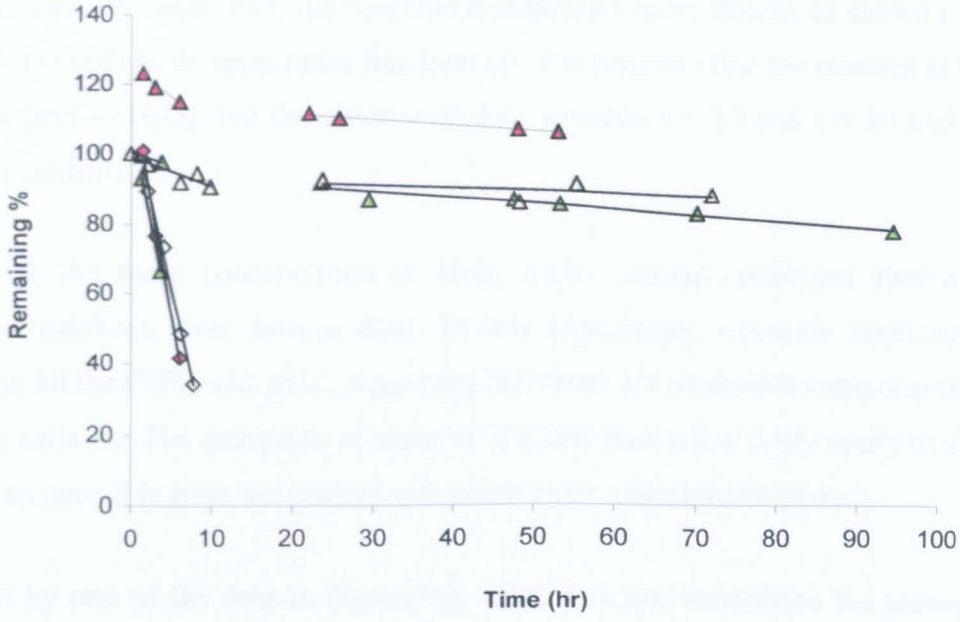


Figure 74 Percentages of CIPC and H_2O_2 remaining over time in distilled water at 30°C. Starting concentrations 2ppm and 10mM respectively.

◇ = CIPC △ = H_2O_2

However, when the data from this experiment was plotted as ln (C_t/C_0) vs time, the data could be fitted to a curve better than a straight line. On closer inspection it transpired that the first point (T_0) was the only one that would fit below the straight line. From this, it seemed the transformation of CIPC progressed slowly in the early stages, before reaching a stable rate. This lag period could be due to the build up of radicals in the solution. Another explanation would be that the first sample was not fully mixed before the first CIPC sample was taken, giving an unrepresentative result, but since this effect was seen consistently in replicate runs (and in data from other experiments) it seems more likely that there is an initial lag period.

In light of this, T_0 data was omitted from the graphs (in addition to values of <5%). This resulted in a straight-line plot for each run, indicating a constant rate of conversion of CIPC.

H_2O_2: When the data for peroxide were plotted as a percentage of the starting concentration vs. time, there appeared to be two rates of breakdown. To further illustrate any differences in the rate of reaction, the data from each run was plotted as two separate sets: one for samples up to ~10 hours, and one for later samples. This showed quite clearly a change in gradient of the disappearance line with time. The fast removal of H_2O_2 (i.e. the steeply sloping line) coincided with the removal of the majority of the CIPC from solution.

Once most of the CIPC was gone, the peroxide disappeared more slowly, as shown by the shallower gradient of the disappearance line later on. It is possible that the reaction is first-order with respect to H_2O_2, but the absence of data between t = 10 and t = 20 makes it impossible to confirm.

A control with the same concentration of H_2O_2 under similar conditions showed no spontaneous breakdown over several days. In this experiment, peroxide continued to disappear after all the CIPC was gone, suggesting that there are oxidisable components still present in the solution. The quick rate of removal of CIPC shows it is fairly easily oxidised by peroxide, so once it is gone the oxidant will attack more resistant compounds.

As illustrated by one of the runs in Figure 74, when data are normalised the remaining percentage can occasionally exceed 100%. This does not mean that more has been produced, merely that the T_0 value was inaccurate. This could be the result of an unrepresentative sample collected at T_0 if, for example, the solution was not fully mixed before the sample was taken. The gradient of the disappearance line is more important than the actual percentages, and all three lines for H_2O_2 have similar slopes, indicating similar rates of decomposition.

Products: The appearance of reaction products was not monitored during the progress of the reaction (only the disappearance of CIPC and H_2O_2), so no comment can be made on the pathway or products of the reaction. However, it can be noted that 3-chloroaniline, a product of microbial and thermal degradation of CIPC [Nagayama and Kikugawa (1992); Kaufman and Kearney (1965)], was not formed by the reaction, suggesting that hydrolysis of the carbamate function is not the primary process. Several samples were re-run under the same GC conditions as described for air samples in Chapter 4, which would allow any 3-CA to be identified on the chromatogram. The absence of 3-CA is encouraging, since it is toxic and listed on the European Community Priority Pollutant Circular No 90-55 (1990).

The disappearance of CIPC from the chromatogram does not imply that the molecule has been fully broken down and mineralised. A slight modification of structure (e.g. the oxidation of one carbon) would result in its not being recognised as CIPC when analysed by the GC. As a result, the concentration in solution would decrease, although it is possible that most of the molecule could remain intact and available for further oxidation. The kinetics of the formation and breakdown of reaction by-products need to be investigated to determine whether any stable intermediates remain

In this work, breakdown products were neither quantified nor identified (due to restrictions on time and equipment), so no mechanism for CIPC transformation can be proposed. Where effluent is monitored by the Environment Agency, there would be no problem meeting specific guidelines for CIPC residues, since no CIPC can be detected within 20 hours of the addition of 10mM H_2O_2. However, it is likely that significant amounts of pesticide breakdown products will remain, and it is important to be able to identify them and their fate. Different methods of extraction and analysis might be required in order to identify all compounds produced. The determination of breakdown products is often more complicated than that of the parent because they are produced in such small quantities. In particular, hydroxyl radicals are non-selective so numerous by-products may be formed at very low concentrations, which makes them difficult to identify [Chiron *et al*, 2000]

Following the success of these initial experiments, a number of parameters considered to be important were investigated in turn. These included temperature, the relative concentrations of CIPC and H_2O_2, and the presence of soil and other components of 'natural' water. These experiments are described in the following sections.

7.3.2. 2ppm CIPC and 10mM H_2O_2 at 20°C

Temperature can affect the rate at which a reaction progresses by providing energy required for the molecules to interact. The previous experiment was repeated with the same concentrations of CIPC and peroxide at 20°C to determine the effect of temperature on the reaction. The reaction was expected to proceed more slowly at the lower temperature, but the significance of the effect was not known.

7.3.2.1 Experimental methods:

The experiment was carried out as described in Section 7.3.1.1, with the exception that the incubator was at 20°C instead of 30°C. Sampling and analysis were carried out as described previously.

7.3.2.2 Results

The results for two replicate runs of the experiment are shown in Tables 63 and 64 and Figure 75 overleaf.

Table 63 CIPC data from 2 replicate runs of 2ppm CIPC in distilled water ; 10mM H_2O_2 ; 20°C

Time (hr)	CIPC in extract (µg)	% remaining
0.00	162.00	100.00
0.17	155.00	95.68
24.00	19.80	12.22
0.00	171.30	100.00
1.00	155.30	90.66
19.00	50.60	29.54
24.00	31.00	18.10

Table 64 H_2O_2 data from 2 replicate runs of 2ppm CIPC distilled water; 10mM H_2O_2; 20°C

Time (hr)	Titre (ml)	mmoles $KMnO_4$	mmoles H_2O_2	H_2O_2 conc (mM)	% remaining
0.17	8.10	0.405	1.013	10.125	100.00
24.00	8.30	0.415	1.038	10.375	102.47
45.50	8.15	0.408	1.019	10.188	98.19
69.00	8.00	0.400	1.000	10.000	98.16
1.00	9.05	0.453	1.131	11.313	100.00
19.00	9.00	0.450	1.125	11.250	99.45
24.00	7.10	0.355	0.888	8.875	78.45

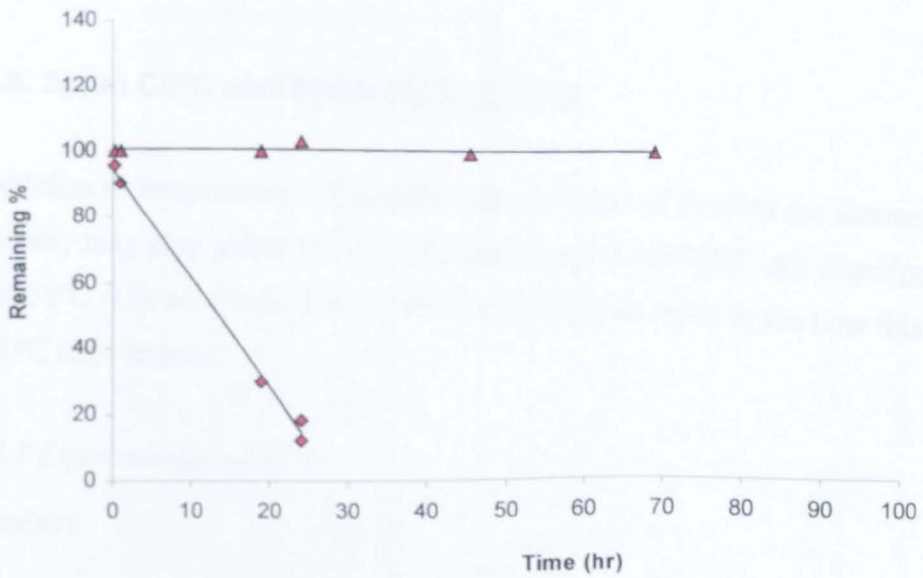


Figure 75 Percentages of CIPC and H_2O_2 remaining in distilled water at 20°C. Starting concentrations 2ppm and 10mM respectively

◇ = CIPC △ = H_2O_2

7.3.2.3 Discussion

Once the T_0 value and values <5% were excluded, there was not enough CIPC data from each individual run to plot two sets of results, so all the data were combined and plotted as one series. Peroxide data were treated in the same way, so it was impossible to tell whether the disappearance of H_2O_2 was constant or followed the pattern seen in the last experiment (i.e. fast removal while CIPC remained followed by a slower breakdown).

The results show that the rate of CIPC conversion is slower, and that less peroxide is consumed when the reaction is carried out at 20°C than over a similar period of time at 30°C. Under these conditions, the transformation of CIPC will still occur, but it will take longer than at a higher temperature. In terms of treatment of wastewater, a fast reaction is desirable given the large volumes produced on a daily basis and the relatively short residence time that would be required in a vessel where this reaction would be carried out.

Although this experiment generated very limited amounts of data, the same patterns of decomposition are seen, and the reaction seems to progress more slowly at a lower temperature. More data would be required to determine whether this is a significant difference in rate.

7.3.3. 2ppm CIPC and 50mM H_2O_2 at 30°C

In addition to temperature effects, the concentration of oxidant (or amount relative to the substrate) may also affect the rate of transformation of CIPC. An experiment was carried out at 30°C with an elevated concentration (50mM) of H_2O_2 to see how this altered the rate of CIPC conversion.

7.3.3.1 Experimental methods

Procedure

Two litres of 2ppm CIPC solution were transferred to a 2 litre conical flask wrapped in aluminium foil (to prevent photolysis by sunlight). The flask was placed in an incubator at 30°C overnight and stirred continuously. 10ml 30% H_2O_2 were added to give a starting concentration of approximately 10mM. 100ml samples were withdrawn at intervals for CIPC analysis, and stored in 4oz screw-cap glass jars with 1ml 1M sodium metabisulphite prior to extraction. 100ml samples for peroxide analysis were withdrawn at the same time.

Extraction and analysis

The sample for CIPC analysis was solid-phase extracted on a C-18 column as described in Section 7.2.4, and analysed by GC under conditions described in Section 7.2.5. Peroxide samples were acidified and titrated with potassium permanganate following the procedure described in 7.2.4.

7.3.3.2 Results

Table 65 CIPC data from 2 replicate runs of 2ppm CIPC in distilled water ; 50mM H_2O_2 ; 30°C

Time (hr)	CIPC in extract (µg)	% remaining
0.00	77.53	100.00
1.83	47.27	60.97
4.25	16.97	21.89
7.00	6.14	7.91
0.00	81.14	100.00
1.50	76.56	94.36
3.66	49.06	60.47
20.75	2.86	3.52
44.00	0.00	0.00

Table 66 H_2O_2 data from 2 replicate runs of 2ppm CIPC distilled water; 50mM H_2O_2; 30°C

Time (hr)	Titre (ml)	mmoles $KMnO_4$	mmoles H_2O_2	H_2O_2 conc (mM)	% remaining
0.00	18.40	0.920	2.30	46.00	100.00
1.92	18.40	0.920	2.30	46.00	100.00
4.33	17.80	0.890	2.23	44.50	96.74
7.17	17.35	0.868	2.17	43.38	94.29
23.50	16.80	0.840	2.10	42.00	91.30
28.33	16.50	0.825	2.06	41.25	92.70
31.91	16.25	0.813	2.03	40.63	93.66
47.50	15.15	0.758	1.89	37.88	90.18
54.75	14.60	0.730	1.83	36.50	88.48
72.75	13.25	0.663	1.66	33.13	81.54
0.00	19.50	0.975	2.44	48.75	100.00
1.42	19.15	0.958	2.39	47.88	98.21
3.58	18.95	0.948	2.37	47.38	97.18
20.75	18.40	0.920	2.30	46.00	94.36
27.08	17.10	0.855	2.14	42.75	87.69
45.00	17.25	0.863	2.16	43.13	88.46
49.17	16.95	0.848	2.12	42.38	86.92
52.33	16.75	0.838	2.09	41.88	85.90
70.67	16.30	0.815	2.04	40.75	83.59

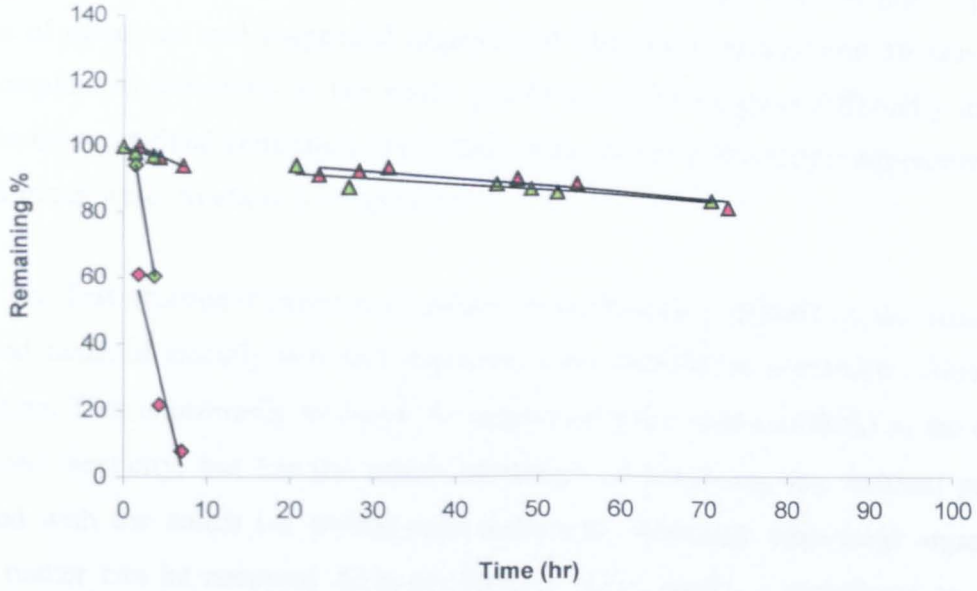


Figure 76 Percentages of CIPC and H_2O_2 remaining over time in distilled water at 30°C. Starting concentrations 2ppm and 50mM respectively

◇ = CIPC △ = H_2O_2

7.3.3.3 Discussion

The rate of CIPC transformation appears to be quicker with 50mM H_2O_2 than 10mM. However, the data from this particular experiment are very limited, and more data points would need to be plotted to determine whether this is a significant effect. Very little of the hydrogen peroxide added is consumed in the breakdown of CIPC, suggesting that peroxide concentration is not rate limiting.

7.4 Decomposition of CIPC by peroxide in 'natural' water samples in the dark at 30°C

The work described in Section 7.3 investigating the transformation of CIPC in aqueous solution by a small amount of peroxide was carried out in distilled water i.e. water free from any dissolved or suspended components.

To more accurately model what would happen in samples of effluent from potato washing operations, some of the experiments were repeated in samples of 'real' water. Tap water in

the West of Scotland (where the experiments were carried out) contains significant amounts of dissolved and suspended organic and inorganic components. Because of the more complicated chemistry of tap water, reactions might progress differently in it than under the more artificial conditions in distilled water. Some of the earlier experiments were repeated in tap water to allow a comparison.

One of the first treatment processes applied to wash-water effluent is the removal of suspended material (mostly soil and sediment, some starch) by settlement, filtration or flocculation. This is primarily to lower the suspended solid load and BOD of the effluent and prevent septicity, but has the added advantage of removing any residual pesticide associated with the solids i.e. sorbed onto sediments. Although suspended organic and mineral matter can be removed from the effluent fairly easily, a significant amount of material could remain dissolved in the water. In order to model this situation more accurately, some of the previous experiments were repeated in water containing dissolved organic matter (extracted from a sample of Barassie soil) in addition to tap water.

7.4.1. 2ppm CIPC and 10mM H_2O_2 in tap water at 30°C

7.4.1.1 Experimental methods

Procedure

2 litres of 2ppm CIPC in tap water were transferred to a 2 litre conical flask wrapped in aluminium foil (to prevent photolysis by sunlight). The flask was placed in an incubator at 30°C overnight and stirred continuously. 2ml 30% H_2O_2 were added to give a starting concentration of approximately 10mM. 100ml samples were withdrawn at intervals for CIPC and peroxide determination.

Extraction and analysis:

Samples for CIPC analysis were solid-phase extracted on a C-18 column as described in Section 7.2.4, and analysed by GC under conditions described in Section 7.2.5. Peroxide samples were acidified and titrated with potassium permanganate following the procedure described in 7.2.4.

7.4.1.2 Results

The tables and figures below describe the disappearance of CIPC and H_2O_2 in tap water.

Table 67 CIPC data from 3 replicate runs of 2ppm CIPC in tap water ; 10mM H_2O_2 ; 30°C

Time (hr)	CIPC in extract (µg)	% remaining
0.00	74.38	100.00
2.08	33.06	44.45
6.00	4.31	5.80
7.67	1.81	2.44
23.58	0.24	0.32
0.00	114.03	100.00
1.58	86.24	75.63
3.83	49.30	43.23
5.17	32.38	28.39
21.42	0.72	0.63
0.00	95.41	100.00
1.17	66.97	70.19
3.50	25.89	27.14
6.50	6.5	6.81
23.42	0	0.00

Table 68 H_2O_2 data from 3 replicate runs of 2ppm CIPC tap water; 10mM H_2O_2; 30°C

Time (hr)	Titre (ml)	mmoles $KMnO_4$	mmoles H_2O_2	H_2O_2 conc (mM)	% remaining
0.00	7.70	0.385	0.963	9.625	100.00
2.00	7.50	0.375	0.938	9.375	97.40
4.12	7.20	0.360	0.900	9.000	93.51
8.08	7.25	0.363	0.906	9.063	94.16
9.67	6.95	0.348	0.869	8.688	90.26
23.58	6.05	0.303	0.756	7.563	78.57
48.17	3.80	0.190	0.475	4.750	50.67
55.17	3.35	0.168	0.419	4.188	46.53
71.92	1.10	0.055	0.138	1.375	15.17
0.00	6.70	0.335	0.838	8.375	100.00
1.58	7.15	0.358	0.894	8.938	106.72
3.75	7.00	0.350	0.875	8.750	104.48
5.00	7.40	0.370	0.925	9.250	110.45
21.42	7.00	0.350	0.875	8.750	104.48
28.00	6.20	0.310	0.775	7.750	92.54
45.67	6.10	0.305	0.763	7.625	91.04
49.75	5.65	0.283	0.706	7.063	84.33
0.00	4.85	0.243	0.606	6.063	100.00
1.17	4.90	0.245	0.613	6.125	101.03
3.42	4.80	0.240	0.600	6.000	97.96
4.83	4.75	0.238	0.594	5.938	97.94
6.42	4.60	0.230	0.575	5.750	94.85
23.42	4.20	0.210	0.525	5.250	86.60
27.50	4.10	0.205	0.513	5.125	84.54

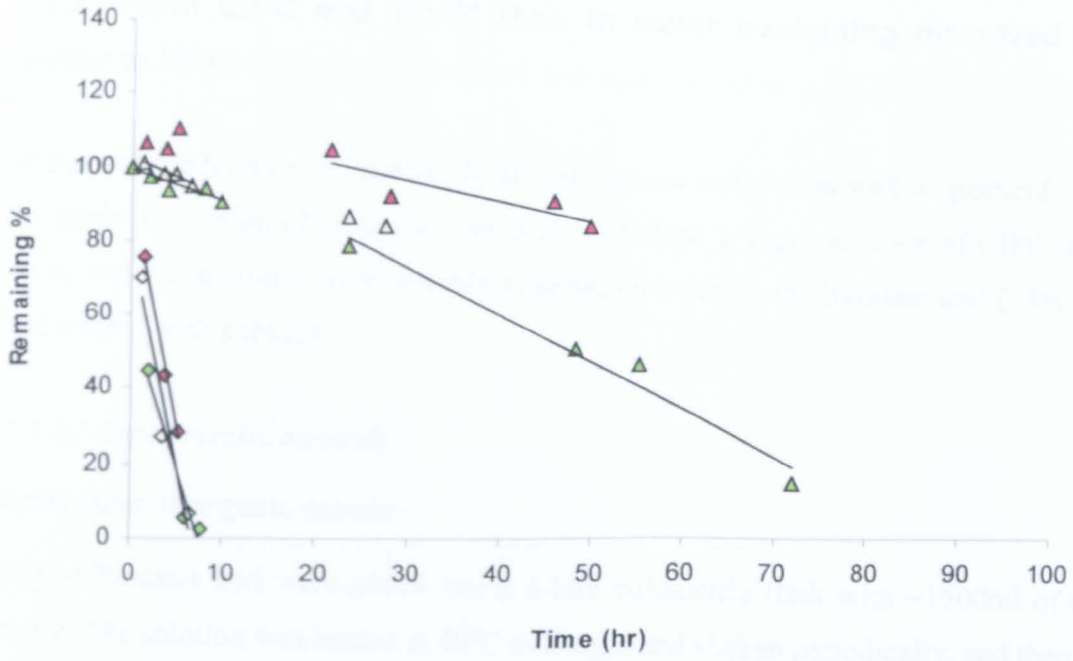


Figure 77 Percentages of CIPC and H_2O_2 remaining in tap water at 30°C. Starting concentrations of 2ppm and 10mM respectively.

◇ = CIPC △ = H_2O_2

7.4.1.3 Discussion

CIPC: The chemical was quickly removed from the solution, and virtually none remained after 10 hours. Each run was plotted as an individual series to demonstrate inter-run variability. All three replicate runs gave similar results for the disappearance of CIPC.

H_2O_2: More peroxide is consumed in tap water than in distilled water. After 70 hours in tap water, <20% of the starting concentration remained compared with ~80% in distilled water. The accelerated breakdown of H_2O_2 is believed to be due to interactions with components of tap water that are not present in distilled water. For example, certain metals present in trace amounts in tap water (e.g. copper and iron) will catalyse the breakdown of peroxide. Tap water will also contain organic material on which the peroxide can act. The two-stage breakdown of peroxide in distilled solution was not observed in tap water because the peroxide has a constant supply of substrate (other than CIPC) on which to act. That the breakdown of CIPC appears quicker in tap than distilled water is perhaps due to the production of other radicals when the peroxide attacks organic molecules in the solution. Hydroxyl and other radicals can be produced on oxidation of organic matter [Mabury and Crosby (1996); Draper and Crosby (1984); Galadi and Julliard (1996)], any/all of which might accelerate the transformation of CIPC.

7.4.2. 2ppm CIPC and 10mM H_2O_2 in water containing dissolved organic matter at 30°C

Wash-water effluent will contain dissolved organic material as well as pesticide residues. To model the action of an oxidant on such a solution, a 2ppm solution of CIPC was made up in water containing water-soluble material extracted from Barassie soil (~5% organic) and treated with peroxide.

7.4.2.1 Experimental methods

Extraction of organic matter:

20g of Barassie soil were added into a 2-litre volumetric flask with ~1500ml of distilled water. The solution was heated at 40°C overnight and shaken periodically, and then filtered through GF/C filter paper followed by a 0.45μm filter to remove all suspended material. The solution was pale yellow in colour, due to the presence of phenolic and other organic compounds extracted from the soil. This solution was then used to prepare a 2ppm solution of CIPC as described in Section 7.2.3.

Procedure

Two litres of 2ppm CIPC solution were transferred to a 2 litre conical flask wrapped in aluminium foil (to prevent photolysis by sunlight). The flask was placed in an incubator at 30°C overnight and stirred continuously. 2ml 30% H_2O_2 were added to give a starting concentration of approximately 10mM. 100ml samples were withdrawn at intervals for CIPC and peroxide determination.

Extraction and analysis:

Samples for CIPC analysis were solid-phase extracted on a C-18 column as described in Section 7.2.4, and analysed by GC under conditions described in Section 7.2.5. Peroxide samples were acidified and titrated with potassium permanganate following the procedure described in 7.2.4.

7.4.2.2 Results

The tables and figures below describe disappearance of CIPC and H_2O_2 in water containing dissolved organic matter (DOM) at 30°C at concentrations of 2ppm and 10mM respectively.

Table 69 CIPC data from 2 replicate runs of 2ppm CIPC in water with DOM ;10mM H_2O_2 ; 30°C

Time (hr)	CIPC in extract (µg)	% remaining
0.00	78.81	100.00
2.00	78.16	99.17
3.83	79.55	100.95
5.92	70.95	90.03
7.45	67.97	86.25
23.42	60.56	76.85
30.42	45.90	58.25
47.92	38.25	48.54
54.84	21.96	27.87
0.00	92.06	100.00
1.58	85.86	93.26
3.92	87.73	95.30
5.17	73.66	80.01
21.67	68.53	74.44
49.83	46.58	50.60

Table 70 H_2O_2 data from 2 replicate runs of 2ppm CIPC water with DOM; 10mM H_2O_2; 30°C

Time (hr)	Titre (ml)	mmoles $KMnO_4$	mmoles H_2O_2	H_2O_2 conc (mM)	% remaining
0.00	7.85	0.393	0.981	9.813	100.00
2.00	7.80	0.390	0.975	9.750	99.36
4.00	7.55	0.378	0.944	9.438	96.18
5.95	7.65	0.383	0.956	9.563	97.45
7.58	7.45	0.373	0.931	9.313	94.90
23.50	7.65	0.383	0.956	9.563	97.45
48.08	7.60	0.380	0.950	9.500	97.44
55.16	7.30	0.365	0.913	9.125	96.69
71.83	7.30	0.365	0.913	9.125	95.42
0.00	7.00	0.350	0.875	8.750	100.00
1.58	6.50	0.325	0.813	8.125	92.86
3.75	7.45	0.373	0.931	9.313	106.43
5.08	7.70	0.385	0.963	9.625	110.00
21.50	7.50	0.375	0.938	9.375	107.14
28.00	7.00	0.350	0.875	8.750	100.00
45.67	7.10	0.355	0.888	8.875	101.43
49.75	6.50	0.325	0.813	8.125	92.86

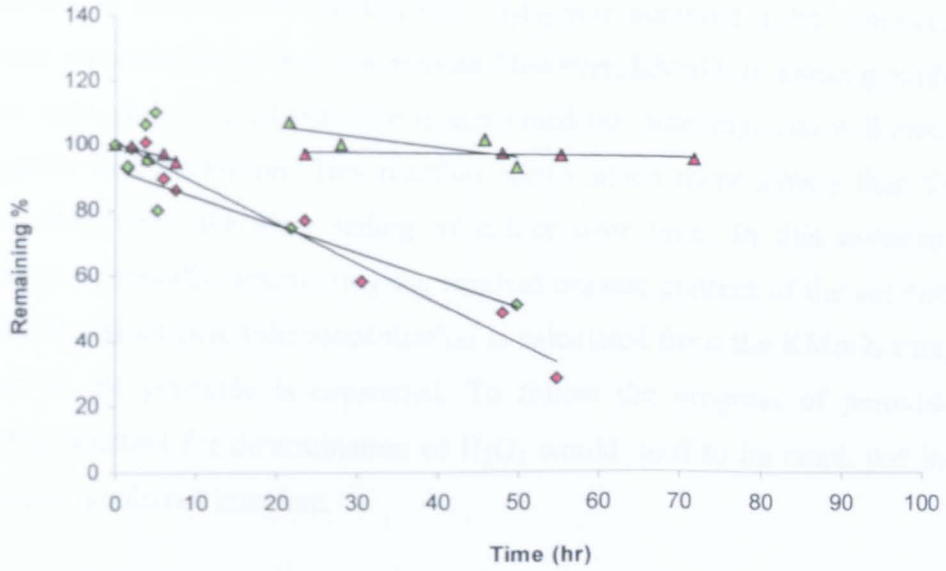


Figure 78 Percentages of CIPC and H_2O_2 remaining over time in water containing DOM. Starting concentrations 2ppm and 10mM respectively.

◇ = CIPC △ = H_2O_2

7.4.2.3 Discussion

Transformation of CIPC occurs more slowly in this solution than in tap water. There also appears to be little breakdown of the peroxide.

CIPC: The slow breakdown of chlorpropham can be attributed to competition between the pesticide and dissolved organics for the oxidant. There may also be a degree of shielding through partitioning onto the organic matter. Bachman and Patterson (1999) observed that hydrophobic partitioning of carbofuran onto dissolved organic matter protected the pesticide from photodecomposition, by drawing it into an aggregate of humic molecules. A similar process might protect the CIPC from chemical oxidation in this instance. Any CIPC held in this way may be recovered by extraction through C-18 columns and elution into acetone, so this process may not be responsible for reducing the solution concentration.

H_2O_2: On initial inspection, it appears that virtually none of the peroxide breaks down over the ~ 80 hours of the experiment. However, this pattern is actually an artefact of the method of peroxide determination. Determination of H_2O_2 by titration with acidified $KMnO_4$ is dependent on the permanganate being reduced by the H_2O_2. The end-point of the reaction usually comes when all the peroxide is used up and the $KMnO_4$ is no longer reduced, resulting in the pink colour persisting in solution. In this experiment, no permanent colour change was achieved – the pink colour faded over time and the solution

returned to yellow. The reaction with H_2O_2 was assumed to be complete when the pink colour remained for at least one minute. However, $KMnO_4$ is a strong oxidising agent in its own right, and once all peroxide is consumed the permanganate will react to oxidise any organics in the solution. This reaction occurs much more slowly than the reaction with peroxide, hence the slow fading of colour over time. In this instance, permanganate titration is actually determining the residual organic content of the solution as well as the peroxide. Since peroxide concentration is calculated from the $KMnO_4$ titre, it appears that none of the peroxide is consumed. To follow the progress of peroxide consumption, another method for determination of H_2O_2 would need to be employed in which organic material would not interfere.

7.5 Decomposition of CIPC by peroxide in distilled water at 30°C in the presence of soil.

'Raw' potato washing effluent will contain significant amounts of suspended material, in particular, soils removed in the washing process and potato components (e.g. skin, starch) as a result of damage to tubers in the washer. At locations where there are permanent washing facilities and some treatment of effluent is carried out, the first stage in the process is to remove the solids by filtration, settlement or flocculation. With the solids, significant amounts of residual pesticide are removed. However, where mobile washers are used on-farm, effluent from washing may be released directly to drain or into watercourses with little or no treatment at all. The addition of peroxide could be useful as a remedial treatment for such effluent. To model this situation, some of the experiments described previously were repeated in a 1% suspension of soil (Barassie) to investigate the effect of the presence of soil on the reaction of H_2O_2 with CIPC.

7.5.1 2ppm CIPC, 10mM H_2O_2 in distilled water at 30°C with 20g soil

7.5.1.1 Experimental methods

Procedure

2 litres of 2ppm CIPC solution (in a conical flask sealed with aluminium foil) were left in an incubator for 24 hours to equilibrate. 20g of Barassie soil (~5% organic matter) were added and the solution stirred, immediately prior to the addition of 2ml of 30% peroxide to start the reaction (concentration ~10mM). The flask was then returned to the incubator, and 100ml samples for CIPC and H_2O_2 determination were removed at intervals. All samples

were filtered through Whatman GF/C paper under vacuum to remove the suspended material before solid-phase extraction (for CIPC) or titration (for H_2O_2).

Extraction and analysis:

Samples for CIPC determination were solid-phase extracted on 500mg C-18 columns as described in 7.2.4, and analysed by GC under the conditions detailed in 7.2.5. Peroxide samples were acidified and titrated with $KMnO_4$ as described in 7.2.4.

7.5.1.2 Results

The tables and figure below describe the disappearance of CIPC and H_2O_2 in a 1% suspension of soil at starting concentrations of 2ppm and 10mM respectively. Data from each run was normalised and plotted as the percentage of the original concentration remaining, to allow CIPC and H_2O_2 data from several experiments to be shown together.

Table 71 CIPC data from 3 replicate runs of 2ppm CIPC in water with 1%soil; 10mM H_2O_2; 30°C

Time (hr)	CIPC in extract (µg)	% remaining
1.50	128.60	100.00
3.00	135.10	105.05
6.00	135.80	105.60
22.00	119.20	92.69
25.75	116.50	90.59
48.00	118.20	91.91
53.00	118.90	92.46
0.00	156.10	100.00
0.17	114.50	73.35
3.50	143.20	91.74
7.25	133.60	85.59
23.50	131.30	84.11
29.50	127.00	81.36
78.00	84.60	54.20
150.83	77.40	49.58
0.00	81.00	100.00
1.08	76.82	94.83
3.17	80.16	98.96
23.00	54.48	67.26
29.00	63.75	78.70
47.08	60.87	75.15
52.92	58.88	72.69
70.00	57.02	70.40
94.33	47.31	58.41

Table 72 H_2O_2 data from 3 replicate runs of 2ppm CIPC water with soil; 10mM H_2O_2; 30°C

Time (hr)	Titre (ml)	mmoles $KMnO_4$	mmoles H_2O_2	H_2O_2 conc (mM)	% remaining
0.00	7.90	0.395	0.988	9.875	100.00
1.50	6.65	0.333	0.831	8.313	84.18
3.00	6.00	0.300	0.750	7.500	75.95
6.00	5.70	0.285	0.713	7.125	72.15
22.00	3.30	0.165	0.413	4.125	41.77
25.75	2.85	0.143	0.356	3.563	36.08
48.00	0.50	0.025	0.063	0.625	6.33
0.00	8.10	0.405	1.013	10.125	100.00
0.17	6.70	0.335	0.838	8.375	82.72
3.50	5.75	0.288	0.719	7.188	70.99
7.25	3.15	0.158	0.394	3.938	38.89
23.50	2.20	0.110	0.275	2.750	27.16
29.50	0.50	0.025	0.063	0.625	6.17
78.00	0.60	0.030	0.075	0.750	7.41
0.00	7.35	0.368	0.919	9.188	100.00
1.25	7.25	0.363	0.906	9.063	98.64
3.58	6.65	0.333	0.831	8.313	90.48
23.75	4.05	0.203	0.506	5.063	55.10
29.75	3.20	0.160	0.400	4.000	43.54
47.75	1.50	0.075	0.188	1.875	20.41
53.50	0.90	0.045	0.113	1.125	12.41

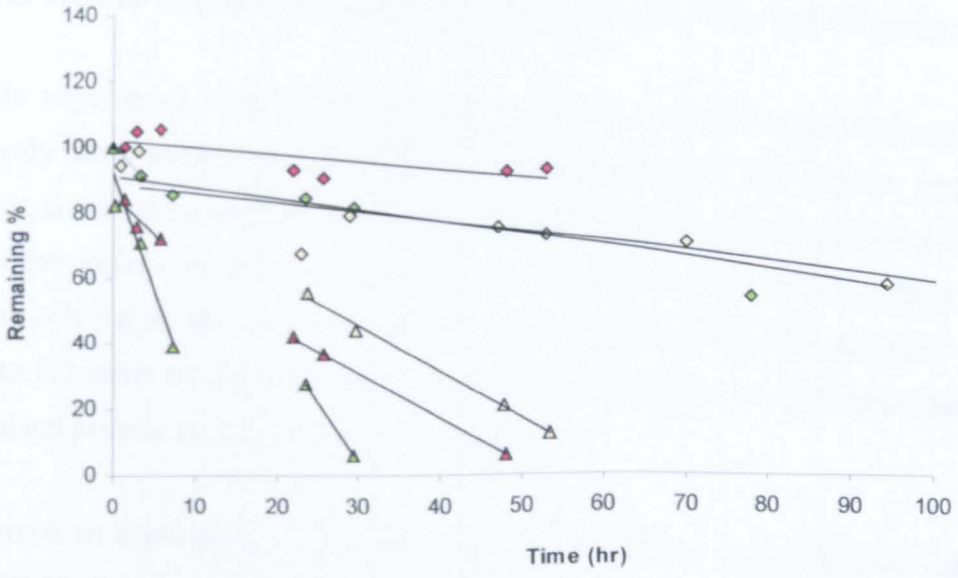


Figure 79 Percentages of CIPC and H_2O_2 remaining over time in 1% suspension of soil. Starting concentrations 2ppm and 10mM respectively.

◇ = CIPC △ = H_2O_2

7.5.1.3 Discussion

This time, a different pattern of breakdown is seen to that in all the previous work. The rate of peroxide consumption is far faster, with almost all consumed within ~50 hours. More than 50% of the starting CIPC remains after 100 hours in each of the three experiments. The presence of soil in the solution has therefore greatly affected the progress of the reactions.

Any oxidisable material in solution will compete with the pesticide molecules for the peroxide, and it is likely that there will be a significant quantity in this solution. 20g of soil were added to 2 litres of CIPC solution to give a 1% suspension. The particular soil added (Barassie) contains ~5% organic matter, so it can be said that ~1g of soil organic matter is present in the solution, in comparison to just 4mg of CIPC i.e. 2,500 times as much organic material is provided by the soil as by the CIPC. The oxidant will attack the most easily oxidised compounds first, which may be compounds present in the soil.

There is also the possibility that sorption onto the solid surfaces of the soil provides the CIPC with protection from attack: sorption studies have shown that CIPC will be taken up from solution onto Barassie's organic components (see Chapter 6). However, since it is a fairly mineral soil this effect is relatively small. Hydrophobic partitioning onto dissolved organic material can also inhibit pesticide breakdown [Bachman and Patterson (1999)].

In this experiment, it is likely that two significant processes are responsible for the relatively slow transformation of CIPC: competition from soil organic matter for the oxidant, and binding onto organic matter affording protection from oxidation. Competition from other molecules is likely to be the most significant effect, because there is so much present relative to the amount of CIPC. Any binding onto solid surfaces would also account for some of the removal of chemical from solution, as these particles would be filtered out prior to extraction on C-18 columns.

In contrast to experiments carried out in water containing only dissolved organics, the apparent breakdown of peroxide can be seen when soil particles are present (i.e. the permanganate titre reduces over time). This is because the total amount of organic material in the soil is very high relative to the small amount that is water-extractable. As a result, peroxide is consumed more quickly, and the interference effect in the titration is lessened.

7.5.2 2ppm CIPC, 50mM H_2O_2 in distilled water at 30°C with 20g soil

7.5.2.1 Experimental methods

The experiment was carried out as described in 7.5.1.1, with the exception that 10ml of 30% H_2O_2 were added to give a starting concentration of ~50mM.

7.5.2.2 Results

Tables 73 and 74, and Figure 80, below describe the disappearance of CIPC and H_2O_2 in a 1% suspension of Barassie soil at 30°C.

Table 73 CIPC data from 3 replicate runs of 2ppm CIPC, 50mM H_2O_2 at 30°C with soil

Time (hr)	CIPC in extract (µg)	% remaining
0.00	155.10	100.00
0.17	140.50	90.59
3.25	128.50	82.85
7.25	124.30	80.14
23.50	82.90	53.45
29.50	52.40	33.78
97.75	6.90	4.45
0.00	127.90	100.00
1.83	139.06	108.73
4.25	122.39	97.42
7.08	124.60	95.69
23.75	100.05	78.22
27.83	90.90	71.07
31.25	81.60	63.80
47.50	32.88	25.70
55.08	17.11	13.38

Table 74 H_2O_2 data from 3 replicate runs of 2ppm CIPC, 50mM H_2O_2 at 30°C with soil

Time (hr)	Titre (ml)	mmoles $KMnO_4$	mmoles H_2O_2	H_2O_2 conc (mM)	% remaining
0.25	19.75	0.988	2.469	49.38	100.00
3.50	17.65	0.883	2.206	44.13	89.37
7.25	15.85	0.793	1.981	39.63	80.25
23.50	13.50	0.675	1.688	33.75	68.35
29.50	12.85	0.643	1.606	32.13	65.06
50.00	9.25	0.463	1.156	23.13	46.84
78.50	4.90	0.245	0.613	12.25	24.81
126.83	0.80	0.040	0.100	2.00	4.05
0.00	18.75	0.938	2.344	46.88	100.00
1.75	17.50	0.875	2.188	43.75	93.33
4.08	16.35	0.818	2.044	40.88	87.20
6.92	15.95	0.798	1.994	39.88	85.07
23.75	13.30	0.665	1.663	33.25	76.00
27.58	12.65	0.633	1.581	31.63	77.37
31.00	12.05	0.603	1.506	30.13	75.55
47.50	10.00	0.500	1.250	25.00	75.19
55.00	9.20	0.460	1.150	23.00	72.73
71.92	6.80	0.340	0.850	17.00	56.43

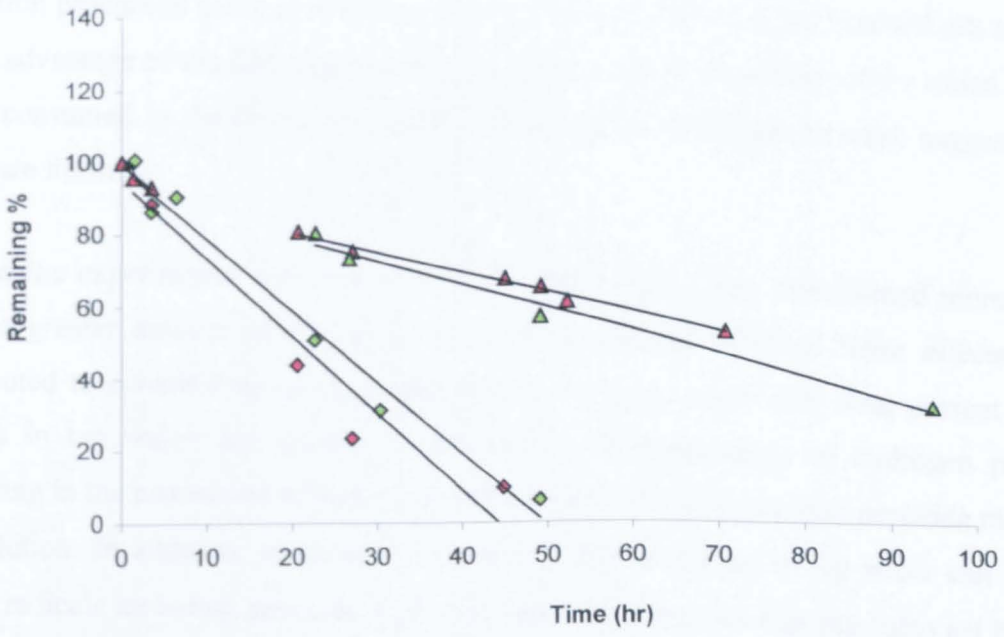


Figure 80 Percentages of CIPC and H_2O_2 remaining over time in a 1% suspension of soil. Starting concentrations 2ppm and 50mM respectively

7.5.2.3 Discussion

CIPC is broken down faster at 50mM H_2O_2 than 10mM in the presence of soil due to the increased concentration of oxidant reducing any competition effects between the CIPC and the soil organic matter. If hydroxyl or other free radicals are produced on destruction of soil organic matter, they too could contribute to the removal of CIPC from the solution.

When this experiment was repeated in tap water under the same conditions, the results were more consistent than in distilled water, although no significant difference in rate can be determined from the fairly limited data (results not shown).

7.6. Summary

The addition of a small volume of peroxide was effective at transforming CIPC in a 2ppm solution in distilled water. The rate of reaction was increased at higher oxidant concentration, but was not proportional to the increase in concentration. At 20°C, the reaction proceeded more slowly than at 30°C. Most of the work was carried out at 30°C to take advantage of the faster rate of reaction. Only a small proportion of the added peroxide was consumed in the reaction (at both concentrations and temperatures), suggesting it is not rate limiting.

When the experiments were repeated in tap water, CIPC was transformed more quickly and a greater amount of the added H_2O_2 was used up. Both of these effects can be attributed to constituents of tap water. Metals such as copper and iron, present at trace levels in tap water, are known to catalyse the decomposition of hydrogen peroxide, resulting in the production of hydroxyl radicals that can then react with pesticide molecules in solution. In addition, oxidation of organic matter dissolved in tap water can produce other radicals including peroxide, hydroxyl and singlet oxygen that may also act on CIPC and increase the rate of transformation relative to distilled water.

When organic matter extracted from soil was also present in solution, the rate of CIPC breakdown was reduced due to competition effects. This experiment also highlighted a limitation of the method of peroxide determination. Organic matter oxidised by potassium permanganate under acid conditions interferes in the analysis, and prevents the end-point of the reaction being accurately determined by titration. In this experiment, the

concentration of peroxide appeared to remain constant although some would actually have been consumed during the reaction.

When a 1% suspension of fairly mineral (5% organic) soil was present in the solution, a similar degradation rate was observed for CIPC. Any binding onto the soil surfaces will also contribute to the reduction of observed solution concentration. This time, the peroxide concentration was seen to decrease, probably because it was consumed very quickly by reaction with the soil. In this instance the effect of interference on the titration was lessened because of the fast breakdown of CIPC, although the end-point problem remained.

In terms of treating potato washing water to remove residual pesticide, the overall results from this series of experiments show that the addition of peroxide may not be as effective as suggested by the original experiments carried out in distilled water. The presence of organic material in the effluent, either suspended or dissolved, as well as potato components such as skin and starch will provide competition for the oxidant and reduce the rate of transformation of CIPC.

Although the concentration of CIPC in solution was seen to decrease over time, it is unlikely that it has been fully mineralised. Slight oxidation of any part of the molecule would prevent it being identified as CIPC by GC. Different methods of extraction and analysis to those used in this study may be necessary to determine the mechanism and products of the transformation. To satisfy environmental regulators, the products of the reaction must be shown to be less toxic and/or less persistent than the parent molecule.

Overall, it seems that the use of peroxide alone may not be effective for the treatment of potato washing effluent. It may be more successful when used in combination with other treatments, for example, UV light. Tirmazi (1998) showed UV light to be effective at removing CIPC residues from solution when used in isolation. A combination of H_2O_2 and UV light may provide an effective method for removing pesticide residues: it was not considered as part of this work because the aim was to investigate the simple, low cost method of H_2O_2 addition, which was not as successful as hoped. Other methods of destruction (e.g. ozonolysis, sonolysis) could be investigated in future for cleaning up washing water contaminated with pesticides. Other oxidants, (e.g. peracetic acid) could also be tested under similar conditions, since the development of a simple, low-cost method for residue removal is still required.

Chapter 8

ESTIMATION OF CHLORPROPHAM LOSS IN AIR FROM TREATED STORES

8.1 Introduction

A large volume of gas is introduced to the store during thermal fog application of chlorpropham. Because stores are leaky, and do not become pressurised during the application, it can be said that an equal volume must also be displaced from the store. In an ideal situation, the volume of fog added to the store would be less than the free air volume in the store and the gas displaced would be mostly air. All the chemical added would remain in the store. In reality, some loss of chemical is inevitable. Some properties and behaviour of the fog can encourage loss; for example, high temperature application encourages fog to accumulate at the top of the store, where most vents and louvres are located. As a result, loss of chemical through leakage is high. Figure 81 below shows fog escaping from a vent during the early stages of a commercial application of chlorpropham.

Figure 81 Fog escaping from a vent

Once all the particles of fog have settled, a small amount of CIPC remains as vapour in the air. When doors are opened or fresh air introduced through vents, this chemical can escape.

A simple model was used to estimate the amount of chemical lost during the application process and as a result of routine venting, based on experimentally derived data. Much of this work has previously been presented as a paper at the 15th Triennial Conference of the European Association of Potato Research in Hamburg, Germany (14-19th July 2002).

8.2 A theoretical 2,000 tonne box store

For the purposes of modelling losses of chlorpropham, the dimensions and volumes in a theoretical 2,000 tonne box store were estimated from measurements of commercial stores and boxes.

8.2.1 Box dimensions and volumes

The dimensions of a one-tonne wooden box were measured and used to calculate the volume of i) the box ii) the crop inside the box iii) the free air space in the box.

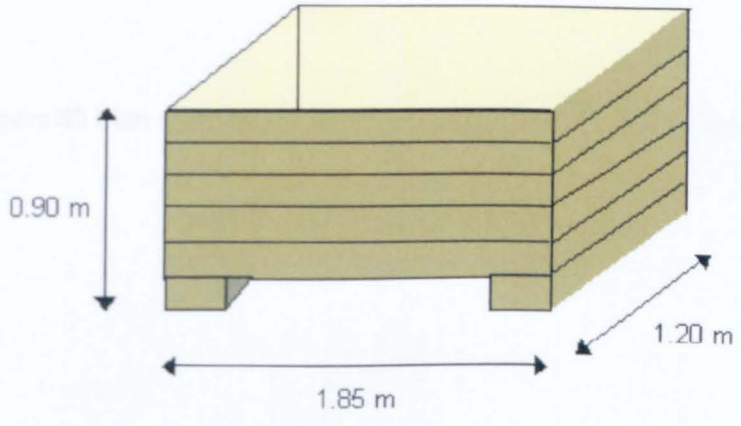


Figure 82 Dimensions of a typical 1-tonne wooden box

A typical one-tonne wooden box has a volume of 1.998m^3 [A. Jina, personal communication]. One tonne of potatoes is assumed to occupy ~1.5m^3 inside the box, of which 0.9m^3 will be tubers and 0.6m^3 inter-tuber spaces [Boyd, unpublished results]. This leaves a free volume at the top of the box of 0.498m^3.

8.2.2 Commercial store dimensions and volume

The layout of the theoretical store was modelled based on a commercial store of similar tonnage described by Boyd (1988). Figure 83 overleaf shows a plan view of the store.

To calculate the total volume of the store, the height and shape of the roof also needs to be considered. Figure 84 shows the end elevation of the store and its proportions.

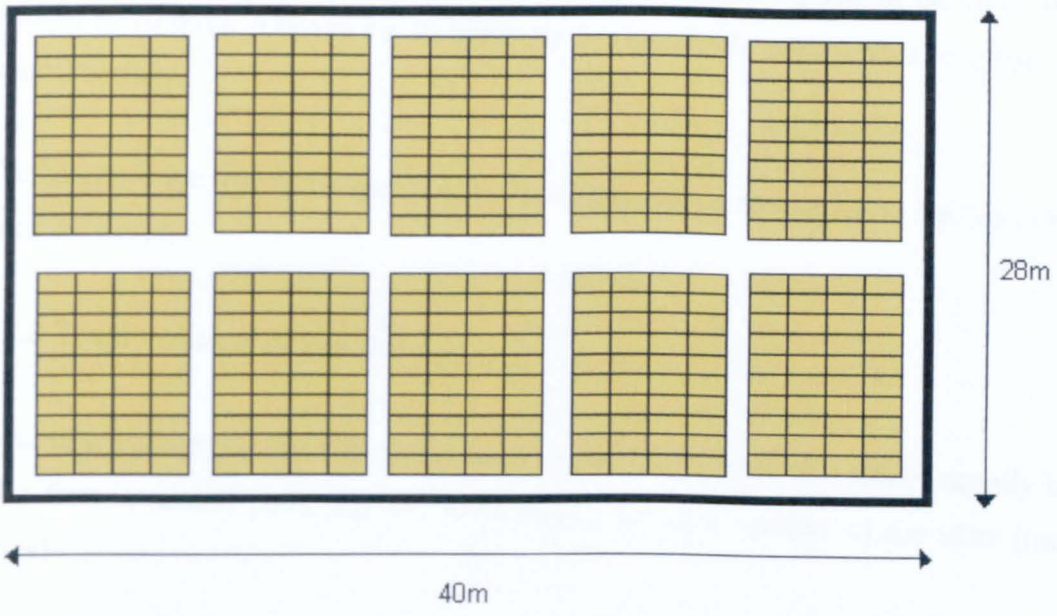


Figure 83 Plan view of the layout of a theoretical 2,000 tonne box store

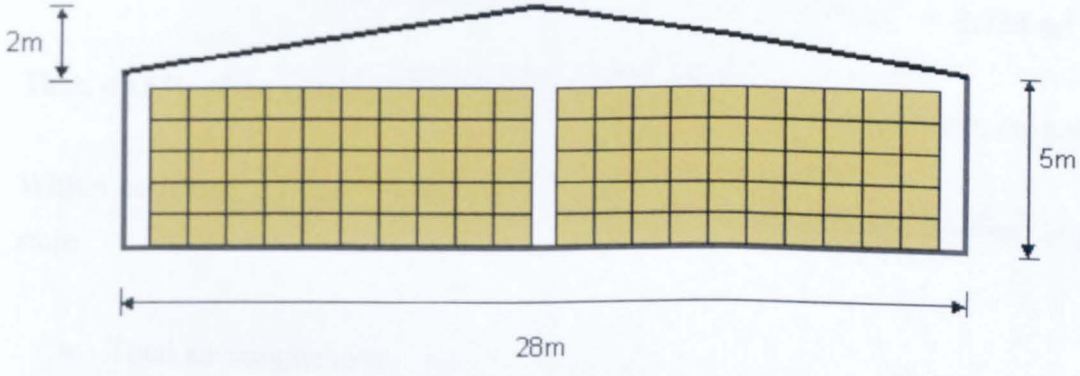


Figure 84 End elevation of a theoretical 2,000 tonne box store

Figure 83 shows the length and width of the store, assuming gaps of 0.5m between each stack; a 2m wide central corridor and 1m clearance round each side of the store. Boxes are stacked in 10 bays, 4 boxes by 10 boxes by 5 boxes high, with 5 bays on either side of a central corridor.

The height to the top of the stack is shown as 5m, with a further 2m to the top of the store from the eaves.

8.2.3 Total volume of the store

Assuming a height to the top of the stack of 5m, and a roof that slopes equally on both sides from a central point 2m above the stack, the total volume of the store (including boxes)

= (40m * 28m * 5m) + (½ * 40m * 28m * 2m) = **6,720 m^3**

Volume occupied by boxes (assuming the store is full)

= 2000 * 1.998m^3 = **3,996 m^3**

Thus, the boxes occupy **59.5%** of the volume of the store

Free air volume above and around boxes = 6,720 m^3 – 3,996 m^3 = **2,724 m^3**

Thus, **40.5%** of the volume of the store is free airspace above and between the boxes.

Within each box, 1.098m^3 of the volume is air, so there is an extra 2,196m^3 of air in the store

- Total air volume in the store is **4,920m^3** (73.2%)
- Total volume occupied by boxes and crop is **1,800m^3** (26.8%)

8.2.4 Types of air space in the store

Figure 85 below shows the different kinds of air space identified in a store. The contribution of each to the total volume of the theoretical store was used to estimate losses through leakage during application, and as a result of vapour phase CIPC loss during routine venting throughout the season.

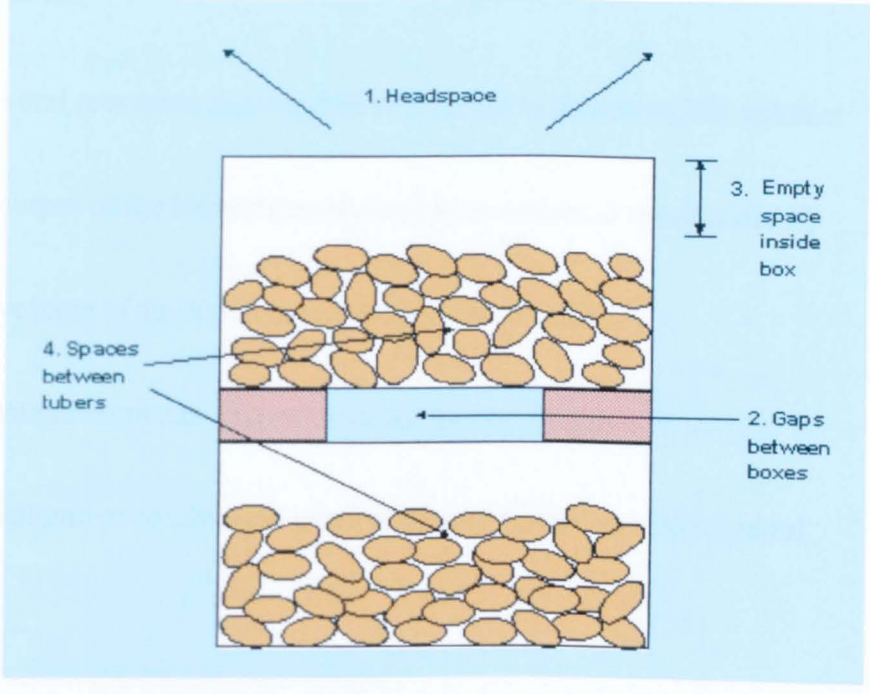


Figure 85 Four types of air space in a potato store, as used in estimates of chlorpropham losses

During application, fog tends to move around and above the column of boxes, rather than into the middle of the box, so the free headspace (1) at the top of the store and gaps between boxes in a stack (2) are the most important spaces. When estimating chemical loss via leakage, these are the only volumes that will be taken into consideration.

Spaces between the tubers themselves (4) and the empty space at the top of the box (3) will become more important when considering chemical loss through routine venting. During venting, the entire volume of the store is refreshed, so vapour phase CIPC within the boxes is assumed to be lost as well as that in the free headspace.

8.3 Estimating the volume of gas produced during thermal fogging – background and theoretical values

To estimate the amount of chemical that is lost through leakage during the application process, the volume of gas introduced to the store during fogging must be known. An equal volume of gas must be lost from the store since pressure in the store does not increase during application.

There are several processes that must be considered to determine the volume:

1. The output of the blower (ascertained from technical specifications)
2. The volume of air drawn in due to the Venturi effect
3. The temperature and expansion properties of the gas
4. The volume of combustion gases produced by the burning of petrol

8.3.1 Blower output

The volume of air produced by the Unifog machine during thermal fogging will be largely dependent on the output of the blower. Information was gathered from several sources to determine the likely output from a typical blower in a commercial fogging machine.

SAM Unifog: blower specification is $500m^3$ per hour at 3,500 rpm [Anon, http]. This volume will be "increased by Venturi effect"

SCC Unifog: Stated blower output is actually measured as inlet flow and is dependent on pressure. It proved impractical to measure this on a Unifog fogger without dismantling the machine, so data from the blower (Hick Hargreaves Series 2033-2000) specification was used instead. Standard operating conditions are 3,600 rpm and pressures between 100 and 420 mbar. Table 75 overleaf shows how the blower output changes with pressure.

Table 75 Variations in Series 2033-2000 blower output over the range of operating pressures

Pressure (mbar)	Blower output (m^3/hr)
100	570
200	540
300	520
420	500

Unifog Model 100 thermal foggers utilise a Roots blower [Anon, 1990]. Information on the blower was obtained from www.rootsblower.com. Performance tables indicate that output volume at 3,600 rpm would be ~540m^3/hr, which is a very similar figure to that obtained from Hick Hargreaves.

The theoretical speed of the airflow exiting the ducting pipe during commercial fogging was first estimated based on blower specification data, as a function of volume and the diameter of the metal ducting pipe. Velocity was calculated using blower output (taken as 530m^3/hr), cross-sectional area of pipe and the relationship velocity = volume/area. (V= Q/A see Continuity equation below)

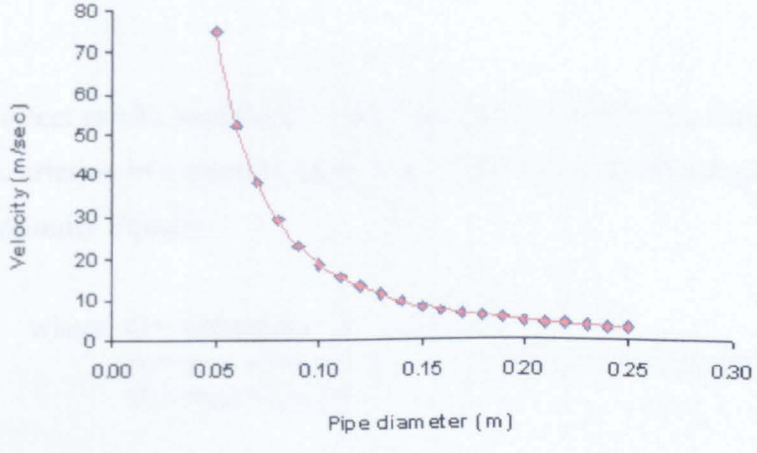


Figure 86 Relationship between air velocity and pipe diameter

8.3.2 Venturi effect

Estimation of the volume of air added to a store during fogging is complicated by the design of the fogger outlet, which incorporates a gap of several centimetres between the fog-head and the ducting pipe, as illustrated overleaf.

Figure 87 Fogger outlet, showing the gap between the fog-head and the metal ducting pipe

This small space between the fog-head and the pipe allows fresh air to be pulled into the air stream (via the Venturi effect) and results in a cooling of the fog and an increase in volume.

The Venturi effect can be explained as the increase in velocity of a fluid stream as it passes through a constriction in a channel, pipe or duct. The increase in velocity can be calculated using the Continuity Equation

$Q = VA$ where Q = volumetric flow rate
A = area of flow (i.e. cross-sectional area of pipe)
V = fluid velocity

Because the volume of gas remains constant, as A gets smaller, so V must increase. This increase in velocity, and resultant change in pressure, draws more air in around the side of the fog stream. Quantifying this effect is very difficult, and so direct measurement of the velocity of the air stream exiting the pipe is the easiest way to determine the total volume of gas.

8.4 Estimating the volume of gas produced during thermal fogging – experimental methods

The blower specification figures alone are not an accurate estimate of the volume of gas added to the store because they take no account of the extra air added to the stream as it enters the ducting pipe. As a result, direct measurement of the velocity of air leaving the fogger was attempted at Sutton Bridge Experimental Unit using an anemometer calibrated to 30m s^{-1}. The study was carried out on 13th June 2002, with the assistance of Stored Crop Conservation.

Table 76 below shows the estimated velocity of the gas exiting a 10cm diameter pipe over the range of volumes expected under normal operating conditions. Figures are based on blower output alone.

Table 76 Blower output and associated gas velocity through 10cm diameter tubing

Blower output (m^3/hr)	Velocity (m/sec)
570	20.04
540	18.99
520	18.28
500	17.58

These figures show that the output from the blower alone can result in air velocities toward the top end of the calibrated range of the anemometer. Any significant increase in volume due to the Venturi effect may take the measurement off-scale.

In practice, the reading was off-scale, suggesting that the volume of gas may have doubled or more as a result of extra air being pulled in. Since no equipment was available that could measure these higher velocities, two approaches were adopted in order to slow the fog down

1. Wider diameter ducting pipe was attached to the 10cm diameter pipe bolted to the fog-head

2. A large box was constructed with 4 apertures, which could be opened and closed in any combination. The combined cross-sectional area of the apertures results in a decrease in velocity

To prevent any damage to instruments and equipment, this study was carried out with no formulation present in the air stream. Therefore, the calculated figures do not include the volume of the fog contributed by the formulation itself. The only other limitation was the maximum operating temperature of the anemometer, which was 80°C. As a result, burner temperature had to be lowered to keep fog temperature within acceptable range. Measurements were made with the burner off or at 125°C, which is considerably lower than the 400-500°C normal under standard operating conditions for the Unifog [Dowd (2003)]. Thus, recorded velocities are likely to be under-estimates since the higher burner temperature during commercial application will increase the volume of fog because of i) expansion of gas at high temperature and ii) increased fuel consumption generating more combustion products.

8.4.1 Air velocity measured through wider diameter ducting pipe

8.4.1.1 Experimental details

As in standard applications, 4" (~10cm) diameter ducting pipe was bolted onto the fog-head of the Unifog machine, leaving a small gap between the two. Short lengths of pipe 6" and 8" in diameter were added at the end of the standard pipe as shown in the diagram below.

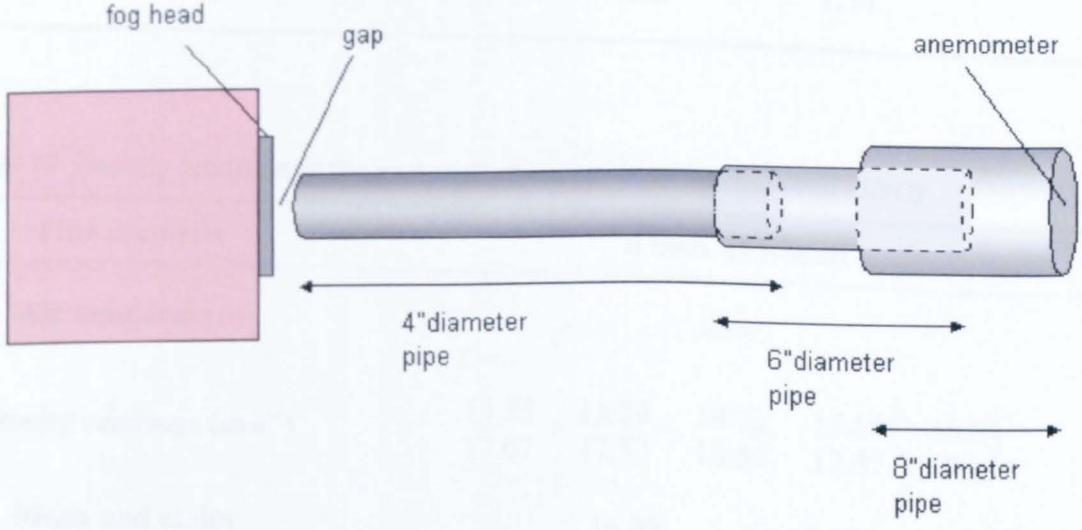


Figure 88 Assembly of pipes for measuring air velocity (not to scale)

Fog velocity reduces as it passes through each section of wider diameter because the cross-sectional area of the pipe increases. The pipes overlapped by ~30cm at each join to reduce the likelihood of leakage, or of extra air getting in, so any change in volume due to the joins in the pipe was assumed to be negligible for the purposes of this study.

It was assumed that the volume and velocity of the fog would vary with instantaneous changes in engine speed and burner temperature, and as a result ten replicate readings were taken each time velocity was measured. Burner temperature, engine revs and air temperatures were recorded for each set of readings.

8.4.1.2 Results with the burner off (~60°C)

Tables 77 to 79 below show recorded velocities at the end of each pipe with the burner off.

Table 77 Velocity readings at the end of 8" diameter pipe; burner cold (60°C)

Pipe diameter	**8 inch (20.6cm)**				
Air temperature	28°C				
Velocity readings (m s^{-1})	5.67	5.66	5.34	7.15	9.17
	10.62	8.60	6.35	8.21	7.71
Mean and st.dev	**7.45**		**1.74**		

Table 78 Velocity readings at the end of 6" diameter pipe; burner cold (60°C)

Pipe diameter	**6 inch (15.4cm)**				
Air temperature	28°C				
Velocity readings (m s^{-1})	14.83	11.34	14.73	15.66	16.64
	17.07	17.39	16.52	17.67	19.14
Mean and st.dev	**16.05**		**2.18**		

Table 79 Velocity readings at the end of 4" diameter pipe; burner cold (60°C)

Pipe diameter	4 inch (10.2cm)				
Air temperature	40°C				
Velocity readings (m s^{-1})	6.83	27.64	26.14	31.60	31.60
	31.60	31.60	30.14	30.32	31.60
Mean and st.dev	27.91		7.65		

The air temperature at the end of the 4" pipe was significantly higher than at the end of the other two pipes. Burner temperature was similar in each case, so the cooler air at the end of the 6" and 8" pipes is probably due to cooling in contact with the metal – the longer the path length through the pipe, the more opportunity for heat loss. In all cases the temperature was within the operating range of the anemometer (80°C maximum). Combustion chamber fuel pressure was fairly constant at 1 bar, and engine revs stayed between 3,390-3,400 rpm. Variation in the ten replicate velocity readings is likely to be due to the difficulty of holding the meter at the same point in the moving air stream. Air in the centre of the flow will be moving fastest, with velocity decreasing out towards the sides of the pipe.

When measurements were made at the end of the 4" pipe bolted directly onto the fogger, the anemometer registered its maximum reading several times – although nominally calibrated to 30 m s^{-1}, the top reading on the meter was 31.60m s^{-1}. The reliability of the data from the 4" pipe is questionable, as there is reason to suspect some of the readings were actually off-scale. What the data does show is that the use of wider diameter piping is effective in bringing the velocity of fog within measurable limits.

Measurements at the end of the 4" pipe were repeated on 27th June 2002 under similar conditions. Table 80 overleaf shows the second data set.

Table 80 Velocity readings at the end of 4" diameter pipe; burner cold, 3,420 rpm

Pipe diameter	4 inch (10.2cm)				
Air temperature	-				
Velocity readings (m s^{-1})	22.80	27.45	27.85	27.27	27.93
	29.53	27.98	27.49	30.35	30.10
Mean and st.dev	**27.89**		**2.12**		

This time, all readings were on scale. The slight reduction in measured velocity could be due in part to the reduced burner temperature (~30°C as compared to 60°C). The mean velocity was very similar to that determined previously, but there was much less variation in the results, as shown by the greatly reduced standard deviation.

8.4.1.3 Results with the burner at 125-130°C

After readings were taken with the burner off (engine temperature 60°C), the work was repeated with the burner on for a more accurate simulation of a commercial application. Under normal operating conditions, the burner can be around 500°C to generate the heat necessary to produce a good quality fog. The temperature at the end of a standard 4" ducting pipe under these conditions was measured as part of this study, and found to be in excess of 200°C. Burner temperature settings of ~130°C and 200°C were investigated in order to keep air within the working range of the anemometer. Because an increase in velocity was expected, readings were taken off the end of the 8" pipe, which previously recorded the lowest mean velocity. Table 81 below shows the recorded velocities at the end of an 8" diameter pipe with the burner set for 130°C.

Table 81 Velocity readings at the end of 8" diameter pipe; burner ~130°C

Pipe diameter	8 inch (20.6cm)				
Air temperature	36.7°C				
Velocity readings (m s^{-1})	8.39	10.11	10.39	11.19	9.83
	11.04	11.58	9.54	9.65	8.39
Mean and st.dev	**10.01**		**1.09**		

Air temperature at the end of the pipe was significantly higher this time, and the measured velocities greater. The pressure and engine revs displayed on the fogger control panel were very similar to under the cold conditions, so expansion of the gas at higher temperature is likely to be responsible for the noted increase in volume.

At burner temperature 200°C (3,360 rpm and 1 bar) air temperature at the end of the pipe was measured with a digital thermometer and found to be 87°C. This is outwith the working range of the anemometer and so velocity of air was not measured. It is anticipated that the velocity of air would have increased relative to the previous readings. In terms of determining how much air is actually produced during a commercial application, it would have been useful to have values for three experimental temperatures to allow extrapolation to commercial conditions.

8.4.2 Measurement of velocity through open ports in a wooden box

Another strategy adopted to reduce the speed of air from the fogger was allowing it to vent through several apertures, each the same diameter as the ducting pipe (4"). Having several exit points for the gas will reduce the velocity through each, and keep values within the working range of the anemometer. To this end, a large wooden box was constructed with four apertures in one side, as shown in Figure 89 below. The ducting pipe carried air into the box at one end, and air vented out through the holes in the side. Each hole had its own cover, allowing any combination of apertures to be open/closed at any one time.

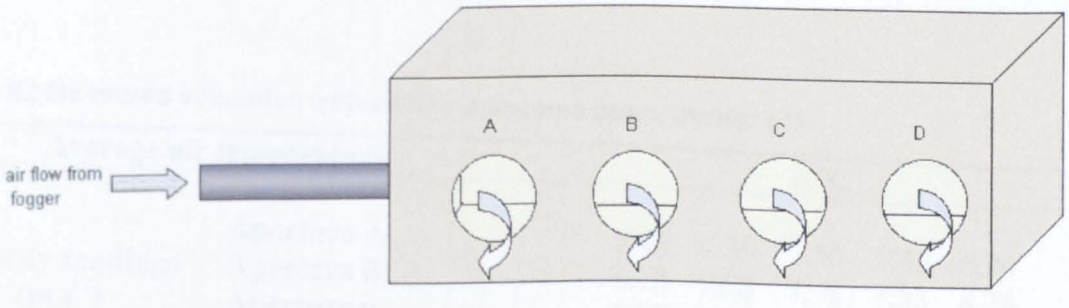


Figure 89 Box arrangement for measuring fog velocity (not to scale)

8.4.2.1 Experimental details

Again, only air was blown through the system. No formulation was added to the air stream to protect equipment and personnel from exposure to the fog. Running conditions were as follows with the burner off:

Machine temperature	~ 43°C
Engine revs	3,420 rpm
Combustion chamber fuel pressure	2 bar.

The average temperature of the air coming out of the apertures was 26°C.

With the burner on at 125-130°C, machine settings were 3,410 rpm and 0.5 bar combustion chamber fuel pressure. Average air temperature ranged between 40 and 70°C, depending on the number of apertures that were open.

Once several sets of measurements had been made with air alone, burner temperature was increased to 200°C and formulation added to the air stream to determine whether the presence of formulation had any effect on the volume of gas produced.

8.4.2.2 Results

For the box work, five replicate readings were taken from each open aperture, except when only one was open, where 10 readings were taken. Tables 82-85 below show the velocities of air measured through a combination of apertures with the burner off and at ~125°C. Table 86 shows the measured velocity of formulation at burner temperature 200°C with all apertures open.

Table 82 Measured velocities with all four apertures open, burner off

Average air temperature		26°C				
Velocity readings ($m\ s^{-1}$)	**Aperture A**	5.42	4.39	3.56	5.40	6.24
	Aperture B	4.72	7.88	7.98	1.33	8.24
	Aperture C	6.95	7.77	6.86	6.47	4.67
	Aperture D	6.65	6.28	7.50	5.28	5.76
Mean and standard deviation		**5.97**		**1.71**		

Table 83 Measured velocities with all four apertures open, burner 125-130°C

Average air temperature		40°C				
Velocity readings ($m\ s^{-1}$)	Aperture A	2.54	3.56	4.35	5.79	4.57
	Aperture B	1.80	7.06	8.23	8.66	7.94
	Aperture C	6.46	4.77	9.41	8.51	5.02
	Aperture D	4.64	4.54	8.47	7.02	4.12
Mean and standard deviation		5.87		2.20		

This time, burner temperature did not significantly affect the velocity of air leaving the box. However, the box was quite leaky around its joints so the figures are considered less reliable than the data direct from the pipes. All later work was carried out with the burner at ~125°C to be as close as possible to commercial application conditions

Table 84 Measured velocities with two end apertures (A and D) sealed, burner 125-130°C

Average air temperature		70°C				
Velocity readings ($m\ s^{-1}$)	Aperture B	13.07	12.75	11.64	10.99	14.32
	Aperture C	9.73	12.36	13.17	14.49	7.51
Mean and standard deviation		12.00		2.14		

Table 85 Measured velocity with three apertures (A,B and D) sealed, burner 125-130°C

Average air temperature		~ 71°C				
Velocity readings ($m\ s^{-1}$)	Aperture C	10.17	20.60	21.38	23.92	18.35
		18.52	23.02	26.40	21.79	23.21
Mean and standard deviation		20.74		4.44		

Table 86 Measured velocities with formulation present, and all 4 apertures open (burner 200°C)

Average air temperature		-				
Velocity readings ($m\ s^{-1}$)	Aperture A	0.52	2.75	2.16	2.97	3.22
	Aperture B	3.65	5.26	5.05	3.97	4.71
	Aperture C	2.99	7.42	6.85	5.37	7.13
Mean and standard deviation		4.27		1.95		

Although all four apertures were open as formulation was vented out of the box, readings were only taken off the first 3. At this point, the measurement was abandoned due to exposure of personnel to the chemical fog.

8.4.3 Calculation of volumes of air produced by the fogger

Pipe measurements and aperture diameters have previously been given in inches, but for the purposes of calculation measurements were converted to into metric units.

4" diameter = 0.102m diameter = 0.00817 m^2 cross sectional area

6" diameter = 0.154m diameter = 0.01863 m^2 cross sectional area

8" diameter = 0.206m diameter = 0.03333 m^2 cross sectional area

8.4.3.1 Volumes determined using metal ducting pipe alone

Tables 87 and 88 below give the calculated volumes exiting ducting pipes of different diameters with the burner off, and the volume produced with the burner at ~125°C (as measured at the end of the 8" diameter pipe). Dimensions have been converted to metric for ease of calculation.

Table 87 Estimated volumes of air produced by fogger through different diameter pipes, with the burner off (60°C)

Pipe diameter (m)	Mean velocity ($m\ s^{-1}$)	Cross sectional area (m^2)	Mean volume of air produced ($m^3 sec^{-1}$)
0.102	27.89*	0.0082	0.228
0.154	16.10	0.0186	0.299
0.206	7.45	0.0333	0.248

* value calculated from the second set of readings

Table 88 Estimated volume produced with burner at 125°C (through 8" pipe)

Pipe diameter (m)	Mean velocity (m s^{-1})	Cross sectional area (m^2)	Mean volume of air produced (m^3 sec^{-1})
0.206	10.01	0.0333	0.333

With the burner off, all three diameters of pipe produced very similar volumes of air, suggesting that any change due to the joins in pipe is negligible. Analysis by ANOVA shows there is no statistical difference between the 4" and 8" data sets ($p = 0.297$), but the 6" data is statistically higher than the other two. That there is no consistent pattern in the results suggests that the joins in the pipes are not having a significant effect on the volumes of air exiting the pipe (either by decrease through leakage or increase through Venturi effect).

Volumes measured through the 8" pipe are statistically higher with the burner at 125°C than with the burner off ($p = 0.001$) and can be attributed to the expansion of gas at the higher temperature since any effect due to joins in the pipe has already been discounted.

8.4.3.2 Volumes calculated using the box with multiple apertures

The total volume of air exiting through apertures was calculated from the mean measured velocity and the total cross-sectional area of all open apertures.

Table 89 Calculated estimates of fogger air production with burner off and at 125°C

Open apertures	Burner temperature (°C)	Total area (m^2)	Mean velocity (m s^{-1})	Mean volume produced (m^3 sec^{-1})
4	Off	0.03268	5.97	0.195
4	125-130	0.03268	5.87	0.192
2	125-130	0.01634	12.00	0.196
1	125-130	0.00817	20.74	0.169

Burner temperature did not have a significant effect on the volume of gas produced by the fogger. However, the box was leaky, and the results from it are not considered as reliable as the data from the pipes.

The number of apertures open also had no consistent effect on the volume.

8.4.4 Summary of findings from experiments to determine the volume of air produced by the fogger

- The box generated lower estimates of air velocity and volume than the pipes, perhaps as a result of leakage around its joints. It did, however, give very consistent results. No significant change in estimated volume was found when measuring off different numbers and combinations of apertures

- Velocities calculated at the end of pipes were higher than box values, perhaps due to a lack of leakage, or the Venturi effect pulling extra air in. Results from the end of pipes were more variable than those from the box, but are thought to be a better estimate of the true volume produced by a fogger

- Increasing burner temperature resulted in an increase in volume. The highest burner temperature used during the experiments was significantly lower than standard application temperature, suggesting that calculated values will under-estimate air production during commercial application. However, maintaining high burner temperature places greater strain on the machinery, which could result in reduced output.

- Extrapolation of the data to a 1-hour average application time gives a range of volumes of 700-1200m^3 hr^{-1}, exclusive of the effect of combustion gases or expansion of gases at high temperature.

8.5 Estimation of loss during application

During application, fog is seen to leak out through vents and louvres. A significant amount of chemical is thought to be lost in this way. The actual amount of chemical lost will depend on

- The volume of air displaced from the store
- The concentration of chemical in the fog
- The degree of mixing between store air and fog

8.5.1 Volume of air displaced from the store

This volume will equal the amount of air produced by the fogger during the 1-hour application. In studies of air velocity (described earlier in this chapter) the volume of air produced by a Unifog machine was estimated between 750 – 1200m^3 hr^{-1}. These figures were derived from experiments carried out at low burner temperature, with no formulation present. As a result, no account has been made of expansion of fluid (both air and formulation) at high temperature and the contribution of combustion gases from the burning of petrol. From fuel consumption trials reported by Dowd (2001), during a 1-hour application under standard operating conditions, ~12.5 litres of petrol will be burned, producing 32,734 litres of combustion gases (32.734m^3).

8.5.2 Concentration of chlorpropham in fog

Assuming a formulation flow rate of 1 litre/min (0.5kg/min), an estimate of the concentration in the fog can be calculated by dividing by the volume of air produced per minute. Figures below are based on the range of flow rates calculated from earlier work reported in this chapter. 33m^3 of combustion gases are assumed to be added to the store along with air from the fogger. This volume was added to the fogger output figures before calculation of concentrations.

$$\frac{783\ m^3\ hr^{-1}}{\text{Fog concentration}} = 13.0\ m^3\ min^{-1}$$

$$\text{Fog concentration} = 0.5kg/13.0m^3 = 0.0385\ kg/m^3/min \text{ or } 38.5mg\ l^{-1} \text{ (ppm)}$$

$\frac{1033m^3\ hr^{-1}}{\text{Fog concentration}} = 17.22m^3\ min^{-1}$
Fog concentration = 0.5/17.22 = 0.0290 kg/m^3/min or 29.0mg l^{-1} (ppm)

$\frac{1133m^3\ hr^{-1}}{\text{Fog concentration}} = 18.88m^3\ min^{-1}$
Fog concentration = 0.5/18.88 = 0.0265 kg/m^3/min or 26.5mg l^{-1} (ppm)

8.5.3 Degree of mixing between fog and store air

It is accepted that the amount of gas displaced from the store will be equal to the amount introduced during the fogging process. This can be estimated using figures for airflow derived experimentally. What is more tricky to predict is the amount of chlorpropham lost with the escaping gas.

The amount of chemical lost will be dependent on both the volume and composition of the escaping gas. Volume is determined by fogger input to the store (air and combustion gases), but composition will be dependent on a number of factors, most importantly the degree of mixing between the 'pure' fog and the free air in the store. Other factors related to the behaviour of the fog (e.g. its movement, due to high temperature) and the whereabouts of the leaky points in the store will have an effect, but these are minor compared with the mixing factor.

In order to model what might be happening, two situations are described which represent the opposite ends of the mixing spectrum. Figures 90 and 91 overleaf show in simple form what is assumed to be happening in each case.

The first gives a 'worst-case' estimate for chemical loss (Figure 90). Here, we assume that fog accumulates at the top of the store and does not mix with the store air. The concentration in the fog is thus not diluted by the free air in the store, and is assumed to equal the concentration as introduced to the store (which can be estimated from fogger air output and formulation introduction rate). Gas most commonly escapes from louvres and vents at the top of the store, so gas escaping from the store will be mostly fog.

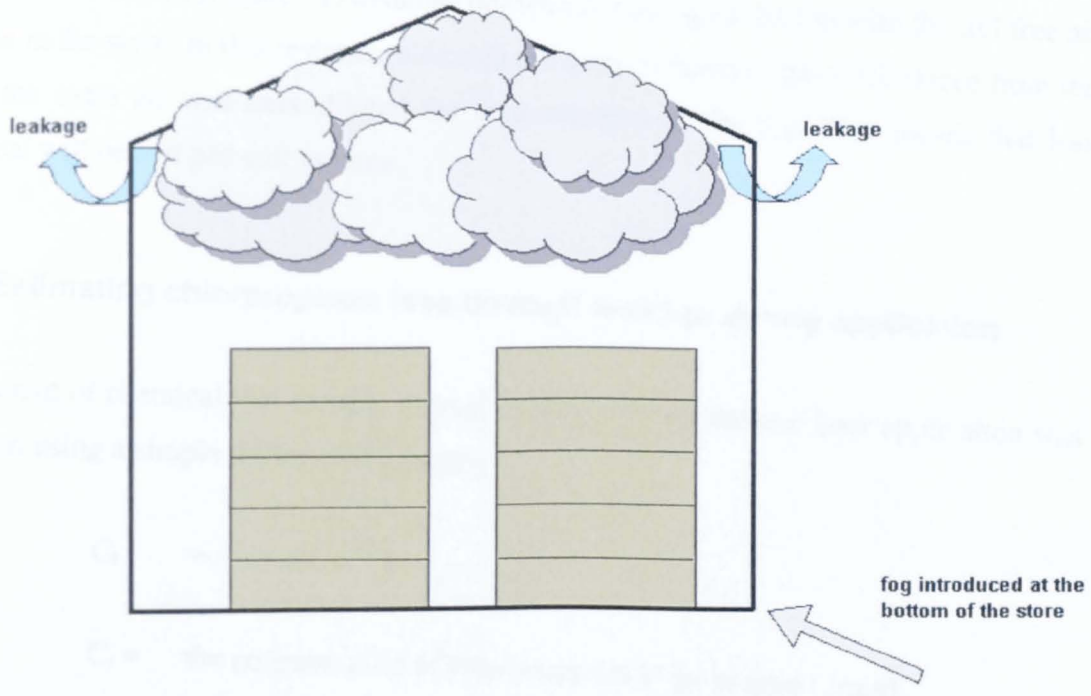


Figure 90 Fog accumulating at the top of the store and not mixing with store volume. Leakage of high-concentration for through the eaves

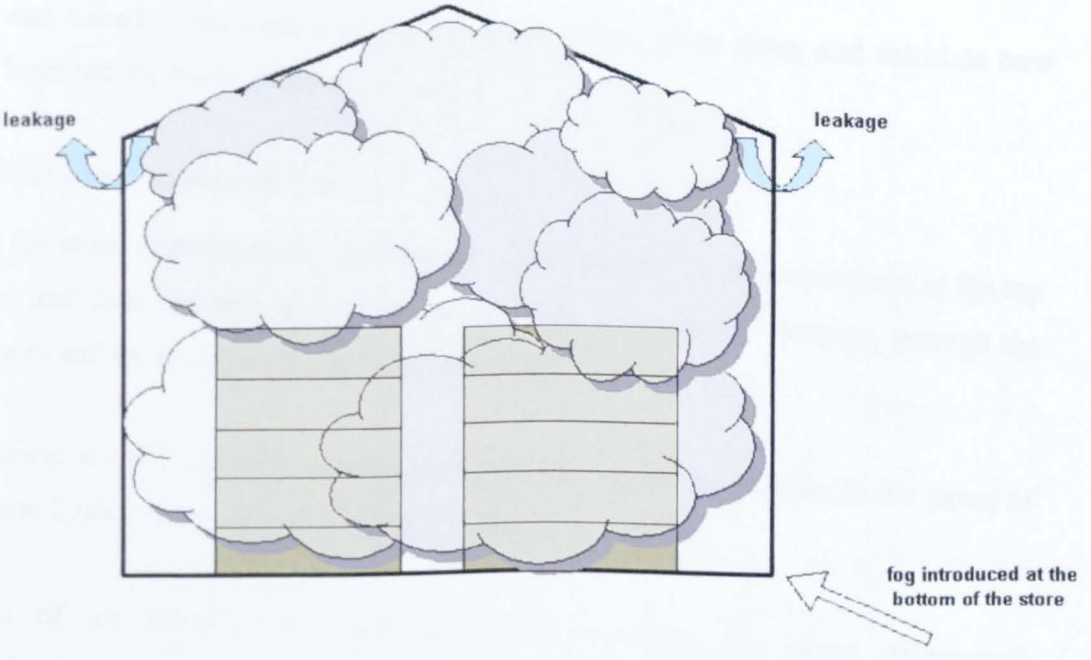


Figure 91 Fog mixing with the entire volume of air in the store. Dilution of chemical concentration resulting in reduced losses.

The second situation (Figure 91) assumes immediate mixing of the fog with the full free air volume in the store. In this instance, although the same volume of gas is displaced from the store, the extra air will have diluted the concentration of the fog. This means that less chemical will be lost per unit volume.

8.5.4 Estimating chlorpropham loss through leakage during application

The amount of chemical that escapes through leakage during the one-hour application was estimated using a simple differential equation

$$C_t = s(1-e^{-ft/v})$$

Where C_t = the concentration of chlorpropham in air at time t (min)

s = starting concentration of chlorpropham in the fog (kg/m^3)

f = fogger flow rate (m^3/min)

v = air volume (m^3) in which chemical is dispersed

Thus, we can calculate the concentration in the air at any given time, and calculate how much has been lost by mass balance.

8.5.4.1 'Worst case' estimate of loss:

Fog enters the store at ground level, and rapidly rises due to heat. It accumulates at the top of the store and does not mix with the store air. Gas is constantly escaping through the eaves, as more and more fog is introduced to the store.

In this instance, we will consider that fog is dispersed only in the volume in the eaves of our theoretical 2,000 tonne store (Section 8.2.3), which is 1,120m^3.

Three rates of air introduction were considered, covering the range determined experimentally (Section 8.5.2). 33m^3 of combustion gases were added onto each fogger output to account for combustion gases produced from the burning of petrol. The concentration remaining in the air at t = 60 minutes (i.e. at the end of the application) was calculated for each.

$\underline{783 m^3 hr^{-1}}$ $C_{60\ min}$ = $0.0385\ (1-e^{-13.00*60/1120})$ = $0.0193\ kg/m^3$

$\underline{1033 m^3 hr^{-1}}$ $C_{60\ min}$ = $0.0290\ (1-e^{-17.22*60/1120})$ = $0.0175\ kg/m^3$

$\underline{1133 m^3 hr^{-1}}$ $C_{60\ min}$ = $0.0265\ (1-e^{-18.88*60/1120})$ = $0.0169\ kg/m^3$

Table 90 Percentage loss of chlorpropham through leakage at 3 fogger flow rates, assuming no mixing of the fog with free air in the store.

Fogger flow* rate (m^3/hour)	Final concentration in air (kg/m^3)	Volume in which chemical dispersed (m^3)	Weight of CIPC left in store (kg)	Percentage loss
750	0.0193	1200	23.16	**22.8**
1000	0.0175	1200	21.00	**30.0**
1100	0.0169	1200	20.28	**32.4**

8.5.4.2 'Best case' estimate

Fog is introduced at the bottom of the store, rises due to heat and immediately begins to mix with the free air in the store. The concentration in the fog is reduced, and chlorpropham is dispersed evenly through the entire volume of air in the store.

In this instance, we will consider that the chemical is distributed through the entire free air volume above and around boxes in our theoretical 2,000 tonne store - 2,724 m^3. Free space at the top of the box and gaps between tubers were not considered accessible in this case.

Three rates of fogger air production were considered, covering the range determined experimentally (as reported earlier in this chapter). $33m^3$ were added to each fogger output to account for the production of combustion products, which will be ducted into store along with the fog. The concentration in the air was calculated at t = 60 minutes i.e. at the end of the application.

* exclusive of combustion gases

$\underline{783m^3\ hr^{-1}}$ $C_{60\ min} = 0.0385\ (1\text{-}e^{-13.00*60/2724}) = 0.0096\ kg/m^3$

$\underline{1033m^3\ hr^{-1}}$ $C_{60\ min} = 0.0290\ (1\text{-}e^{-17.22*60/2724}) = 0.0091\ kg/m^3$

$\underline{1133m^3\ hr^{-1}}$ $C_{60\ min} = 0.00265\ (1\text{-}e^{-18.88*60/2724}) = 0.0090\ kg/m^3$

Table 91 Percentage loss of chlorpropham through leakage at 3 fogger flow rates, assuming complete mixing of the fog with free air in the store.

Fogger flow* rate (m^3/hour)	Final concentration in air (kg/m^3)	Volume in which chemical dispersed (m^3)	Weight of CIPC left in store (kg)	Percentage loss
750	0.0096	2,724	26.15	**12.8**
1000	0.0091	2,724	24.78	**17.4**
1100	0.0090	2,724	24.51	**18.3**

8.5.4.3 Summary

From the calculated figures, the estimated amount of chlorpropham lost through leakage of fog ranges between 13 and 33%, depending largely on the degree of mixing between free air in the store and the fog.

In both cases, the concentration of chemical in store air at the end of the application is considerably less than the starting concentration of the fog, indicating that a significant quantity of chlorpropham has been lost from the store over the duration of the application.

* exclusive of combustion gases

8.6 Estimation of loss through routine venting during the storage season

8.6.1 Introduction

To determine losses through leakage during application, only the volume of parts of the store where the fog was expected to reach were taken into consideration i.e. the free headspace above and around the columns of boxes, and the gaps between boxes in a stack (total volume 2,724 m^3). Movement of fog into the body of boxes was assumed to be negligible, since there is no incentive for fog to find its way there (a fact borne out by the low residue values reported within boxes).

However, when considering losses of chemical due to intentional venting of stores, we must assume that the entire volume of air in the store is replaced each time venting takes place (total air volume 4,920m^3). Thus, free space at the top of each box, and the gaps between tubers within the box are considered as well as the 'free volumes' outside the boxes.

In processing stores, it is good practice to vent stores daily to prevent the build up of carbon dioxide produced during respiration at high storage temperatures. Crisping crop in particular can suffer from dark fry colours because of the accumulation of reducing sugars, which can be prevented by adequate ventilation during storage.

A numerical value for the amount of venting carried out in commercial stores has been difficult to obtain, because standard practice in industry seems to vary considerably. The fans in large stores have the capacity to exchange the entire volume of store air in a matter of minutes. It has been suggested that in practice, fans in processing stores might run for ~10 minutes per day, although not all growers do this and not every day [Coleman, personal communication]. Changing the air completely once a day to flush out CO_2 will not affect residual store temperature, and should not cause condensation problems.

Venting may also be necessary if crop temperature rises above target. In most processing stores, ambient air is used for cooling (although some more modern installations do have refrigeration). Cool, fresh air will be drawn in from outside through louvres and mixed with existing store air to produce a cooling mixture, which is then circulated around the store. Assuming the temperature differential is not significant (e.g. 0.5°C or less) condensation should not be an issue [Coleman, personal communication].

In pre-pack stores ('cold stores'), operating at <4°C, it is not common practice to vent stores once at holding temperature, because the rate of crop respiration (and hence CO_2 production) is significantly reduced. In addition, reducing sugar concentration is not critical in ware crop since fry colour is not an issue.

Vapour phase losses of chlorpropham from pre-pack stores will be significantly less than from processing stores because

- The amount of ventilation carried out is less
- Lower air temperature means a lower concentration of chemical
- Fewer applications of CIPC are necessary to maintain sprout control at low temperature

A 5-minute running of fans can replace the entire air volume of the store several times over [Cunnington, personal communication]. Where one episode of venting results in more than one complete air change, the loss of chlorpropham vapour was considered to be equal to one complete change. Because no information is available on how quickly vapour concentration builds up, it is assumed that instantaneous replenishment of saturated (or equilibrium) concentration does not occur and that the concentration of chlorpropham in air escaping after the first flush will be negligible. Thus, one running of fans per day is assumed to result in the loss of equilibrium concentration ($\mu g\ l^{-1}$) multiplied by store volume (l) of CIPC.

As with leakage during application, the amount of chemical lost from the store through venting will be a function of the concentration in the air and the volume of air replaced. Concentration will depend in turn on i) air temperature ii) the reservoir of chemical in the store (i.e. the amount applied plus the amount held in store fabrics).

8.6.2 Calculation of estimated loss through venting

Our theoretical 2,000 tonne store was considered as being both a processing store at 8°C, and as a pre-pack store at 3°C. Figures of potential loss were calculated on the basis of one complete air exchange per day using vapour concentrations at 3°C and 8°C determined in

experimental stores at Sutton Bridge Experimental Unit (as described in Chapter 4). Table 92 shows the estimated amounts of chlorpropham lost over a 6-month (180 day) storage period.

Table 92 Weights of CIPC lost during venting at 3°C and 8°C for a 6-month period, assuming one complete air exchange per day

Air temperature (°C)	Vapour concentration (μg l^{-1})	CIPC lost per air change (g)	Loss during 6-month storage (g)
3	0.04	0.197	35.46
8	0.08	0.394	70.92

8.6.2.1 Pre-pack store estimate

The calculated loss at low temperature will be an over-estimate, since air is not likely to be exchanged on a daily basis under pre-pack storage conditions.

8.6.2.2 Processing store estimate

Estimated loss from a processing store amounts to 0.24% of the chemical applied in one application. However, the concentration in the air might increase with successive applications, and repeat applications are often necessary when crop is held at high temperatures for long periods of storage. Air sampling in commercial stores throughout the season would be necessary to confirm if there is any cumulative effect on air concentration.

8.6.2.3 Passive air leakage

Potato stores are inherently leaky, and even in well-sealed stores air is constantly being lost and replaced. However, passive air leakage was not considered as part of the model for estimating losses, mainly because accurate figures were not available in this literature. Indeed, conflicting data was received from different sources. Values varied by approximately an order of magnitude.

Data in Table 93 below comes from The Farm Electric Handbook (1983), and shows how the estimated volume of air exchanged through passive leakage is expected to increase with store volume.

Table 93 Amount of passive air exchange as related to store volume

Volume of building (m^3)	Air changes/hour	Volume exchanged per hour (m^3)
150	0.18	27
300	0.12	36
600	0.09	54
1200	0.06	72
3000	0.03	90

Pringle (personal communication) estimates that between 0.7 to 0.9 air changes occur every hour in well-sealed stores, with up to 1.5 air changes/hr in less sophisticated buildings. In addition to the 'leakiness' of the store, the magnitude of air loss will depend on a number of other factors including building orientation, wind speed and direction and roof pitch. The influence of such factors will vary enormously among different stores (and with season at any one location) so there was no straightforward way to incorporate them into this simple model for loss.

Previous work on CIPC vapour concentration (as described in Chapter 4) has been carried out in airtight experimental stores at Sutton Bridge Experimental Unit, where the concentration in air was found to remain constant over time. Store air appeared to reach equilibrium within 2 hours of a rise in temperature. Importantly, no air exchange occurred between the store and the outside.

The effect of constant leakage on the concentration of chemical in air is unknown at present, and more work would need to be done to clarify this point. It is possible that in a store where the atmosphere is not stable, the build up of a significant chemical concentration in air could be suppressed. The degree to which this happens would depend on the relative rates of vapour concentration increase and air loss from the store, as well as other factors such as air temperature and the amount of CIPC in the store available for volatilisation. As a result, it is possible that less chemical could be lost from a constantly leaking store than one that is stable and vented periodically, even though more air exchange is taking place. More work will need to be done to confirm this hypothesis.

Chapter 9

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

9.1 Changes to the commercial situation since the work was commissioned

Since work on this project was started in November 1999, there have been a number of developments affecting the potato industry and the use of sprout suppressants.

In 1999, tecnazene was available as an alternative to chlorpropham for post-harvest treatment of potatoes. However, support for tecnazene in the EU was withdrawn, and it has not been available for use since the 2001 storage season, leaving CIPC as the only sprout suppressant for use in store. In 1999, chlorpropham itself was undergoing an EU review (supported by Aceto and Luxan) and its future was uncertain. However, in December 2003 chlorpropham achieved Annex 1 listing, which secures it as an acceptable active ingredient in EU countries. The Maximum Residue Level (MRL) has not yet been set, but is expected to fall in the range 5-10 mg kg^{-1} based on past guidelines.

A number of alternatives to conventional thermal fogging of CIPC formulations are coming onto the market that will afford the industry some flexibility in sprout control:

A method of applying CIPC as a solid briquette has been developed, and will be used commercially in the 2003-4 season. The application time is reduced using this method, resulting in less stress to the crop due to the presence of combustion products of petrol [Aceto Agricultural Chemicals Corp press release, 20th August 2003 accessed through Global Potato News*]. The absence of solvent is an advantage in environmental and product safety terms.

A new sprout suppressant application and monitoring system ('Restrain') using ethylene has been developed and marketed in the UK by Greenvale AP plc [press release accessed through Global Potato News*]. This treatment is only available for cold stored potatoes at present because of its effects on the sugar content of the crop.

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* www.potatonews.com/pressreleases/press_detail.asp?id=411

* www.potatonews.com/trends/trends_detail.asp?id=180

1,4-dimethylnaphthalene (DMN) is commonly used in the US (alone and in combination with CIPC), where it has MRL-free status because it is seen as a natural product used to enhance dormancy. The process of registration of DMN in the EU is underway, and the product is expected to be available for limited commercial use in UK and Holland during the 2004/5 storage season.

The development of other sprout suppression strategies takes some of the pressure off CIPC, and should allow sprout control to be maintained with minimal chemical residues. Both ethylene and DMN are seen as 'natural' alternatives to the use of synthetic agrochemicals.

Although chlorpropham has now achieved Annex 1 listing, that alone may not be enough to guarantee its future. Many of the larger retailers (e.g. Marks and Spencer, Sainsbury's and Tesco) are now demanding produce free of any detectable chemical residue, which presents a particular problem for the pre-pack industry. Ethylene and DMN may go a long way to meeting this demand.

Reducing CIPC residues to zero will be virtually impossible, since even storing crop in buildings or boxes that have been treated with CIPC in the past can result in detectable residues. With detection limits on modern analytical equipment getting ever smaller, it will be a real challenge to produce potatoes with no chemical residues at all.

Although reducing residues may be a problem for CIPC, the situation for maleic hydrazide is worse. CIPC has the advantage of being almost completely removed on peeling, whereas residues of maleic hydrazide are virtually impossible to get rid of because the chemical is distributed throughout the whole tuber, rather than being held on the skin. The processing industry will not be so affected by the zero tolerance approach to CIPC residues, since most processing is carried out after removal of the peel.

9.2 Suggestions for future work

It is clear there is significant scope for improving the application of chlorpropham. When dose rates are considered, one efficient application should provide enough chemical to maintain sprout control for the whole season. In other countries (e.g US and Scandinavia) the industry uses significantly less chemical than we do in the UK. The main problems

identified in this work with regards to distribution are the accumulation of chemical at the top of the store, and lack of movement of chemical into boxes. The significant losses estimated through leakage also need to be addressed.

Modifications to the fogging procedure may improve the distribution of chemical around the store. The high temperature and large amount of force used to get the chemical into the store are both believed to play important roles in determining how the chemical moves around the store. Lowering the temperature of the fog may reduce the tendency for chemical to accumulate in the roof space. However, the quality of the fog produced by conventional fogging equipment may be adversely affected if the temperature is reduced by to much: the dry, buoyant fog considered desirable is not achievable at low temperature.

Changing the patterns of turbulence in the store e.g. by applying through a number of ports simultaneously or sequentially, or by running the fogger in pulses rather than continuously may also benefit the distribution, and reduce the tendency for chemical to accumulate at one end of the store. This may also help reduce the compounding effect of several identical applications on residue levels.

The process by which 3-chloroaniline is produced in stores needs to be identified: reducing the burner temperature in the fogger may help confirm whether the presence of 3-chloroaniline in air is a result of thermal degradation during the application process. 3-chloroaniline is listed on the EU Priority Pollutants Circular 90-55 (Directive No. 76.46/EEC) and its presence in treated store is a cause for concern. It is important for the industry to identify the way in which it is produced, and to change their working practice to minimise its production, if appropriate. It is possible, however that the application process is not responsible for the presence of 3-chloroaniline and that degradation occurs via some other mechanism during storage.

More detailed study of the amount of CIPC present as vapour in treated stores and the factors that influence it is required. Work reported in this thesis centred on experimental stores, which were operated under quite different conditions to commercial stores. Although the values obtained in these experimental stores are similar to those available in the literature from commercial stores [Boyd (1984); Boyd and Duncan (1986)] more detailed study of the effect of various store conditions is recommended. Routine monitoring of a commercial store throughout the season would shed light on the influence of factors such as temperature (e.g. sampling during curing and during storage), ventilation, humidity and length of time since last application. The treatment history of the

store may determine the extent of the 'reservoir' of chemical held in the fabrics, which may have an important effect on the air concentration early in the season i.e. during curing and before an application is carried out in the store. We may expect more chemical in the air in stores that have been regularly and recently treated than in one that has not been treated for many years. At-loading application of CIPC would be attractive in terms of distribution of chemical, but is not possible because it inhibits wound healing, but it would be interesting to know if any significant quantity is present in air during this time when store temperature is high.

The rate at which the chemical concentration builds up in air in commercial stores is not known. This will be important in determining how much chemical is lost through venting, and is likely to be influenced by temperature and possibly humidity.

The vapour concentration of sprout suppressant chemicals in air has been shown to reduce in the presence of materials such as soil, potato peel and water. These small experiments suggest that chemical vapour is as likely to be taken up onto soil and store fabrics as onto the crop, and as a result significant contamination of store fabrics is possible.

Contaminated store fabrics and boxes are thought to be an important source for the chemical residue found in air, and the problems of loss to the environment and possible crop contamination could be reduced if a way of removing these residues could be found. The possibility of reducing residues by chemical treatment (e.g. UV/H_2O_2) or by physical means (e.g. cleaning with water at high pressure and/or high temperature; or by increasing store temperature and venting to encourage volatilisation) would be worthy of consideration. The effect of standard store disinfection and cleaning procedures on such residues is not known, and would also be of interest.

In addition, the sealing of such surfaces in some way to prevent future contamination or to trap any chemical already present might provide a solution. It may prove difficult to reach chemical that has penetrated deep within the fabrics with chemical treatments, so surface sealing may be an attractive option if practical. Another benefit of this type of approach would be greater flexibility for the grower: at present untreated material and seed cannot be stored in CIPC treated boxes or stores without residue and growth problems.

The treatment of washing effluent is an area in which interest is growing for a number of reasons. The increasing cost of maintaining a fresh water supply means that recycling of water around a site is becoming a more attractive option. In order to be able to re-use water

in a food production area, all chemical residues must be minimised. In addition, the EA (and SEPA in Scotland) are monitoring outputs to watercourses and to drain more and more closely, and their attention will soon turn to mobile washers and the increasing number of small sites where potatoes are washed. It is vital that the industry has solutions to the problem if they are to avoid environmental pollution and large fines for violation of discharge consents. It is suggested that efforts should focus on low-cost straightforward methods that could be implemented on-farm.

Bio-beds have been used in Sweden for containing pesticide pollution in rinsate and spills and are fairly simple to construct and maintain [Tortensson (2000); Fogg *et al* (2003)]. The Environment Agency has recently issued guidelines on their use where pesticides are handled or mixed [Anon (2003)]. Although designed to cope with small volumes of high concentration waste, the applicability of a similar approach to the treatment of the large volumes of low-concentration waste produced by crop washing is worthy of consideration.

In April 2003, the BPC commissioned a further 2-year study "Review and development of the CIPC application process and evaluation of environmental issues" (Project 807/243). The basis of this grant application was progress made during the studies described in this thesis. They also commissioned another project (807/235), in which different methods of application (i.e. vapour and controlled release) are being investigated as an alternative to thermal fogging.

Appendix 1 Raw data from distribution studies

2000-2001 control store

J2-8 top half deposit	J2-8 top half residue	J2-8 bottom half deposit	J2-8 bottom half residue
33.84	18.58	5.96	6.07
23.77	3.23	2.61	3.14
10.47	13.72	3.46	4.08
31.71	18.36	5.99	8.97
29.41	15.55	1.17	2.71
J2-8 whole deposit	**J2-8 whole residue**	**J2-4 whole deposit**	**J2-4 whole residue**
12.51	17.11	1.41	2.42
16.58	11.72	0.85	3.97
9.54	7.95	0.48	0.65
20.02	5.64	1.65	1.20
15.31	5.67	1.42	1.88
J2-1 whole deposit	**J2-1 whole residue**	**A14-7 top half deposit**	**A14-7 top half residue**
1.73	1.11	5.11	12.63
1.61	1.60	14.26	10.11
1.82	2.82	10.74	6.98
1.14	1.03	6.48	7.77
0.37	1.89	3.00	14.61
A14-7 bottom deposit	**A14-7 bottom residue**	**A14-7 whole deposit**	**A14-7 whole residue**
3.58	3.60	3.06	4.23
2.71	1.70	3.59	4.93
2.24	1.36	6.10	2.52
1.17	3.29	2.83	2.46
1.62	3.41	5.03	4.60
A14-4 whole deposit	**A14-4 whole residue**	**A14-1 whole deposit**	**A14-1 whole residue**
*	2.63	1.69	1.25
1.41	1.82	1.07	1.32
2.36	1.17	1.12	2.32
1.20	2.53	1.83	2.14
1.86	1.72	1.83	1.41

2000-2001 fan store

J12-8 top half deposit	J12-8 top half residue	J12-8 bottom half deposit	J12-8 bottom half residue
11.18	13.88	6.69	4.21
18.54	18.40	3.79	3.98
22.95	10.31	3.70	3.50
10.54	31.46	3.45	4.10
22.98	9.38	4.44	4.66
J12-8 whole deposit	**J12-8 whole residue**	**J12-4 whole deposit**	**J12-4 whole residue**
7.23	7.18	2.49	2.49
6.66	8.88	1.49	1.49
11.66	6.94	1.08	1.05
4.52	6.12	1.40	1.40
8.80	6.02	2.85	2.74
J12-1 whole deposit	**J12-1 whole residue**	**A2-7 top half deposit**	**A2-7 top half residue**
4.59	3.79	14.73	10.70
5.10	*	11.89	24.40
3.98	3.65	10.37	22.20
3.40	0.61	16.36	18.60
1.18	0.53	8.41	12.04
A2-7 bottom deposit	**A2-7 bottom residue**	**A2-7 whole deposit**	**A2-7 whole residue**
4.49	3.75	4.58	7.60
*	3.81	4.92	10.62
2.54	3.45	4.32	8.11
3.87	4.89	3.30	8.05
4.45	1.97	6.90	8.58
A2-4 whole deposit	**A2-4 whole residue**	**A2-1 whole deposit**	**A2-1 whole residue**
1.91	5.68	2.12	2.42
4.18	4.68	0.90	2.31
6.42	3.96	2.34	1.63
2.41	5.30	1.91	1.98
2.29	4.13	3.28	2.28

2001-2002 fan store

A2-7 top half deposit	A2-7 top half residue	A2-7 bottom half deposit	A2-7 bottom half residue
2.44	4.14	3.09	11.47
36.68	14.54	0.94	6.87
18.81	15.51	5.29	5.73
33.64	12.73	14.56	7.86
29.04	13.2	3.19	2.46
A2-7 whole deposit	**A2-7 whole residue**	**A2-4 whole deposit**	**A2-4 whole residue**
14.28	4.92	6.08	4.40
13.07	4.24	1.41	2.14
8.70	1.52	1.04	3.31
12.76	9.66	1.42	2.46
21.15	5.04	6.18	2.02
A2-1 whole deposit	**A2-1 whole residue**	**J11-8 top half deposit**	**J11-8 top half residue**
5.61	4.54	37.16	7.59
1.39	3.19	58.57	16.92
1.93	1.67	92.58	52.52
7.04	5.03	37.37	12.42
4.22	0.69	21.72	27.46
J11-8 bottom half deposit	**J11-8 bottom half residue**	**J11-8 whole deposit**	**J11-8 whole residue**
6.46	3.52	3.19	3.61
6.11	3.44	20.78	6.25
6.63	12.19	13.98	3.79
1.26	10.34	30.25	12.22
35.68	9.14	12.56	6.90
J11-4 whole deposit	**J11-4 whole residue**	**J11-1 whole deposit**	**J11-1 whole residue**
2.09	2.50	1.96	1.49
2.57	3.10	1.89	1.39
6.34	1.74	3.39	0.80
2.61	2.54	2.03	1.91
2.22	2.00	1.68	1.71
B11-7 whole deposit	**B11-4 whole deposit**	**B11-1 whole deposit**	**J2-8 whole deposit**
17.42	19.80	1.12	15.16
16.05	2.13	1.26	16.58
5.51	12.74	0.95	6.22
7.53	10.71	1.30	10.58
14.77	10.55	1.93	8.69
J2-4 whole deposit	**J2-1 whole deposit**		
24.66	2.92		
25.23	9.38		
5.50	6.70		
6.21	13.00		
7.46	5.68		

2001-2 plenum store

B5-7 top deposit	B5-7 top residue	B5-7 bottom deposit	B5-7 bottom residue
34.65	18.84	4.58	2.74
34.85	18.13	4.40	*
40.20	19.48	40.32	4.91
28.04	13.65	1.75	3.57
1.96	14.16	4.00	4.08
B5-7 whole deposit	**B5-7 whole residue**	**B5-4 whole deposit**	**B5-4 whole residue**
29.88	7.44	6.40	6.96
9.39	2.15	1.06	2.60
12.09	*	2.64	2.71
11.42	12.36	2.05	2.22
17.41	8.18	7.52	1.54
B5-1 whole deposit	**B5-1 whole residue**	**J14-8 top deposit**	**J14-8 top residue**
1.28	1.61	20.68	1.88
2.05	1.27	24.20	0.60
2.46	1.56	23.80	18.11
3.36	1.36	19.81	11.78
1.39	1.42	7.91	13.39
J14-8 bottom deposit	**J14-8 bottom residue**	**J14-8 whole deposit**	**J14-8 whole residue**
5.20	2.83	7.93	*
4.38	1.14	7.19	2.37
3.89	1.24	7.04	6.18
2.32	3.58	8.26	3.72
*	0.50	6.26	*
J14-4 whole deposit	**J14-4 whole residue**	**J14-1 whole deposit**	**J14-1 whole residue**
1.06	5.14	5.21	0.86
6.99	4.49	1.29	2.33
3.40	5.92	1.16	1.13
4.97	2.75	1.70	*
10.04	2.20	2.09	1.26
A14-7 whole deposit	**A14-4 whole deposit**	**A14-1 whole deposit**	**J5-8 whole deposit**
10.16	0.99	3.62	5.59
14.18	26.89	2.49	3.47
9.20	2.48	1.41	0.90
6.24	3.39	1.86	5.85
*	2.51	8.08	4.74
J5-4 whole deposit	**J5-1 whole deposit**		
6.19	21.62		
5.02	3.48		
4.80	1.78		
5.25	2.68		
5.19	1.96		

2000-1 control store all surface samples

	A14 BD	A14 BR	A14 TD	A14 TR	J2 BD	J2 BR	J2 TD
A14 BR	-10.64 8.33						
A14 TD	**-31.49** **-12.52**	**-30.33** **-11.36**					
A14 TR	**-19.54** **-0.57**	-18.38 0.59	**2.47** **21.44**				
J2 BD	-7.91 11.06	-6.76 12.22	**14.09** **33.06**	**2.14** **21.11**			
J2 BR	-9.32 10.65	-7.16 11.81	**13.68** **32.65**	**1.73** **20.70**	-9.89 9.08		
J2 TD	-13.57 5.41	-12.41 6.56	**8.44** **27.41**	-3.52 15.46	-15.14 3.83	-14.73 4.24	
J2 TR	-16.07 2.90	-14.91 4.06	**5.94** **24.91**	-6.02 12.95	-17.64 1.33	-17.23 1.74	-11.99 6.98

2000-1 control store all subsurface samples

	A14-1 D	A14-1 R	A14-4 D	A14-4 R	A14-7 D	A14-7 R	J2-1 D	J2-1 R	J2-4 D	J2-4 R	J2-8 D
A14-1 R	-4.51 4.15										
A14-4 D	-4.79 4.39	-4.61 4.57									
A14-4 R	-4.80 3.86	-4.62 4.04	-4.86 4.33								
A14-7 D	-6.94 1.72	-6.76 1.90	-7.01 2.18	-6.48 2.18							
A14-7 R	-6.57 2.09	-6.39 2.27	-6.63 2.55	-6.10 2.56	-3.96 4.70						
J2-1 D	-4.16 4.50	-3.98 4.68	-4.22 4.97	-3.69 4.97	-1.54 7.12	-1.92 6.74					
J2-1 R	-4.51 4.15	-4.33 4.33	-4.58 4.61	-4.05 4.61	-1.90 6.76	-2.27 6.39	-4.69 3.97				
J2-4 D	-3.98 4.68	-3.80 4.86	-4.05 5.14	-3.52 5.14	-1.37 7.29	-1.74 6.92	-4.16 4.50	-3.80 4.86			
J2-4 R	-4.85 3.81	-4.67 3.99	-4.91 4.28	-4.38 4.28	-2.23 6.43	-2.41 6.05	-5.02 3.64	-4.66 4.00	-5.19 3.47		
J2-8 D	**-17.61** **-8.95**	**-17.43** **-8.77**	**-17.68** **-8.49**	**-17.15** **-8.49**	**-15.00** **-6.34**	**-15.37** **-6.71**	**-17.79** **-9.13**	**-17.43** **-8.77**	**-17.96** **-9.30**	**-17.10** **-8.44**	
J2-8 R	**-12.44** **-3.78**	**-12.26** **-3.60**	**-12.50** **-3.32**	**-11.97** **-3.31**	**-9.83** **-1.17**	**-10.20** **-1.54**	**-12.61** **-3.95**	**-12.26** **-3.60**	**-12.79** **-4.13**	**-11.92** **-3.26**	**0.84** **9.50**

2000-2001 fan store all surface samples

	A2 BD	A2 BR	A2 TD	A2 TR	J12 BD	J12 BR	J12 TD
A2 BR	-9.90 10.42						
A2 TD	-18.67 1.64	-18.36 0.80					
A2 TR	**-23.91** **-3.59**	**-23.59** **-4.44**	-14.81 4.34				
J12 BD	-10.74 9.58	-10.42 8.74	-1.64 17.52	**3.60** **22.75**			
J12 BR	-10.41 9.91	-10.09 9.06	-1.32 17.84	**3.92** **23.08**	-9.25 9.90		
J12 TD	**-23.56** **-3.24**	**-23.24** **-4.09**	-14.46 4.69	-9.23 9.93	**-22.40** **-3.25**	**-22.73** **-3.57**	
J12 TR	**-23.01** **-2.69**	**-22.69** **-3.53**	-13.91 5.24	-8.68 10.48	**-21.85** **-2.69**	**-22.17** **-3.02**	-9.03 10.13

2000-2001 fan store all sub-surface samples

	A2-1 D	A2-1 R	A2-4 D	A2-4 R	A2-7 D	A2-7 R	J12-1 D	J12-1 R	J12-4 D	J12-4 R	J12-8 D
A2-1 R	-3.01 2.99										
A2-4 D	-4.33 1.67	-4.32 1.68									
A2-4 R	-5.64 0.36	-5.63 0.37	-4.31 1.69								
A2-7 D	-5.69 0.31	-5.68 0.32	-4.36 1.64	-3.05 2.95							
A2-7 R	**-9.48** **-3.48**	**-9.47** **-3.47**	**-8.15** **-2.15**	**-6.84** **-0.84**	**-6.79** **-0.79**						
J12-1 D	-4.54 1.46	-4.53 1.47	-3.21 2.79	-1.90 4.10	-1.85 4.15	**1.94** **7.94**					
J12-1 R	-3.22 3.15	-3.20 3.16	-1.89 4.48	-0.58 5.79	-0.52 5.84	**3.27** **9.63**	-1.68 4.69				
J12-4 D	-2.75 3.25	-2.74 3.26	-1.42 4.58	-0.11 5.89	-0.06 5.94	**3.73** **9.73**	-1.21 4.79	-2.90 6.47			
J12-4 R	-2.72 3.28	-2.71 3.29	-1.39 4.61	-0.08 5.92	-0.03 5.97	**3.76** **9.76**	-1.18 4.82	-2.87 3.49	-2.97 3.03		
J12-8 D	**-8.66** **-2.66**	**-8.65** **-2.65**	**-7.33** **-1.33**	**-6.02** **0.02**	-5.97 0.03	-2.18 3.82	**-7.12** **-1.12**	**-8.81** **-2.45**	**-8.91** **-2.91**	**-8.94** **-2.94**	
J12-8 R	**-7.92** **-1.92**	**-7.90** **-1.90**	**-6.59** **0.59**	-5.28 0.72	-5.22 0.78	-1.44 4.65	**-6.38** **-0.38**	**-8.07** **-1.70**	**-8.17** **-2.17**	**-8.19** **-2.19**	-2.25 3.75

2001-2002 fan store all surface samples

	A2 BD	A2 BR	A2 TD	A2 TR	J11 BD	J11 BR	J11 TD
A2 BR	-29.81 26.88						
A2 TD	-47.05 9.64	-45.59 11.10					
A2 TR	-34.96 21.74	-33.49 23.20	-16.25 40.44				
J11 BD	-34.16 22.53	-32.70 24.00	-15.45 41.24	-27.55 29.14			
J11 BR	-30.66 26.03	-29.19 27.50	-11.95 44.74	-24.05 32.64	-24.84 31.85		
J11 TD	**-72.41** **-15.72**	**-70.95** **-14.26**	-53.70 2.99	**-65.80** **-9.11**	**-66.60** **-9.91**	**-70.10** **-13.41**	
J11 TR	-46.31 10.38	-44.85 11.84	-27.61 29.09	-39.70 16.99	-40.50 16.19	-44.00 12.69	-2.25 54.44

2001-2002 fan store all sub-surface samples

	A2-1 D	A2-1 R	A2-4 D	A2-4 R	A2-7 D	A2-7 R	B11-1 D	B11-4 D	B11-7 D	J11-1 D	J11-1 R	J11-4 D	J11-4 R	J11-8 D	J11-8 R	J2-1 D	J2-4 D
A2-1 R	-9.37 11.40																
A2-4 D	-9.57 11.20	-10.59 10.18															
A2-4 R	-9.21 11.56	-10.23 10.54	-10.02 10.74														
A2-7 D	-20.34 0.43	**-21.35** **-0.59**	**-21.15** **-0.38**	**-21.51** **-0.74**													
A2-7 R	-11.42 9.35	-12.44 8.33	-12.23 8.53	-12.59 8.17	-1.47 19.30												
B11-1 D	-7.66 13.11	-8.67 12.10	-8.47 12.30	-8.83 11.94	**2.30** **23.06**	-6.62 14.15											
B11-4 D	-17.53 3.24	-18.55 2.22	-18.34 2.42	-18.70 2.06	-7.58 13.19	-16.49 4.27	-20.26 0.51										
B11-7 D	-18.60 2.17	-19.62 1.15	-19.41 1.35	-19.77 0.99	-8.65 12.12	-17.56 3.20	**-21.33** **-0.56**	-11.45 9.31									
J11-1 D	-8.54 12.23	-9.55 11.22	-9.35 11.42	-9.71 11.06	**1.42** **22.19**	-7.50 13.27	-11.26 9.51	-1.39 19.38	-0.32 20.45								
J11-1 R	-7.81 12.96	-8.82 11.95	-8.62 12.15	-8.98 11.79	**2.15** **22.92**	-6.77 14.00	-10.53 10.24	-0.66 20.11	**0.41** **21.18**	-9.65 11.11							
J11-4 D	-9.51 11.26	-10.53 10.24	-10.32 10.44	-10.68 10.08	**0.44** **21.21**	-8.47 12.29	-12.24 8.53	-2.36 18.40	-1.29 19.47	-11.36 9.41	-12.09 8.68						
J11-4 R	-8.72 12.05	-9.74 11.03	-9.53 11.23	-9.89 10.87	**1.22** **22.00**	-7.68 13.08	-11.45 9.32	-1.57 19.19	-0.50 20.26	-10.57 10.20	-11.30 9.47	-9.59 11.17					
J11-8 D	**-22.50** **-1.73**	**-23.51** **-2.75**	**-23.31** **-2.54**	**-23.67** **-2.90**	-12.54 8.22	**-21.46** **-0.69**	**-25.22** **-4.46**	-15.35 5.42	-14.28 6.49	**-24.35** **-3.58**	**-25.08** **-4.31**	**-23.37** **-2.60**	**-24.16** **-3.39**				
J11-8 R	-12.90 7.87	-13.91 6.85	-13.71 7.06	-14.07 6.70	-2.95 17.82	-11.86 8.91	-15.63 5.14	-5.75 15.02	-4.68 16.09	-14.75 6.02	-15.48 5.29	-13.77 7.00	-14.56 6.21	-0.79 19.98			
J2-1 D	-13.88 6.89	-14.90 5.87	-14.69 6.07	-15.05 5.71	-3.93 16.84	-12.84 7.92	-16.61 4.16	-6.73 14.03	-5.66 15.10	-15.73 5.04	-16.46 4.31	-14.75 6.01	-15.54 5.22	-1.77 19.00	-11.37 9.40		
J2-4 D	-20.16 0.61	**-21.17** **-0.41**	**-20.97** **-0.20**	**-21.33** **-0.56**	-10.20 10.56	-19.12 1.65	**-22.88** **-2.12**	-13.01 7.76	-11.94 8.83	**-22.01** **-1.24**	**-22.74** **-1.97**	**-21.03** **-0.26**	**-21.82** **-1.05**	-8.04 12.72	-17.64 3.13	-16.66 4.11	
J2-8 D	-17.79 2.98	-18.80 1.96	-18.60 2.16	-18.96 1.80	-7.84 12.93	-16.75 4.01	-20.52 0.25	-10.64 10.12	-9.57 11.19	-19.64 1.13	-20.37 0.40	-18.66 2.10	-19.45 1.31	-5.68 15.09	-15.28 5.49	-14.29 6.47	-8.02 12.75

2001-2002 plenum store all surface samples

	B5 BD	B5 BR	B5 TD	B5 TR	J14 BD	J14 BR	J14 TD
B5 BR	-12.52 26.89						
B5 TD	-35.51 1.65	**-43.82** **-4.41**					
B5 TR	-24.42 12.74	-32.74 6.68	-7.49 29.67				
J14 BD	-12.65 26.77	-20.90 20.65	**4.28** **43.70**	-6.81 32.61			
J14 BR	-9.43 27.73	-17.74 21.68	**7.50** **44.66**	-3.59 33.58	-17.62 21.80		
J14 TD	-26.85 10.31	-35.16 4.25	-9.92 27.24	-21.01 16.15	-35.04 4.38	-36.00 1.16	
J14 TR	-16.72 20.44	-25.04 14.38	**0.21** **37.37**	-10.88 26.28	-24.91 14.51	-25.88 11.29	-8.45 28.71

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Appendix 2 Survey questionnaires

POTATO INDUSTRY CIPC QUESTIONNAIRE

UNIVERSITY of GLASGOW

If you use CIPC sprout suppressant on your potatoes, your assistance in completing this questionnaire would be greatly appreciated. The results will be used to provide industry information for a BPC-funded research project being carried out at Glasgow University and Sutton Bridge Experimental Unit.

Section A: Your Details

1) Name/Company title: _____

Address: _____

Telephone number: _____

e-mail address: _____

Section B: Storage capacity and management

2) Please enter the approximate tonnage you hold in

Box storage _____ Bulk storage _____

3) What is the approximate breakdown of your cop in terms of sales to market sectors?

Pre-pack _____% Processing/chipping _____% Other _____ %

4) Approximately what percentage of the crop do you treat with CIPC? _____ %

5) Do you use any other sprout suppressant chemicals in addition to CIPC?

Tecnazene granules ☐ Maleic hydrazide (eg Fazor) ☐

PLEASE ANSWER THE REMAINING QUESTIONS IN THIS SECTION BASED ON THE ONE STORE WHERE YOU KEPT CROP THE *LONGEST* LAST SEASON (ie 1999/2000)

PLEASE INDICATE THE TYPE AND SIZE OF THIS STORE:

BOXES ☐ **BULK** ☐ **CAPACITY:** _____ **TONNES**

6) How long did you cure the crop for? _____ days

7) What was the holding temperature of the store? _____ °C

PTO

8) How long was the crop stored for?

Less than 1 month	☐	1-3 months	☐
4-5 months	☐	6-7 months	☐
More than 8 months	☐		

9) How many treatments of CIPC did the crop receive? _____

10) Who carried out the application?

Self / own staff ☐ Specialist contractor ☐

Name of contractor (if known) _____

11) Which type of fogging equipment was used (if known)?

Swingfog ☐ Unifog ☐

Superfog ☐ Don't know ☐

Other (please state) _____

12) Did you re-circulate air during application?

Yes ☐ No ☐

How soon after application did you switch the store back on? _____ hours

13) Did you wash crop from this store before it left the site?

Yes ☐ No ☐

14) Finally, would you be happy for us to contact you about the answers you have given?

Yes ☐ No ☐

MANY THANKS FOR YOUR HELP.

Please return completed forms using the reply paid envelope. If you have any questions regarding this questionnaire please feel free to contact us at one of the addresses below.

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POTATO INDUSTRY CIPC QUESTIONNAIRE

UNIVERSITY of GLASGOW

If you use CIPC sprout suppressant on your potatoes, your assistance in completing this questionnaire would be greatly appreciated. The results will be used to provide industry information for a BPC-funded research project being carried out at Glasgow University and Sutton Bridge Experimental Unit.

Section A: Your Details

1) Name/Company title: _____

Address: _____

Telephone number: _____

e-mail address: _____

2) Contact name: _____

Position in company: _____

3) Tick the box which best describes your company:

Merchant ☐ Producer ☐

Other (please state) _____

Section B: Storage capacity

4) Please give an indication of the nature of your storage facilities:

Purpose-built ☐ Converted buildings ☐

5) What type of insulation do you have in your store(s)?

Polyurethane sprayfoam ☐ Extruded polystyrene (eg Styrofoam Polyfoam, Styrodur) ☐

Straw ☐ Other (please state) _____

6) Is the insulating material?

Exposed ☐ Covered (eg with panelling) ☐

7) Please enter the approximate tonnage you hold under the following sets of conditions:

	Box storage	Bulk storage
Buildings without fan ventilation		
Buildings with forced draught ambient (outside air) cooling only		
Buildings with refrigeration only		
Buildings with both ambient cooling and refrigeration		

Section C: Store management

8) How long on average does it take to fill your store(s)

less than 1 week ☐ 1-2 weeks ☐
2-3 weeks ☐ more than 3 weeks ☐

9) What are the main end uses for your crop?
(please tick as many as apply)

Washed pre-pack ☐ Processing / chip shop ☐
Pre-pack dry-brush ☐ Seed ☐
General ware ☐

Other (please state) _____

10) Please indicate what percentage of your crop you store for the following lengths of time:

< 1 month	%	1-3 months	%
4-5 months	%	6-7 months	%
≥ 8 months	%		

Approximately what percentage of your crop do you treat with CIPC?

100% ☐ Other (please state) _____

11) Do you use any other sprout suppressant chemicals in addition to CIPC?

Tecnazene ☐ Maleic hydrazide (eg Fazor) ☐ None ☐

PLEASE ANSWER THE REMAINING QUESTIONS IN THIS SECTION BASED ON THE ONE STORE WHERE YOU KEPT CROP THE LONGEST IN 1999/2000

Please indicate the type and size of the store:

Boxes ☐ **Bulk** ☐ **Capacity:** _____ **tonnes**

12) How long did you cure your crop for ?

1 week ☐ 10 days ☐
2 weeks ☐

Other (please state) _____

13) What target temperature did you use last season for

a) Curing / wound healing? ____°C **or** ☐ not cured

b) Holding? ____°C

14) How many different varieties did you keep in the store?

1 ☐ 2 ☐
3 ☐ more than 3 ☐

15) Did you wash crop from this store ***before*** it left your site?

Yes ☐ No ☐

16) If YES, which of these methods for clean-up of crop washing water did you use?

Settlement ☐ Digestion ☐
Filtration ☐ None ☐

Other (please state)_____

17) Approximately what volume of water do you use for washing of crop?

_____ litres/day or don't know ☐

18) What happens to the sediment from wash water?

Stored onsite ☐ Offsite disposal by self ☐
Contractor removal ☐

Other (please state) _____

19) Please state the trade name(s) of any CIPC formulation(s) used in your store last season

MSS CIPC 50M ☐ MSS Warefog 25 ☐

MSS CIPC 50LF ☐ Luxan Gro-Stop HN ☐

Other (please state) _____

Don't know ☐

20) How many applications of CIPC did your crop receive last season?

1 ☐ 2 ☐

3 ☐ 4 ☐

Other (please state) _____

21) How long after store loading did you apply the first CIPC treatment?

2-4 weeks ☐ 4-6 weeks ☐

6-8 weeks ☐ at eyes open ☐

Other (please state) _____

22) What criteria do you use for timing of re-application?

Apply at timed intervals ☐

Visual inspection of tuber condition ☐

Other (please state) _____

23) Who carries out the application?

Self / own staff ☐ Specialist contractor ☐

Name of contractor (if known) _____

24) Which type of fogging equipment is used?

Swingfog gun ☐ Sands/SAM Unifog ☐

Superfog ☐ other Unifog ☐

Don't know ☐ Other (please state) _____

25) If you store the crop at less than 5°C, do you warm your stores up prior to CIPC application?

Yes ☐ No ☐

26) If YES, at what crop temperature do you apply CIPC? _____°C

27) If you warm your stores prior to application, please give a brief explanation of WHY:

28) Did you re-circulate air during application?

Yes ☐ No ☐

29) If NO, how soon after application did you switch the fans back on?

6 hours ☐ 12 hours ☐
24 hours ☐

Other (please state) _____

30) Do you alter your application when you apply CIPC if the store is only part full?

Yes ☐ Don't apply CIPC to part-full stores ☐
No ☐

31) If YES, what do you do differently?

32) Finally, would you be happy for us to contact you about the answers you have given?

Yes ☐ No ☐

MANY THANKS FOR YOUR HELP.

If you have any questions regarding this questionnaire please feel free to contact me at the address below

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References

Anon (1990) Unifog work manual (Model 100). Unifog UK Ltd, Gravesend Kent.

Anon (1996) EXTOXNET Pesticide Information Profile: Chlorpropham http://ace.orst.edu/cgi-bin/mfs/01/pips/chloropro.htm

Anon (2000) Optimisation of CIPC application and distribution in stored potatoes. BPC Project S104 information leaflet

Anon (2001a) Online Statistical Database Food and Agriculture Organisation of the united Nations (UN) http://www.apps.fao.org/page/collections?subset=agriculture

Anon (2001b) Treatment of effluent now high priority. *Potato Review* September 2001 p19-22

Anon (2001c) Liquid Assets. *Potato Business World* July/August 2001 p50-56

Anon (2002) www.samltd.co.uk/unifogdata.html

Anon (2003) Interim guidance on agricultural pesticide handling and washdown areas in relation to the protection of controlled waters. http://www.environment-agency.gov.uk/commondata/105385/biobeds_526534.pdf

Afek U, Orenstein J and Kim JJ (2001) " Control of silver scurf disease in stored potato by using hydrogen peroxide plus (HPP)" *Crop Protection* **V20** p69-71

Afek U, Orenstein J and Nuriel E (2000) "Using HPP (hydrogen peroxide plus) to inhibit potato sprouting during storage" *American Journal of Potato Research* **V77** p63-65

Alexandrova LG and Klisenko MA, (1982) Identification and determination of some urea, carbamate and thiocarbamate derivatives in air *Journal of Chromatography* **V247** p255-262

Babić S, Petrović M and Kaštelan-Macan M (1998) Ultrasonic extraction of pesticides from soil *Journal of Chromatography A* **V823** p3-9

Bachman J and Patterson HH, (1999) Photodecomposition of the carbamate pesticide carbofuran: Kinetics and the influence of dissolved organic matter. *Environmental Science and Technology* **V33** p874-881

Bailey GW and White JL (1964) Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioavailability. *Journal of Agricultural and Food Chemistry* **V12** p324-332

Bauer R, Fallman H, Krutzler T, Malato S and Blanco J (1999) Applicability of the photo-Fenton method for treating water containing pesticides. *Catalysis Today* **V54** p309-319

Bidleman TF (1984) Estimation of vapour pressure for non-polar organic chemicals by capillary gas chromatography. *Analytical Chemistry* **V56** p2490-6

Blenkinsop RW, Copp LJ, Yada RY and Marangoni AG (2002) Effect of chlorpropham (CIPC) on carbohydrate metabolism of potato tubers during storage. *Food Research International* **V35** p651-655

Boyd IMG (1988) Studies on the potato sprout suppressant chlorpropham. PhD Thesis, University of Glasgow.

Boyd WD (1984) The headspace analysis of potato volatiles. PhD Thesis, University of Glasgow.

Boyd WD and Duncan HJ (1986) Studies on potato sprout suppressants. 7: Headspace and residue analysis of chlorpropham in a commercial box potato store *Potato Research* **V29** p217-223

Briddon A and Jina A (2000) The deposition of thermal fog applied CIPC on stored potatoes. Paper in preparation.

Burfoot D, Smith DLO, Butler-Ellis MC and Day W (1996) Modelling the distribution of isopropyl N-(3-chlorophenyl) carbamate [CIPC] in box potato stores *Potato Research* **V39** p241-251

Burge WD and Gross LE (1972) Determination of IPC, CIPC and propanil, and some metabolites of these herbicides in soil incubation studies. *Soil Science* **V114** p440-443

Burrows HD, Canle M, Santaballa JA and Steenken S (2002) Reaction pathways and mechanisms of photodegradation of pesticides. *Journal of Photochemistry and Photobiology B: Biology* **V67** p71-108

Camire ME, Bushway RJ, Zhao J, Perkins B and Paradis LR (1995) Fate of thiabendazole and chlorpropham residues in extruded potato peels. *Journal of Agricultural and Food Chemistry* **V43** p495-7

Celis R, Koskinen WC, Hermosin MC and Cornejo J (1999) Sorption and desorption of triadimefon by soils and model soil colloids. *Journal of Agricultural and Food Chemistry* **V47** p776-781

Chiron S, Fernandez-Allba A, Rodriguez A and Garcia-Calvo E (2000) Pesticide chemical oxidation: state-of-the-art. *Water Research* **V34** p366-377

Clark CG and Wright SJL (1970) Detoxication of isopropyl N-phenylcarbamate (IPC) and isopropyl N-3-chlorophenylcarbamate (CIPC) in soil, and isolation of IPC-metabolising bacteria. *Soil Biology and Biochemistry* **V2** p19-26

Coleman P (Ed) (2001) Exclusive Agronomy News V1 Issue 13 November 2001 Greenvale AP plc

Coleman WK (1998) Carbon dioxide, oxygen and ethylene effects on potato tuber dormancy release and sprout growth *Annals of Botany* **V82** p21-7

Coleman WK, Lonergan G and Silk P (2001) Potato sprout growth suppression by menthone and neomenthol, volatile oil components of *Minthostachys*, *Satureja*, *Bystropogon* and *Mentha* species. *American Journal of Potato Research* **V78** p345-354

Conte E and Imbroglini G (1995) Presence of sprout inhibitor residues in potatoes in relation to application techniques. *Journal of Agricultural and Food Chemistry* **V43** p2985-7

Corsini D, Stallknecht G and Sparks W (1979) Changes in chlorpropham residues in stored potatoes. *American Potato Journal* **V56** p43-56

Corti P, Dreassi E, Politi N and Aprea C (1991) Comparison of an HPTLC and an HPLC procedure for the determination of chlorpropham, propham and thiabendazole residues in potatoes. *Food Additives and Contaminants* **V8** p607-616

Coxon DT and Filmer AAE (1985) The fate and distribution of chlorpropham when applied to stored potatoes as a sprout suppressant. *Pesticide Science* **V16** p355-363

David B, Lhote M, Faure V and Boule P (1998) Ultrasonic and photochemical degradation of chlorpropham and 3-chloroaniline in aqueous solution. *Water Research* **V32** p2451-2461.

deBertrand N, Durand G and Barceló D (1991) Extraction, cleanup and liquid chromatographic-diode array determination of carbamate pesticides in soil samples. *Journal of Environmental Science and Health A* **V26** p575-597

Dennison HH, Garthwaite DG and Thomas MR (2003) Potato Stores in Great Britain 2000. Pesticide Usage Survey Report 174. MAFF and SERAD www.csl.science/organ/pvm/puskm/potstores2000.pdf

DiCorcia A and Marchetti M (1991) Multiresidue method for pesticides in drinking water using a graphitised carbon black cartridge extraction and liquid chromatographic analysis. *Analytical Chemistry* **V63** p580-5

Dowd G (2002) An investigation into the effects of CIPC use on the processing quality of stored potatoes – 2. Contract report to the BPC (Project Report 2002/3)

Dowd G (2003) Project Report: An investigation into the effects of CIPC use on the processing quality of stored potatoes – Final Report August 2003. BPC Project Report 2003-08

Draper WM and Crosby DG (1981) Hydrogen peroxide and hydroxyl radical: intermediates in indirect photolysis reactions in water. *Journal of Agricultural and Food Chemistry* **V29** p699-702.

Draper WM and Crosby DG (1984) Solar photooxidation of pesticides in dilute hydrogen peroxide. *Journal of Agricultural and Food Chemistry* **V32** p231-237

Duncan HJ (1999) Explosion and combustion processes associated with the fogging of stored potatoes. *Potato Research* **V42** p25-9

Eleftheriou EP and Bekiari E (2000) Ultrastructural effects of the herbicide chlorpropham (CIPC) in root tip cells of wheat. *Plant and Soil* **V226** p11-19

Ercegovich CD and Witkonton S (1972) An improved method for the analysis of residues of isopropyl N-(3-chlorophenyl) carbamate (chlorpropham) in alfalfa. *Journal of Agricultural and Food Chemistry* **V20** p344-7

European Union (1990) Circular 90-55 on pollution caused by certain dangerous substances discharged into the aquatic environment. Annex 1 (Directive No 76.46/EEC)

Ferguson CE and Gard LN (1969) IPC and CIPC residue analysis. *Journal of Agricultural and Food Chemistry* **V17** p1062-5

Ferguson CE, Gard LN, Shupe RH and Dress KS (1963) Infrared analysis for residues of isopropyl N-(3-chlorophenyl) carbamate in white potatoes. *Journal of Agricultural and Food Chemistry* **V11** p428-431

Filmer AAE and Land DG (1978) The accumulation of volatile substances in a large modern potato store. *Journal of the Science of Food and Agriculture* **V29** p219-224

Fletcher CL and Kaufman DD (1979) Hydrolxylation of monochloroaniline pesticide residues by *Fusarium oxysporum* Schlecht. *Journal of Agricultural and Food Chemistry* **V27** p1127-1130

Fletcher WW and Kirkwood RC (1982) Herbicides and plant growth regulators. Granada

Fogg P and Boxall ABA (2003) Degradation of pesticides in biobeds: The effect of concentration and pesticide mixtures. *Journal of Agricultural and Food Chemistry* **V51** p5344-5349

Foster DM, Rachwall AJ and White SL (1991) New treatment processes for pesticides and chlorinated organics control in drinking water. *Journal of the Institute of Water and Environmental Management.* **V5** p466-477

Fox EA, Garthwaite DG and Thomas MR (2000) Potato Stores in Great Britain 1998. Pesticide Usage Survey Report 161. MAFF and SERAD. www.csl.gov.uk/science/organ/pvm/puskm/potstores1998.pdf

Franzaring J, Kempenaar C and van der Eerden LJM (2001) Effects of vapours of chlorpropham and ethofumesate on wild plant species. *Environmental Pollution* **V114** p21-8.

Galadi A and Julliard M (1996) Photosensitised oxidative degradation of pesticides *Chemosphere* **V33** p1-15

Gard LN (1959) Determination of isopropyl N-(3-chlorphenyl) carbamate residues in potatoes treated for sprout inhibition. *Journal of Agricultural and Food Chemistry* **V7** p339-341

Gard LN and Ferguson CE (1963) Determination of micro amounts of isopropyl N-(3-chlorophenyl) carbamate in milk and urine excreted from dairy cows. *Journal of Agricultural and Food Chemistry* **V11** p234-237

Gard LN, Pray BO and Rudd NG (1954) Residues in crops receiving pre-emergence treatment with isopropyl N-(3-chlorophenyl) carbamate. *Journal of Agricultural and Food Chemistry* **V2** p1174-1176

Gard LN and Reynolds JL (1957) Residues in crops treated with isopropyl N-(3-chlorophenyl) carbamate. *Journal of Agricultural and Food Chemistry* **V5** p39-41

Gard LN and Rudd NG (1953) Isopropyl N-(3-chlorophenyl) carbamate (CIPC) in soil and crops. *Journal of Agricultural and Food Chemistry* **V1** p630-632

Goring CAI and Hamaker JW (Eds) (1972) Organic Chemicals in the Soil Environment. Marcel Dekker Publishers, New York.

Gou Y, Eisert R And Pawliszyn J (2000) Automated in-tube solid-phase micro-extraction-high-performance liquid chromatography for carbamate pesticide analysis. *Journal of Chromatography A* **V873** p137-147

Gutenmann WH and Lisk DJ (1964) Electron affinity residue determination of CIPC, monuron, diuron and linuron by direct hydrolysis and bromination. *Journal of Agricultural and Food Chemistry* **V12** p46-8

Guzik FF (1978) Photolysis of isopropyl 3-chlorocarbanilate in water. *Journal of Agricultural and Food Chemistry* **V26** p53-55

Hajslova J and Davidek J (1986) Sprout inhibitors IPC and CIPC in treated potatoes. *Die Nahrung* **V30** p75-9

Hamaker JW and Kerlinger HO (1969) 'Vapour pressure of pesticides' *in* Pesticidal formulations research. RF Gould (Ed) American Chemical Society

Hance RJ (Ed) (1980) Interactions between herbicides and the soil. Academic Press

Hartley GS and Graham-Bryce IJ (1980). Physical principles of pesticide behaviour Vols 1 and 2. Academic Press.

Heikes DL (1985) Mass spectral identification of a metabolite of chlorpropham in potatoes. *Journal of Agricultural and Food Chemistry* **V33** p246-9

Hidalgo C, Sancho JV, López FJ and Hernández F (1998) Automated determination of phenylcarbamate herbicides in environmental waters by on-line trace enrichment and reversed-phase liquid chromatography-diode array detection. *Journal of Chromatography A* **V823** p121-8

Huston PL and Pignatello JJ (1999) Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction. *Water Research* **V33** p1238-1246

Javier Benitez F, Beltran-Heredia J, Gonzalez T and Real F (1995) Photooxidation of carbofuran by a polychromatic UV irradiation without and with hydrogen peroxide. *Industrial Engineering and Chemical Research* **V34** p4099-4105

Junker-Buchheit A and Witzenbacher M (1996) Pesticide monitoring of drinking water with the help of solid-phase extraction and high-performance liquid chromatography. *Journal of Chromatography A* **V737** p67-74

Kaufman DD (1967) Degradation of carbamate herbicides in soil. *Journal of Agricultural and Food Chemistry* **V15** p582-591

Kaufman DD and Kearney PC (1965). Microbial degradation of isopropyl-N-3-chlorophenyl-carbamate and 2-chloroethyl-N-3-chlorophenyl carbamate. *Applied Microbiology* **V13** p443-446

Kearney PC and Kontson A (1976) A simple system to simultaneously measure volatilisation and metabolism of pesticides from soils. *Journal of Agricultural and Food Chemistry* **V24** p424-426

Kerstholt RPV, Ree CM and Moll HC (1997) Environmental life cycle analysis of potato sprout inhibitors. *Industrial Crops and Products* **V6** p187-194.

Khan Baloch WA (1999) The distribution and fate of chlorpropham in commercial potato stores. PhD Thesis, University of Glasgow

Khanbari OS and Thompson AK (1996) Effect of controlled atmosphere, temperature and cultivar on sprouting and processing quality of stored potatoes. *Potato Research* **V39** p523-531

Kleinkopf GE, Brandt TL, Frazier MJ and Möller G (1997) CIPC residues on stored Russet Burbank potatoes 1. Maximum label application. *American Potato Journal* **V74** p107-117

Lawrence JF and Laver GW (1975) Analysis of some carbamate and urea herbicides in food by gas-liquid chromatography after alkylation. *Journal of Agricultural and Food Chemistry* **V23** p1106-9

Lewis DJ, Thorpe SA and Reynolds SL (1996) The carry-through of residues of thiabendazole, tecnazene and chlorpropham from potatoes following manufacture into potato crisps and jacket potato crisps. *Food Additives and Contaminants* **V13** p221-9

Lentza-Rizos C and Balokas A (2001) Residue levels of chlorpropham in individual tubers and composite samples of postharvest treated potatoes. *Journal of Agricultural and Food Chemistry* **V49** p710-4

Liška I and Biliková K (1998) Stability of polar pesticides on disposable solid-phase extraction precolumns. *Journal of Chromatography A* **V795** p61-9

Mabury SA and Crosby DG (1996) Pesticide reactivity toward hydroxyl and its relationship to field persistence. *Journal of Agricultural and Food Chemistry* **V44** p1920-4

Martin D (2002) Water Quality Consenting Guidance Appendices Dangerous Substances in Discharges to Surface Waters. Version 2.www.netregs.environment-agency.gov.uk/commondata/105385/ds_appendix_solutions_v2_17May02

McCarthy AI, Palmer JK, Shaw CP and Anderson EE (1963) Correlation of gas chromatographic profiles of fresh banana fruit" *Journal of Food Science* **V28** p379-385

Meigh DF, Filmer AAE and Self R (1973) Growth-inhibitory volatile aromatic compounds produced by *Solanum tuberosum* tubers. *Phytochemistry* **V12** p987-993

Miles CJ and Moye HA (1988) Postcolumn photolysis of pesticides for fluorometric determination by high-performance liquid chromatography. *Analytical Chemistry* **V60** p220-6

Miller GC and Zepp RG (1979a) Effects of suspended sediments on photolysis rates of dissolved pollutants. *Water Research* **V13** p453-9

Miller GC and Zepp RG (1979b) Photoreactivity of aquatic pollutants sorbed on suspended sediments. *Environmental Science and Technology* **V13** p860-3

Mondy NI, Munshi CB and Seetharaman K (1992) Residue levels of isopropyl N-(3-chlorophenyl) carbamate (CIPC) in potatoes as affected by level of application, storage time and temperature, and method of cooking. *Food Research International* **V25** p375-9

Mondy NI, Reddy U and Munshi CB (1993) Effect of packaging material on the quality of potatoes treated with isopropyl N-(3-chlorophenyl) carbamate (CIPC). *Journal of Food Quality* **V16** p393-403

Mondy NI, Sharada D, Munshi CB and Wurm CM (1992) Effect of storage time, temperature, and cooking on isorpropyl N-(3-chlorophenyl) carbamate levels in potatoes. *Journal of Agricultural and Food Chemistry* **V40** p197-9

Mondy NI, Wurm CM and Munshi CB (1993) Moist and dry heat reduce isopropyl N-(3-chlorophenyl) carbamate (CIPC) residue in potatoes. *Journal of Food Science* **V58** p132-133

Montgomery M and Freed VH (1959) Determining micro amounts of isopropyl N-phenylcarbamate. *Journal of Agricultural and Food Chemistry* **V7** p617-8

Nagayama T and Kikugawa K (1992) Influence of frying and baking on chlorpropham residue. *Japanese Journal of Toxicology and Environmental Health* **V38** p78-83

O'Hagan N (1991) Substituted naphthalenes and their role as potato sprout suppressants. PhD Thesis University of Glasgow

Park L (2001a) Optimisation of the application of CIPC to stored potatoes and evaluation of environmental issues -1. British Potato Council Project Report 2001-11

Park L (2001b) Optimisation of the application of CIPC to stored potatoes and evaluation of environmental issues – 2. British Potato Council Project Report 2001/16

Parochetti JV and Warren GF (1966) Vapor losses of IPC and CIPC. *Weeds* **V14** p281-5

Pellizzari ED, Bunch JE, Carpenter BH and Sawicki E (1976) Collection and analysis of trace organic vapour pollutants in ambient atmospheres *Analytical Letters* **V9** p45-63

Pena-Heras A and Sanchez-Rasero F (1982) Determination of carbamic herbicides by high performance liquid chromatography. *Journal of Liquid Chromatography* **V5** p327-335

Pignatello JJ and Xing C (1996) Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science and Technology* **V30** p1-11

Ponnampalam R and Mondy NI (1986) Effect of sprout inhibitor isopropyl N-(3-chlorophenyl) carbamate (CIPC) on phenolic and ascorbic acid content of potatoes. *Journal of Agricultural and Food Chemistry* **V34** p262-3

Pringle R and Cunnington AC (2002) BPC Store Managers' Guide.

Ritchie W, Boyd IMG and Duncan HJ (1983) A method for the determination of chlorpropham residues in crisps and crisp frying oil. *Potato Research* **V26** p73-7

Romagnoli RJ and Bailey JP (1966) Direct gas chromatographic determination of isopropyl N-(3-chlorophenyl) carbamate (CIPC). *Analytical Chemistry* **V38** p1928-9

Ross RD and Crosby DG (1973) Photolysis of ethylenethiourea. *Journal of Agricultural and Food Chemistry* **V21** p335-337

Rouillon R, Poulain C, Bastide J and Coste CM (xxxx) Degradation of the herbicide chlorpropham by some ectomycorrhizal fungi in pure culture. *Agriculture, Ecosystems and Environment* **V28** p421-4

Russell (1975) Analysis of air pollutants using sampling tubes and gas chromatography. *Environmental Science and Technology* **V9** p1175

Sakodynskii K, Panina L and Klinskaya N (1974) A study of some properties of Tenax, a porous polymer sorbent. *Chromatographia* **V7** p339-344

Sawata S (1998) Removal of tecnazene from water using UV light and hydrogen peroxide. MSc Thesis, University *of Glasgow*

Sherma J (1999) Pesticide residue analysis: 1997-1998. *Journal of AOAC International* **V82** p561-574

Sowokinos J and Glynn M (2002) New potato clones maintain low sugars in cold storage. Published by Valley Potato Grower Magazine accessed at www.potato.org.uk/MarchPotatoClones.pdf

Spencer WF and Cliath MM (1983) Measurement of pesticide vapour pressures. *Residue Reviews* **V85** p57-71

Spencer WF, Cliath MM, Jury WA and Zhang L-Z (1988) Volatilization of organic chemicals from soil as related to their Henry's Law constant. *Journal of Environmental Quality* **V17** p504-7

Storey RMJ, Cunnnington AC and Michalski KH (1994) Technical Survey: Potato Storage Practices in Great Britain. Potato Marketing Board Research and Development Department Report

Sun L and Lee HK (2002) Microwave-assisted extraction behaviour of non-polar and polar pollutants in soil with analysis by high-performance liquid chromatography. *Journal of Separation Science* **V25** p67-76

Taylor AW and Spencer WF (1990) "Volatilisation and vapour transport processes" In "Pesticides in the Soil Environment: Processes, Impacts and Modelling" HH Cheng (Ed)

Tirmazi SH (1998) The fate and behaviour of isopropyl-N-(3-chlorophenyl) carbamate (chlorpropham) herbicide in the environment. PhD Thesis, University of Glasgow.

Torstensson L (2000) Experiences of biobeds in practical use in Sweden. *Pesticide Outlook* **V5** p206-211

Tsumura-Hasegawa Y, Tonogai Y, Nakamura Y and Ito Y (1992) Residue levels of dichlorvos, chlorpropham and pyrethrins in postharvest treated potatoes during storage and processing into starch. *Journal of Agricultural and Food Chemistry* **V40** p1240-4

Turner BC and Glotfelty DE (1977) Field air sampling of pesticide vapours with polyurethane foam. *Analytical Chemistry* **V49** p7-10

Turner BC, Glotfelty DE, Taylor AW and Watson DR (1978) Volatilization of microencapsulated and conventionally applied chlorpropham in the field. *Agronomy Journal* **V70** p933-7

Valange B and Henriet J. (1973) Meded. Fac. Landbouwwet Rijksuniv. Gent V38 p929-949. Cited by Coxon and Filmer (1985) Pesticide Science V16 p355-363

van Vliet WF and Sparenberg H (1970) The treatment of potato tubers with sprout inhibitors. *Potato Research* **V13** p223-227

Volante M, Cattaneo M, Bianchi M and Zoccola G (1998) Some applications of solid phase microextraction (SPME) in the analysis of pesticide residues in food. *Journal of Environmental Science and Health Part B* **V33** p279-292

Wang L and Pritchard MK (1997) Ethylene contamination during CIPC application increases respiration and sugars of stored potatoes. *American Potato Journal* **V74** p475

Wilson AM, Bushway AA and Bushway RJ (1981) Residue analysis of isorpropyl N-(3-chlorophenyl) carbamate in fruits and vegetables using high-performance liquid chromatography. *Journal of Agricultural and Food Chemistry* **V29** p746-9

Wolfe NL, Zepp RG and Paris DF (1978) Carbaryl, propham and chlorpropham: A comparison of the rates of hydrolysis and photolysis with the rate of biolysis. *Water Research* **V12** p565-571

Worobey BL and Sun W-F (1987) Isolation and identification of chlorpropham and two of its metabolites in potatoes by GC-MS. *Chemosphere* **V16** p1457-1462

Wright SJL and Maule A (1982) Transformation of the herbicides propanil and chlorpropham by microalgae. *Pesticide Science* **V163** p253-6

Xu Y and Burfoot D (2000) Modelling the application of chemicals in box potato stores. *Pest Management Science* **V56** p111-9

Zhu H and Selim HM (2000) Hysteretic behaviour of metolachlor adsorption-desorption in soils. http://www.agronomy.lsu.edu/pdf/SELIM1.pdf