



Research Report

Review and development of the CIPC application process and evaluation of environmental issues

Part 1

Work undertaken between July 2003 and September 2004

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Aims of the project

This project follows on from British Potato Council Project 197 (“Optimisation of CIPC application and evaluation of environmental issues relating to its use as a sprout suppressant in Great Britain”).

This project aims to provide data in the following areas:

- Improving the efficiency of the CIPC application process and reducing the need for repeat applications during the season
- Lowering residues on crop to ensure guidelines on Maximum Residue Levels (MRL) and Acceptable Daily Intake (ADI) are not exceeded
- Assessing methods of removing or reducing residues in commercial washing water effluent, with a view to developing a simple, cost-effective way of keeping residue levels within environmental legislative guidelines.
- To determine the levels of CIPC present in store atmospheres at different times in the season.
- To investigate methods of residue removal from contaminated store fabric (e.g. floor, walls, boxes, insulation).

Summary of work undertaken between July 2003 and September 2004

In the first year of the study, particular emphasis was placed on investigating the amount of CIPC present in store atmospheres, and the potential for contamination of untreated potatoes through contact with air containing the chemical. Work was carried out in a combination of experimental and commercial stores under a range of conditions.

We investigated the possibility for CIPC to be lost during application as a result of high-temperature breakdown. Manipulation of various fogger settings was used to investigate the thermal degradation process. In addition to the fogger itself (e.g. burner temperature and formulation flow rate), it has been suggested that the use of a metal pipe might encourage the catalytic breakdown of chemical. Although significant amounts of a product of thermal degradation was identified in store atmospheres immediately after application, simple measures can be adopted to minimise its production.

With an increasing amount of crop now washed on-farm, potential environmental contamination of surface waters is a potential problem for the industry. To this end, we have surveyed samples of effluent from a number of sites at various stages in the treatment process in order to establish the likely level of contamination.

Summary of conclusions

CIPC in air and crop contamination: The amount of CIPC taken up onto potatoes in experimental stores was found to be much higher than that in commercial stores

because i) only a small amount of crop was present in stores ii) stores were sealed so leakage was not an issue and iii) there was a large, readily-available source of chemical in the freshly treated store fabrics.

When one tonne boxes full of untreated potatoes were left in a CIPC contaminated atmosphere, surface potatoes took up significant amounts of chemical but none reached through to sub-surface tubers. This led to the suggestion that perhaps the potatoes act like a kind of sponge to mop up the residue from the atmosphere. When 10-kg trays were left in similar stores, the individual tubers took up more chemical than those in the one-tonne boxes, probably because they were exposed to the atmosphere over their entire surface. There was no difference between three cultivars used (*c.v.* Maris Piper, Saturna and Russet Burbank) in terms of the chemical residues.

Thermal degradation during application: A series of experiments were carried out to determine the influence of burner temperature, formulation flow rate and the use of a metal pipe on the amount of 3-chloroaniline (3CA) produced as a result of CIPC breakdown. High burner temperature (600°C) causes more breakdown than lower (e.g. standard operating condition 475°C), with none occurring when the burner was at 190°C. More 3CA was found when a metal pipe was used than when a plastic pipe or no pipe was attached to the fogger. The effect of formulation flow rate was not clear.

Washing effluent studies: Washing water samples were obtained from a number of locations, and chemical levels were found to be around 10mg/litre (or ppm) in most cases. Predictably, the concentration in washing water increased the more crop was washed. Evidence suggested that low-level contaminated of the washer barrel itself is common. A small study was conducted to investigate the decline in residue levels after effluent had been spread onto land. Difficulties arising from the method of soil sampling and analysis meant that it was not possible to quantify CIPC in the soil. However, visual evidence suggested that the chemical had affected germination of covering vegetation, and thus has a reasonable residence time in the soil. This study was repeated, with modifications, in Year 2 (see Part 2).

Experimental Section

Analysis

This section details the conditions under which samples collected in the following studies were prepared and analysed

Tuber samples

Because of the low levels of CIPC expected in most cases, only the peel from each tuber was analysed (rather than a sub-sample of the whole tuber as in MRL protocols).

Peel was diced and weighed, then Soxhlet extracted with HPLC grade hexane for 2 hours following the method of Khan [1999].

GC conditions were as follows:

Temperatures:

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

Gas flow rates:

Nitrogen carrier	30ml/minute
Flame hydrogen	30ml/minute
Flame air	180ml/minute

Under these conditions CIPC has a retention time on the column of ~3 minutes.

Air samples collected on Tenax

Air samples were analysed by thermal desorption onto the same GC column with the same gas flows as above. However, air samples require a different oven temperature programme to allow an effective separation of the volatiles present in the atmosphere. A programme devised in previous work is as follows:

130°C for 7 minutes

16°C per minute to 190°C

Hold for 5 minutes

Under these conditions, CIPC has a retention time of approximately 11 minutes and 3-chloroaniline approximately 3 minutes.

Air samples collected in methanol traps

Air samples collected in methanol were analysed by gas chromatography on a Hewlett-Packard Model HP5890, equipped with a 15m megabore column (DB1) and flame ionisation detector.

Temperatures:

Injector 220°C
Detector 250°C
Oven program 40°C for 2 minutes
 55°C/minute to 190°C
 Hold for 7 minutes

Gas flow rates:

Helium carrier 2 ml/minute
Nitrogen make-up gas 30ml/minute
Flame hydrogen 30ml/minute
Flame air 180ml/minute

Under these conditions, CIPC has a retention time of ~10.4 minutes

Washing water samples

250ml of the sample was centrifuged at 4,200rpm for 10 minutes, and then filtered through a GF/C filter paper to remove suspended solids. The solution was then passed through a 500mg C-18 solid phase extraction (BondElut) cartridge at a rate of ~2ml per minute. Once all the solution had been passed through, the cartridge was vacuum dried for one hour to remove residual water. CIPC was eluted from the column in 2ml acetone, which was then analysed by either packed column or capillary GC under the conditions described above for potato and air samples.

Soil samples

Fresh soil is air dried in the laboratory, then passed through a 2mm sieve and mixed well. A 30g sub-sample is then Soxhlet extracted with HPLC grade dichloromethane for 3 hours. After extraction, the dichloromethane is evaporated off under vacuum, and the residue re-dissolved in 2ml HPLC grade hexane. This extract is then used for analysis.

Contamination of untreated crop held in 6-tonne stores previously treated with sprout suppressants

Aims

The aim of this experiment was to determine whether untreated potatoes (*cv* Cara) would pick up a detectable residue when moved into a CIPC contaminated store. The study began in July 2003, by which point the stores had received multiple treatments with sprout suppressants. Samples were collected at intervals over a 56-day storage period to examine how the chemical residue builds up in the tuber. Washed and unwashed potatoes were included to determine whether soil cover influences the amount of CIPC taken up.

Stores and treatments

Crop was held in two 6-tonne stores at Sutton Bridge Experimental Unit (SBEU). Each store had been treated with sprout suppressants during the season 2002-3 (as part of another contract study), and this experiment was conducted at the end of the season once the trial crop had been removed. The two stores had received different sprout suppressant treatments:

Store A: Treated with a mixture of CIPC (at ~9.5 g/tonne) and another sprout suppressant (denoted as SS in later diagrams) on 4 occasions.

Store B: Treated four times with CIPC at ~14g/tonne.

All applications were made using a Swingfog fogging machine. Visual inspection suggested that more fog escaped from Store A than Store B during the application process, which might mean that the amount of chemical present in each store was more equal than suggested by dose rate alone.

Stores were maintained at 10°C and 95% relative humidity during the study. While the doors remained closed throughout the study (except for sample collection), the stores were not airtight – it is possible that some leakage of chemical could occur over the five-week period.

Sampling

Crop

50kg of crop was placed in each store in a single layer in six trays. The trays were laid out on shelves as shown in Figure 1. Half the potatoes were washed before they went into store, which differs from normal protocol, where half the sampled tubers are washed in the laboratory prior to analysis and half remain unwashed. MRL guidelines are based on washed tubers (as described in Codex Alimentarius guidelines), while unwashed values give a better picture of how the chemical is distributed around the store.

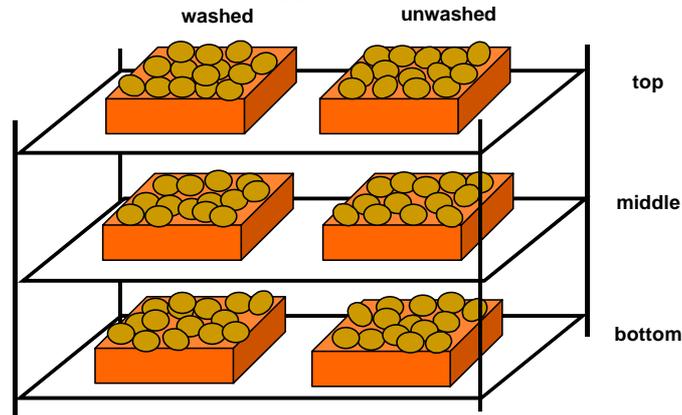


FIGURE 1: LAYOUT OF TRAYS IN SAMPLED STORES

3 tubers were removed from each tray on every sampling occasion, yielding 18 tubers per store.

In the first week of the study, intensive crop sampling was carried out after 1, 3 and 7 days to investigate whether uptake is rapid in the initial stages. For the rest of the eight-week study, sampling was scheduled at wider intervals (Days 14, 30 and 56).

Air

Samples of the store atmosphere were collected throughout the study to determine whether store conditions were stable throughout the study. Monitoring in this way can allow changes in air concentration to be correlated with chemical uptake onto crop. Air samples were collected on the same day as tuber samples to minimise disruption to the stores at all other times.

A sample volume of around 10 litres is required for analysis, so samples were collected at a rate of ~100ml/minute for 100 minutes. The Tenax resin traps were analysed by thermal desorption following a validated method [Boyd (1986)].

Results:

Control samples analysed before crop went into store showed mean CIPC concentrations of 0.29ppm (unwashed) and 0.33ppm (washed). This probably indicates low levels of contamination in other stores at SBEU where crop was held before this trial began. Concentrations in the graphs are shown uncorrected for this background level.

Data from top, middle and bottom shelves showed no significant height effect, so values from all three heights were taken together and plotted as one set of data. Each graph on the following page therefore shows all results from a single store to allow comparison of washed and unwashed values. The bars represent the mean of nine replicate analyses, and error bars are one standard deviation.

In Figure 4, no error bars are shown because each bar represents a single value. No replicate air samples were collected in the stores.

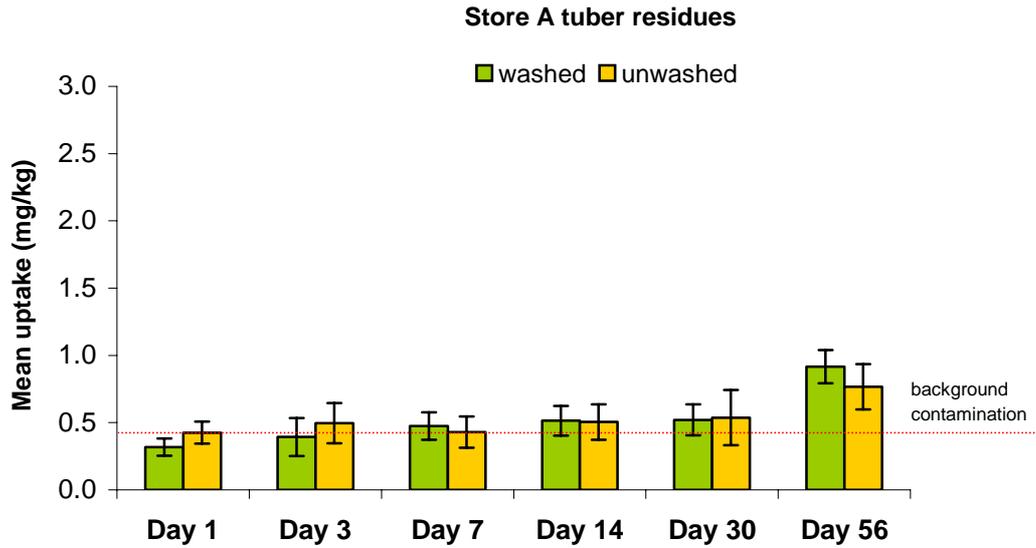


FIGURE 2: WASHED AND UNWASHED TUBER RESIDUES IN STORE A (MIXTURE OF CHEMICALS)

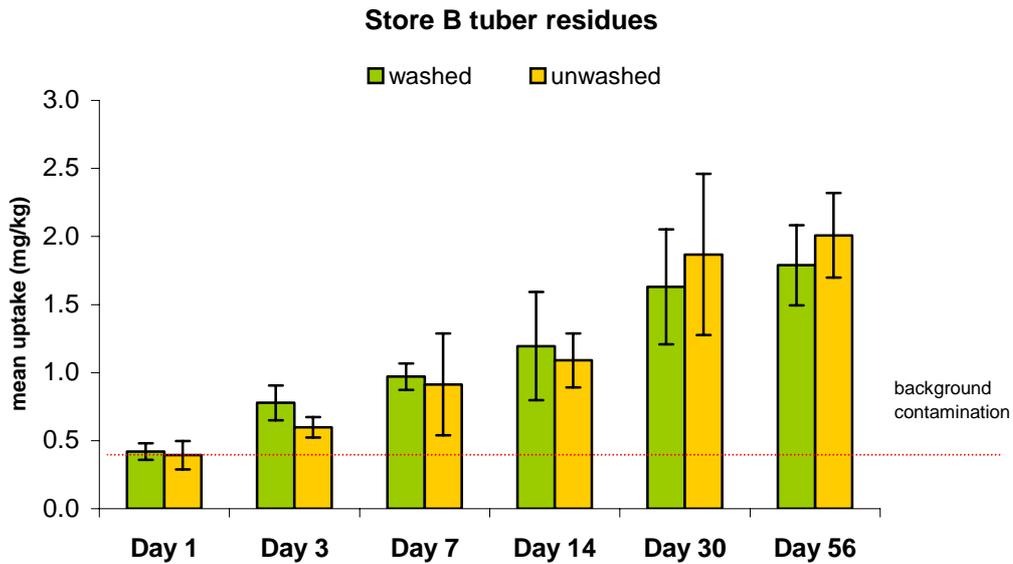
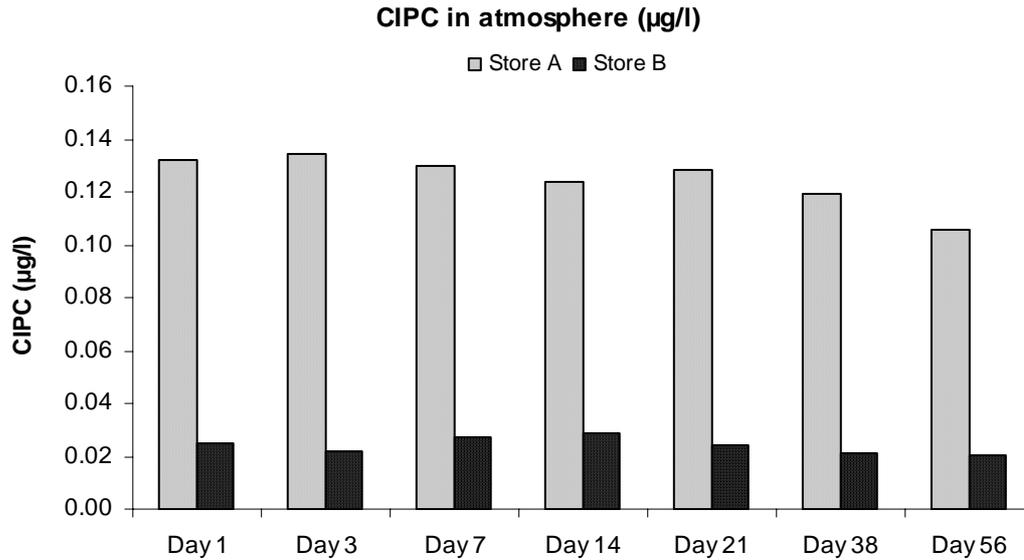


FIGURE 3: WASHED AND UNWASHED TUBER RESIDUES IN STORE B (CIPC ONLY)



Discussion:

In both stores, there was no significant difference between tubers held at different heights. Whether the crop was washed or not does not affect the amount of CIPC taken up. The only factor that seems to influence uptake onto the potatoes is which store they were held in.

As shown above, the store that received a mixture of chemicals, and the least amount of CIPC (Store A), has more CIPC in its atmosphere than the store that received CIPC alone. Analysis of a standard solution containing both compounds confirmed that they would appear at the same time on the chromatogram and produce a bigger peak than CIPC alone.

Next, a different method of sample collection and a different GC capable of separating the two was used for the analysis. Another sample of the store atmosphere was collected in a methanol trap and analysed on a capillary GC [Model HP 5890, equipped with flame ionisation detector and 15m DB1 column]. CIPC was present in this sample, but the other sprout suppressant was not found. The efficiency of the trapping medium was checked by collecting a further sample using two different traps in series: first a methanol trap, followed by a Tenax. On analysis, CIPC was identified in the methanol but nothing was found on the second trap. These results suggest that only CIPC was present in the samples after all.

Previous work carried out in experimental stores [Park (2004)] produced similar concentrations to Store A. In empty stores, an equilibrium concentration of CIPC in air of $\sim 0.1\mu\text{g/l}$ was consistently found at 10°C . So it appears that the concentration in Store B is much lower than anticipated ($\sim 0.02\mu\text{g/l}$), rather than Store A being unusually high. In addition, tuber residues in Store B build to a greater extent than in Store A, suggesting that CIPC's partitioning behaviour between the atmosphere and the potatoes is different in this store. There is no obvious reason for this difference, and

a variety of factors including differences in store history and amounts of leakage may contribute. These effects would be very difficult to quantify.

In Store A (treated with a mixture of chemicals), it appears that CIPC tends to remain in the atmosphere and not be taken up onto the potatoes, while the opposite happens in Store B (CIPC alone).

Store A (mixture of chemicals): Crop residues levels increase slightly during storage, reaching ~1ppm at the end of 56 days storage. The levels became significantly ($p < 0.01$) higher than the background contamination after 14 days. The concentration of CIPC in the air was fairly stable and similar to the levels found previously under similar conditions. No residue of the second sprout suppressant was identified in the tubers or in samples of the atmosphere.

Store B (CIPC only) Crop residues increased significantly over the 8-week storage period, reaching 2 mg/kg and above by the end of the study. Levels were significantly higher than background at 4 days ($p < 0.01$). The concentration of CIPC in the air was around five times lower than expected under these conditions. There is no obvious explanation for this.

Conclusions:

This study has shown that previously untreated potatoes can pick up a detectable CIPC residue within a short time of being moved into a CIPC contaminated store. In the study, chemical levels reached up to 2ppm over a period of 8 weeks, which is a lot considering no direct applications of chemical were made. However, conditions in this trial were specifically manipulated to encourage uptake onto the crop, and as such concentrations are much higher than we would expect under 'normal' conditions in a commercial store. Possible explanations for these high residues include:

- The very small amount of crop that was placed in each store. Potatoes were laid out in a single layer so that the entire tuber surface was exposed to the atmosphere. In commercial stores, there may be hundreds or thousands of tonnes of crop, the majority of which is not in contact with the atmosphere.
- The stores remained sealed throughout the entire 8-week storage period. In commercial stores, opening of doors and replacement of the atmosphere through venting will disrupt the conditions in the store and remove chemical from the atmosphere. If conditions are not stable then crop may be less likely to become contaminated.
- These stores have a relatively small volume (12-tonne capacity) and as such chemical concentration can build up quickly in the atmosphere, particularly because leakage has been reduced to virtually zero. In commercial stores, leakage is inevitable and is difficult to control or quantify.
- No cleaning was carried out between the end of the storage season and the start of this trial – therefore, there was no opportunity for residues in contaminated fabric to decline.

- Commercial stores may not receive as many applications in such a short period of time as these experimental stores i.e. there is a bigger pool of available CIPC in this case.
- The combined area of surfaces in commercial stores (e.g. boxes, floors, walls, and crop) will be much greater, allowing contamination to be more widely distributed.

Contamination of untreated crop held in 12-tonne experimental stores previously treated with CIPC

Aims:

Following on from the previous study, this trial further investigated the uptake of chemical residues onto untreated crop over a five-week storage period. The trial began in July 2004, by which time all six stores had received a number of CIPC applications during the season 2003-4. Tubers and samples of the store atmosphere were removed at intervals to investigate the changing store conditions.

Six stores were used to investigate the influence of a number of factors:

- Cultivar – three cultivars were placed in each store to investigate whether differences between them (e.g. in skin type and tuber shape) influence the amount of CIPC taken up.
- Store temperature – previous work was carried out at 10°C and 95% RH. This treatment was repeated, and a 4°C treatment was introduced to replicate conditions in a pre-pack type store. CIPC contamination leading to residues on crop is more of a problem in cold stores than processing stores because i) the potatoes are sold in their skins [CIPC is largely removed by peeling] and ii) only in cold stores can CIPC feasibly not be used (the level of crop activity is lower and the use of ethylene is possible to maintain sprout control). The amount of CIPC in the air is expected to be less at 4°C than 10°C, and this may be reflected in the tuber residues.
- Extent of store loading: In the previous trial, we demonstrated that a single layer of potatoes (held in untreated plastic trays) would take up chemical from the atmosphere. This time, full one-tonne wooden boxes were also included to examine how far the chemical will penetrate into the crop.

Stores and treatments

Crop was held in six 12-tonne experimental stores at Sutton Bridge Experimental Unit. In each store, three one-tonne wooden boxes were laid out on the floor. In two of the stores, the boxes were filled with crop – one box for each of Russet Burbank, Saturna and Maris Piper. In the remaining stores, three plastic trays were placed in the bottom of each box, and each tray had a single layer of potatoes laid out in it (one tray for each cultivar).

TABLE 1 STORE TEMPERATURES AND LOADINGS

Store	Temperature	Loading
A	4°C	Trays
B	4°C	Boxes
C	10°C	Trays
D	10°C	Boxes

Treated boxes were used to provide an extra source of CIPC contamination. Air was not drawn deliberately through the potatoes, but was allowed to circulate as necessary to maintain the desired temperature in store.

Sampling

Crop: Potatoes were removed from stores at Day 1, 4, 7, 14, 28 and 35 of the storage period. In stores containing only trays of crop, three tubers were removed from each tray on each occasion. In the boxes, potatoes were removed from the surface of the pile, keeping away from the edges, and also from a depth of ~10cm. During the trial, samples were collected from only one half of the box, allowing the other half to remain untouched until the end of the study. This allowed any differences related to a tuber's position in the box to develop during the storage period, and be investigated at the end (discussed later).

Air: A sample of air was taken from each store once they reached the desired temperature, but before the crop was put in. During storage, air samples were collected on the same day as potatoes to minimise disruption to the stores at all other times. A sample of ~10 litres was drawn through Tenax resin and analysed as previously described. It was expected that the concentration in the atmosphere might reduce as the residue on crop increased.

End of trial: In both stores containing boxes of potatoes, the box containing Russet Burbank was selected for intensive sampling (cultivar selected at random). Samples were taken from two locations in the undisturbed portion of the box.

- touching the side of the wooden box
- in the centre of the box, as far as possible from the sides and edges

It was suggested prior to this study that perhaps contact with the wooden box would allow transfer of residues from the box to the crop. Potatoes were also selected from five depths within the box

- at the surface
- sub-surface (~10cm depth)
- middle (midway between top and bottom of box)
- middle-bottom (midway between middle and bottom of box)
- bottom (touching the wooden base)

The depth within the box will limit the extent of a potato's contact with the atmosphere or other potential sources of contamination, for example, the floor.

Results:

The graphs on the following pages illustrate how the CIPC content of potatoes increases with time in each store. All data from an individual store is shown on one graph to allow comparisons among cultivars. Values shown are the mean of three replicate analyses.

Note that some values are missing from the air sampling data due to problems with the analysis.

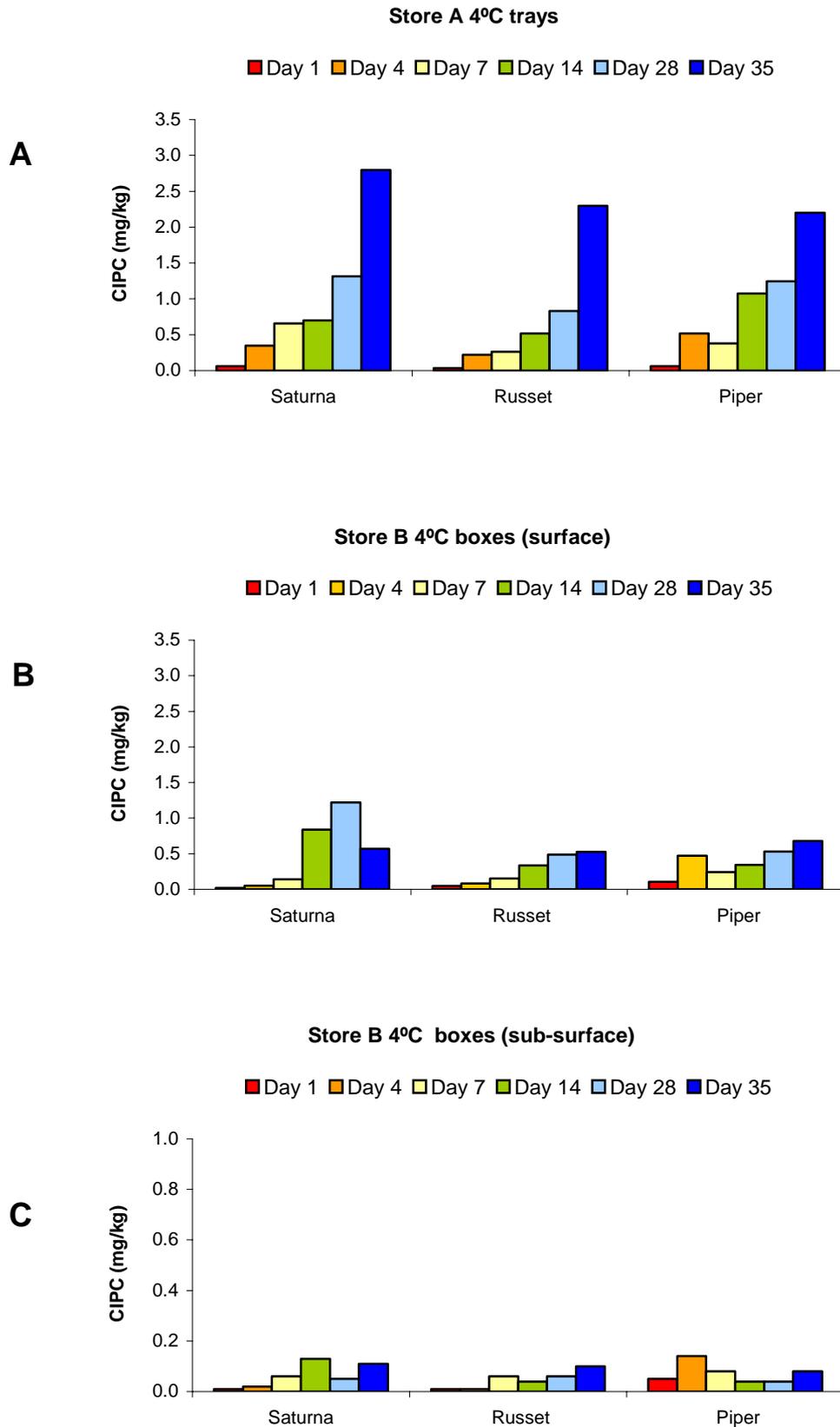


FIGURE 5: INCREASE IN TUBER RESIDUES OVER 35-DAY STORAGE PERIOD AT 4°C A: crop in trays. B: surface tubers from one-tonne box. C: sub-surface tubers from 20cm depth in box. Note that C is on a different scale than A and B

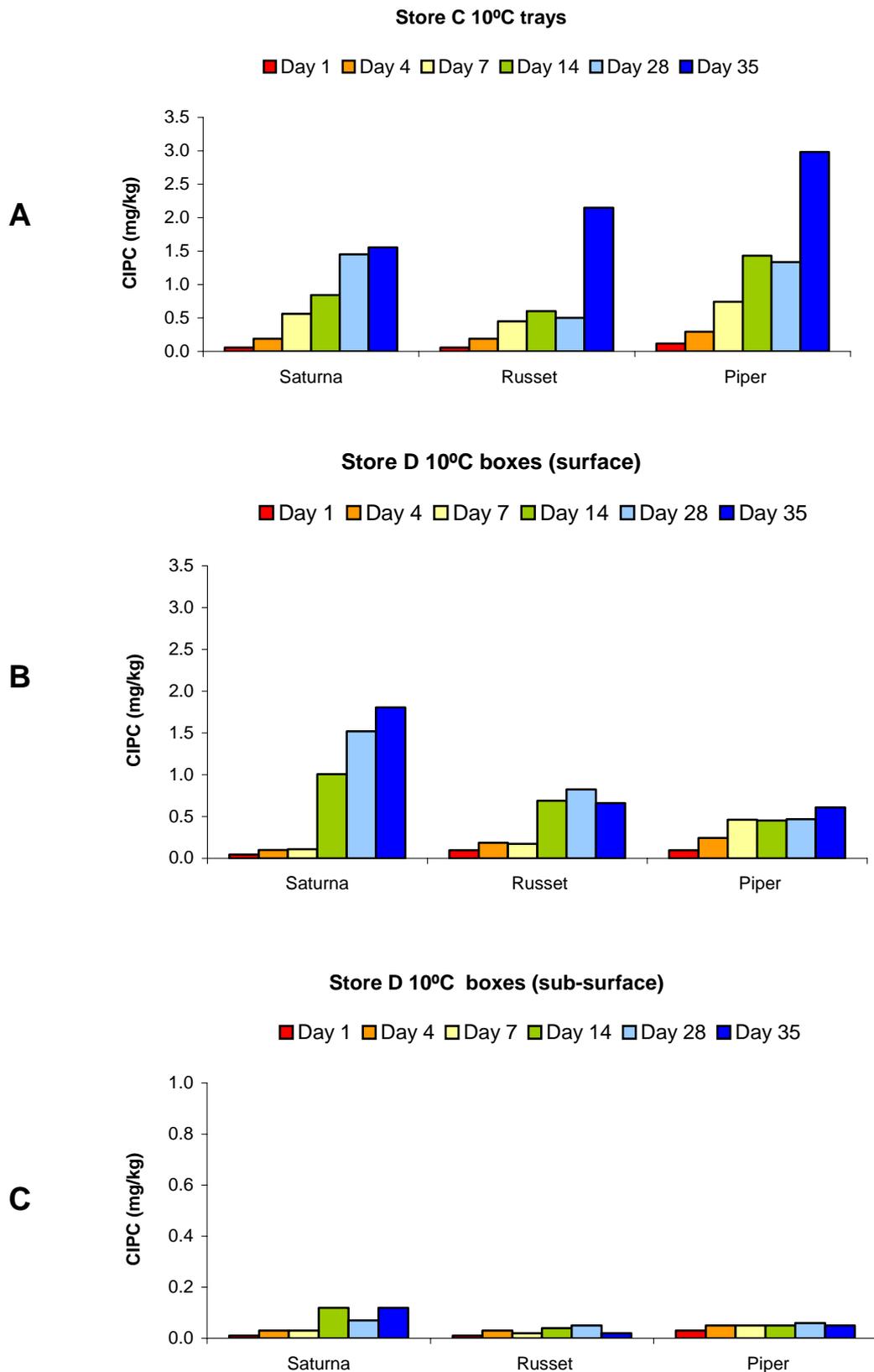


FIGURE 6: INCREASE IN TUBER RESIDUES OVER 35-DAY STORAGE PERIOD AT 10°C. A: crop in trays. B: surface tubers from one-tonne box. C: sub-surface tubers from 20cm depth in box. Note that C is on a different scale than A and B.

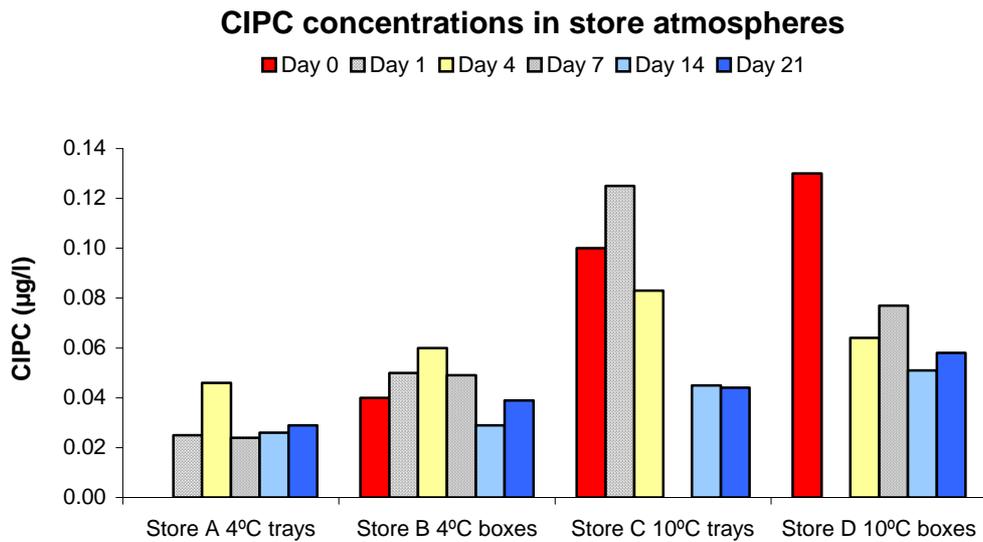


FIGURE 7: CONCENTRATIONS OF CIPC IN STORE ATMOSPHERES OVER THE 35-DAY STORAGE PERIOD. NOTE THAT SOME VALUES ARE MISSING

Tubers (cv. Russet Burbank) sampled from different depths in box at end of trial (Day 35)

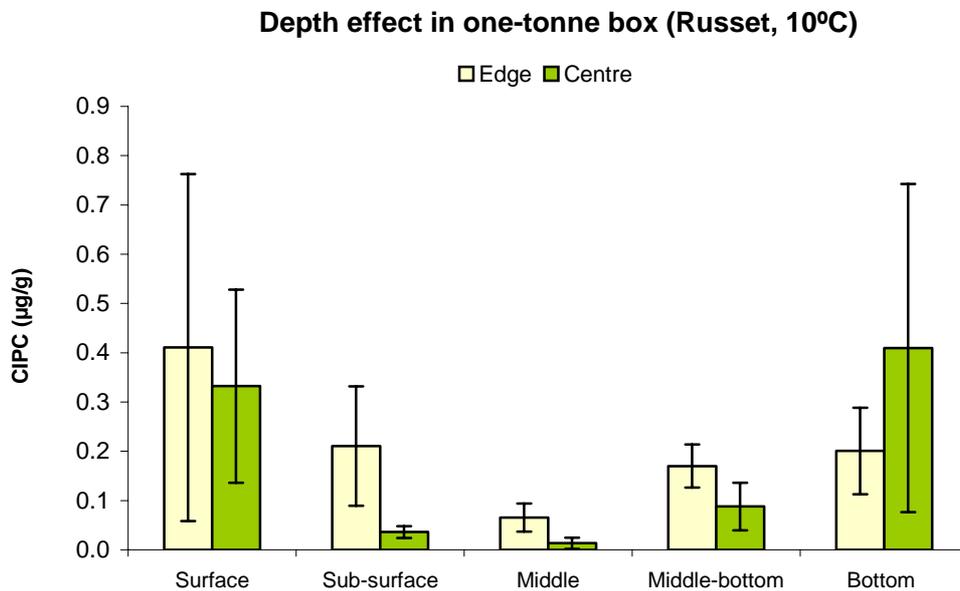


FIGURE 8: MEAN CIPC CONTENT OF UNTREATED POTATOES AT DIFFERENT DEPTHS IN A ONE-TONNE BOX AFTER STORAGE IN A CIPC CONTAMINATED STORE AT 10°C FOR 35 DAYS.

Discussion:

Air samples: Initial values from Day 0 show the expected differences in the concentration in the atmosphere at 4°C and 10°C. Starting values are similar to those found in previous work under similar conditions: 0.02-0.03µg/l at 4°C, and ~0.1µg/l at 10°C [Park (2004)]. By Day 35, however, there appears to be no such difference. It was expected that the concentration in the air might decrease as chemical was taken up onto the potatoes. This effect was seen in the 10°C stores, where concentrations dropped to around half of that seen in empty stores, but not in the cold stores. There was no difference between stores containing different amounts of crop (30kg trays vs. 3 tonne boxes) at the same temperature.

Crop samples: In all stores, there was no significant difference in the amount of chemical taken up by the different cultivars.

The amount of crop did seem to affect the degree of contamination, with higher levels found in potatoes from the stores with only 30kg instead of 3 tonnes. This is probably because the potatoes in the trays were exposed to the atmosphere over their entire surface. In addition, the surface area of the potatoes in these stores is significantly less than in the 3-tonne stores, where the contamination can be spread over a larger area, reducing the contamination on an individual potato basis.

The most significant effect within a single store was whether potatoes were sampled from the surface or the sub-surface of the box. Virtually no CIPC was found to penetrate to ~10cm depth in a box. This suggests that the first layer of potatoes ‘mops up’ the available chemical and prevents it reaching any deeper. It is perhaps significant that in these stores, airflow was not directed through the pile, so any transfer of residues would have to occur as a result of passive air movement into the box. Although fans in the store will switch on and off periodically to maintain temperature control, it is unlikely that significant amounts of air will be moving through the boxes, since there is no incentive for air to move through the pile rather than circulate outside it where it can mix more easily.

In terms of crop residue levels, there was little difference between crop held at 4°C and 10°C by the end of the five-week period, with potatoes in trays containing around 2.5 mg/kg, and potatoes from the surfaces of the one-tonne boxes averaging around 1 mg/kg. This is perhaps surprising considering the initial differences in air concentration, but given the similarities from around Day 7, perhaps not. It can be difficult to draw conclusions from the air concentration data, because only one sample is taken at a time from each store, which can lead to considerable variability within one store over the storage period. In future work, it would be helpful to collect duplicate samples at more regular intervals to get a better picture of what happens in the atmosphere over time.

Position in box: Residue levels clearly depend on the position of the tuber in the box. There is a clear gradient in both directions in the box, with levels highest at the top and bottom of the box, decreasing towards the middle. At the surface, potatoes are in direct contact with the contaminated atmosphere. Bottom potatoes are closest to the floor, which is believed to be a significant source of the chemical residues in the atmosphere. It appears as if the crop is ‘filtering’ the CIPC out of the air as it passes through the box: the predominant direction of air movement through the crop will be

from bottom to top, because of heat generated by the respiring crop. Very little chemical is expected to reach into the centre of the pile of potatoes via this passive process.

Conclusions:

This study has shown the extent of tuber contamination to be

- proportional to the storage time (ie the longer in store, the higher the residue)
- inversely proportional to the amount of crop in store (the more potatoes, the lesser the concentration)
- influenced by the position of the tuber in a box (surface vs. sub-surface)

but not significantly affected by differences in

- cultivar
- air temperature

The levels of contamination found in this trial are significant, considering a likely Maximum Residue Level (MRL) of 5-10 mg/kg and the fact that this crop has received no direct treatment with CIPC. In addition, this was a relatively short storage period (5 weeks) when compared with up to 10 months in commercial stores. However, levels like these are not expected to accrue in commercial crops for the reasons described in the discussion of the previous experiment.

Contamination of untreated potatoes held in commercial stores previously treated with sprout suppressants.

Aims

Where the previous experiments showed the contamination potential under experimental conditions, this piece of work investigated the actual levels of contamination in crop held in full-scale commercial stores.

Over the last couple of seasons, ethylene has emerged as an alternative to CIPC for maintaining sprout control in low temperature storage. Although its effect on fry colour makes it unsuitable for use in processing stores, it is not a consideration for the pre-pack market. As a result, there are now a number of stores with a long history of CIPC use which are no longer receiving CIPC treatment. This presents the opportunity to investigate CIPC contamination of untreated crop under genuine commercial conditions.

We expect the accumulation of residues on crop to be less of a problem in a commercial situation for a number of reasons. Firstly, the concentration of CIPC in the atmosphere at 2-3°C should be considerably less than at 10°C as in the studies in experimental stores, meaning that less CIPC is available to the crop at any given time. In addition, the surface area of crop relative to the volume of the atmosphere is much larger meaning that contamination can be more widespread. Commercial stores are also much leakier than experimental stores, and may be actively vented to prevent the accumulation of products of respiration, allowing loss of chemical from the atmosphere.

Stores and treatments

Crop was taken from a number of commercial stores where CIPC was not used in 2003/4. Details of the stores are shown in Table 2 below.

TABLE 2: DESCRIPTION OF SAMPLED COMMERCIAL STORES

Location	Size (tonnes)	Temperature (°C)	Last CIPCd	Cultivar
1	1,200	2-3	Nov 00	Desiree
2	1,200	2-3	Jan 02	Desiree
3	1,400	2.5	Jan 03	King Edward/Desiree
4	1,550	3	Mar 03	Sante
5	1,200	3	Pre-July 03	Maris Piper/Desiree
6	No details	No details	No details	No details

In addition to the contamination of the store building (e.g. floors, walls, insulation material) as a result of past applications, all crop was held in boxes that had been CIPC treated in the past.

Sampling

Samples were collected from commercial stores by staff from Sutton Bridge Experimental Unit on a number of occasions in June 2004.

Sample tubers were taken from the surface of boxes in most cases, although in a few instances sub-surface tubers were also collected for comparison. It was expected that only surface tubers would be affected by accumulation of residues from the atmosphere. Most of the tubers were removed from store after 8-10 months storage.

In most stores, tubers were sampled from the front and back of the store. Store 3 contained 150 tonnes of CIPC treated crop (which was moved into this store after chemical treatment) in addition to the majority untreated material. In this case, potatoes were sampled from boxes next to the treated crop and also from the opposite end of the store. No details were received regarding the conditions in Store 6, but it is believed that a considerable amount of CIPC treated material was also present in that store.

Results:

The graph overleaf shows the mean CIPC content in potatoes taken from 6 commercial stores. This value is the mean of three analyses, carried out on individual potatoes.

‘Near’ denotes samples collected from close to the CIPC treated material held in store, while ‘far’ denotes samples from the other side/end of the store. ‘Back’ and ‘front’ relate to the front and back of the store. ‘Surface’ and ‘sub’ describe where in the box samples were taken from (sub-surface = 10cm below the surface)

Values shown are parts per million (mg/kg) based on the fresh weight of potato, as in MRL determination. Potatoes were not washed prior to analysis.

A level of 0.05mg/kg or above was considered a potential problem, which may include rejection of the crop and losses to the supplier.

Mean CIPC content of untreated potatoes from commercial stores

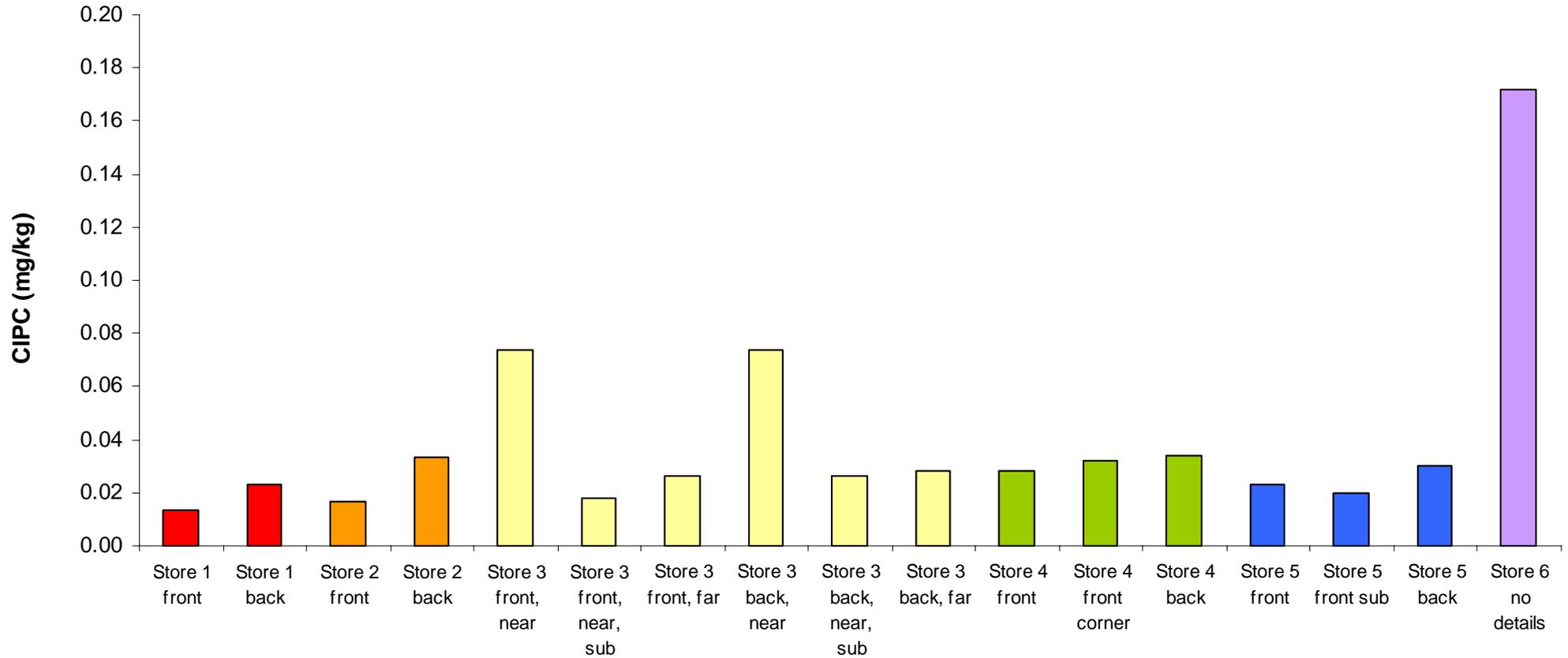


FIGURE 9: MEAN CIPC CONTENT OF UNTREATED POTATOES FROM COMMERCIAL STORES IN WHICH CIPC HAS BEEN USED IN THE PAST

2.5 Discussion:

Figure 9 shows that in most cases, the amount of CIPC determined on the crop is too low to present a problem (taking 0.05mg/kg as a borderline value). In previous work, crop that has neither been treated with CIPC nor held in contaminated stores has been analysed as a blank. When analysed by GC, such material generally gives a response of ~0.02 mg/kg. Very low levels like this are normally considered as 'trace' and are not quantified because of limits on the sensitivity of analysis.

For the purposes of this study, only three samples are considered to show evidence of CIPC contamination: From Store 3, the two surface samples collected close to the 150 tonnes of treated material (at both the front and back of the store) and the sample from Store 6, about which very little is known. It is believed, however, that this store also contained substantial amounts of treated crop.

The results suggest that contaminated store fabrics may not present as much of a contamination problem as suspected. Compared with the results from the experimental stores, the amount of chemical picked up by these tubers is very low (5-10 times less), even after a much longer storage period (6-10 months as compared with 8 weeks). Explanations for this may include:

- i) the lower air temperature in these stores (~3°C, compared with 10°C in experimental stores). The concentration of CIPC in the air has previously been shown to be temperature dependent [Park (2004)]. Air samples were not collected from these stores so we have no information on the concentration in the atmosphere in these particular stores. At present, only low-temperature stores can be used for this kind of study due to the lack of alternative sprout suppressants for processing-type storage. It would be interesting to compare with a higher temperature situation if possible.
- ii) the large volume of crop in the store relative to the volume of headspace. Potato skin presents the largest surface in the store (when compared with the floor, the walls and even the boxes) and may allow the chemical residues from the atmosphere to be more widely distributed, resulting in low values on an individual potato basis.
- iii) leakage or venting of air from the commercial store, which may prevent the build up of CIPC in the atmosphere by providing a pathway for chemical loss.

Surface vs. sub-surface: Further evidence that the atmosphere is the source of crop contamination is provided by the fact that subsurface values were considerably lower than the corresponding surface values from the same position where contamination was identified. Contamination from the wood of treated boxes appears to be less significant – volatilisation from contaminated wood might be a source of the residues in the atmosphere, but direct transfer of chemical from the box to the tubers does not seem to occur.

Crop stored near treated material contains significantly higher residues than potatoes further away, which suggests some movement of residues. Volatilisation from the surface of the CIPC-treated crop or the recently treated boxes they are contained in may be responsible. Although all boxes had been treated in the past, only those containing CIPCd potatoes had been treated this season. Boxes left outside to weather over the summer may experience a reduction in residues during this time, particularly in the easily accessible surface layer. CIPC remaining in the wood after weathering

may be less likely to find its way into the store atmosphere easily. In most cases, boxes had also been sprayed with Jet 5 (used for disinfecting stores between seasons), whose oxidising action may also help reduce surface residues.

Contamination arising from freshly CIPC treated material appears to be more of a problem than surfaces where the residues have been allowed to 'age' for any length of time. It is a common feature of environmental materials (eg soil, plant material and wood) that aged residues are more difficult to extract [Hatzinger and Alexander (1995)] This also implies that they are less likely to dissipate into the atmosphere of their own accord.

Investigation of potential breakdown of CIPC during the thermal fogging process

Background

In previous studies, when CIPC was monitored in the atmosphere of treated stores, another compound was routinely detected as well [Park (2004)]. Following investigation, this compound was identified as 3-chloroaniline (3CA), which is a known product of the microbial and thermal breakdown of the CIPC molecule [e.g. Nagayama and Kikugawa (1992), Worobey and Sun (1987)].

Its presence in potato stores could result from either or both of two processes: the action of microbes in the store gradually breaking CIPC down over the storage period, or thermal degradation during application. Prior to this study, 3CA had been identified in samples taken from stores at various times throughout the storage season, which made it impossible to tell which process was responsible. In this study, the store atmosphere was sampled immediately after the application was complete, allowing no time for microbial action. Any 3CA found at this time is assumed to be a result of thermal breakdown. Some may also be present in the CIPC formulation, but this amount will be very small, and is strictly controlled (i.e. 0.05% of CIPC by weight).

Aims

The aim of the reported work was to investigate several factors in the thermal fogging process and assess their involvement in the production of 3-chloroaniline from CIPC. The factors looked at included burner temperature (conventionally ~475°C) for obvious reasons. In addition, the use of a metal pipe is suspected of having a catalytic effect on breakdown, so applications were made in which the pipe was excluded. The rate at which formulation passes through the fogger may also be involved, as the presence of solvent may have a cooling effect and be expected to reduce the breakdown of CIPC to 3CA.

These factors were combined and investigated in a series of experiments

Stores and treatments

Three sets of experiments have been carried out to date:

Experiment 1 (Feb 04): Burner temperature 190°C vs. 600°C. Also presence/absence of metal pipe

Experiment 2 (April 04): Flow rate (0.25 to 1.0 litre/minute) and burner temperature (400 to 600°C)

Experiment 3 (Sep04): Comparisons of i) Plastic pipe vs. metal pipe ii) Machine (A vs. F) and iii) Burner temperature (475°C vs. 600°C).

Experiment 1: Effect of burner temperature and presence/absence of pipe

Applications were carried out on 11th February 2004, using MSS CIPC 50M and SCC Machine A. Each application lasted 30 seconds, and was carried out under a different set of conditions. The stores were empty during the study.

Prior to application, the fogger was run outside at different burner temperatures and formulation flow rates to assess the fog quality. After this, two temperature set-points were selected covering as wide a range as practicable.

Low: 190°C

High: 600°C

One application was made at each temperature with fog carried into store through 4” diameter metal ducting pipe (~7m length) as in standard applications. The fogger was outside the building in this case.

For the other two applications, the fogger was inside the building (in the corridor behind the stores) and chemical was vented into store directly from the fog-head. In order to achieve this, the fogger had to be propped up on wooden slats to line up the fog-head and the port. All exhaust products produced while getting the fogger up to temperature were also introduced into the store, while usually the fogger is run until stable before the pipe is put through the port.

At 190°C, the optimum flow rate for formulation was 0.25 litre/min (1/4 of the standard rate) and the intention was to use this rate for all four applications. However, it proved difficult to control and chemical was delivered more quickly into some stores.

TABLE 3: APPLICATION CONDITIONS AND CHEMICAL ADDED TO STORES (FEB 04)

Store	Conditions	CIPC added to store (g)
A	Low temperature No pipe	120
B	High temperature No pipe	100
C	Low temperature With pipe	55
D	High temperature With pipe	60

Sampling

To minimise the effect of background contamination (since all stores had been CIPC treated fairly recently), all stores were opened with the fans running on the morning of the study to purge the atmosphere. Stores were only closed immediately prior to application to minimise the accumulation of chemicals in the air.

Samples were collected at intervals after application to investigate what was happening in the atmosphere over time:

1. Immediately after application finished, duplicate samples of atmosphere were collected on Tenax resin (100ml/min for 1 minute)
2. After Tenax sampling was complete, a solvent trap (15ml HPLC grade methanol) was dropped into store via a port in the roof. Running conditions were ~1100 ml/minute for as long as available between applications (varied from 11 to 40 minutes).
3. At 18 hours post-application, more air samples were collected on Tenax (100 ml/min for 60 min)
4. Stores remained sealed with store control switched off and a further sample was collected after 6 days (100ml/min for 100 min).

Two types of samples were taken at T_0 to provide the best chance of getting a quantifiable result: the two types of trap are analysed by different methods, which should provide the widest range for quantification. Tenax (by thermal desorption) is better for small amounts as the entire sample is used at once, while solvent trapping is better where large amounts are expected because only a small proportion of the sample (e.g. 2 μ l of 2ml sample) is injected onto the GC, effectively diluting the sample by a factor of 1000. Trapping in methanol also allows identification of compounds by GC-MS, and does not involve high temperature treatment of the sample during analysis.

Results

The table below shows the concentrations of CIPC and 3CA determined in air samples collected in methanol. The following graphs show 3CA and CIPC at various times post-application

TABLE 4: CONCENTRATIONS OF CHEMICAL IN AIR SAMPLES TRAPPED IN METHANOL.

Store conditions	Concentration (μg/l)	
	3CA	CIPC
190°C no pipe	0.17	65.4
190°C with pipe	nd	32.7
600°C no pipe	0.56	83.3
600°C with pipe	1.21	35.4

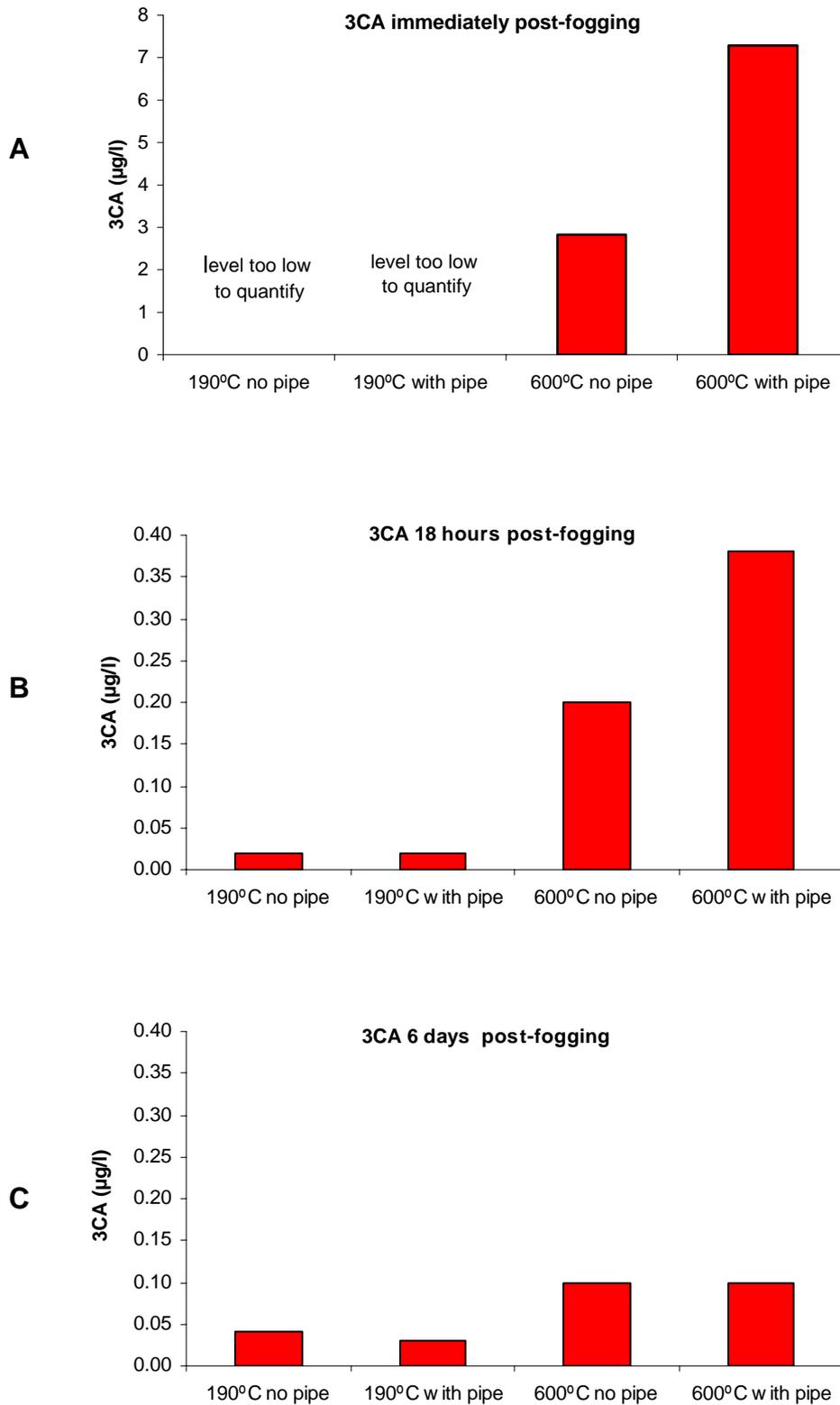


FIGURE 10: 3-CHLOROANILINE CONCENTRATIONS IN SAMPLES COLLECTED ON TENAX A) IMMEDIATELY B) AT 18 HOURS AND C) 6 DAYS POST-APPLICATION

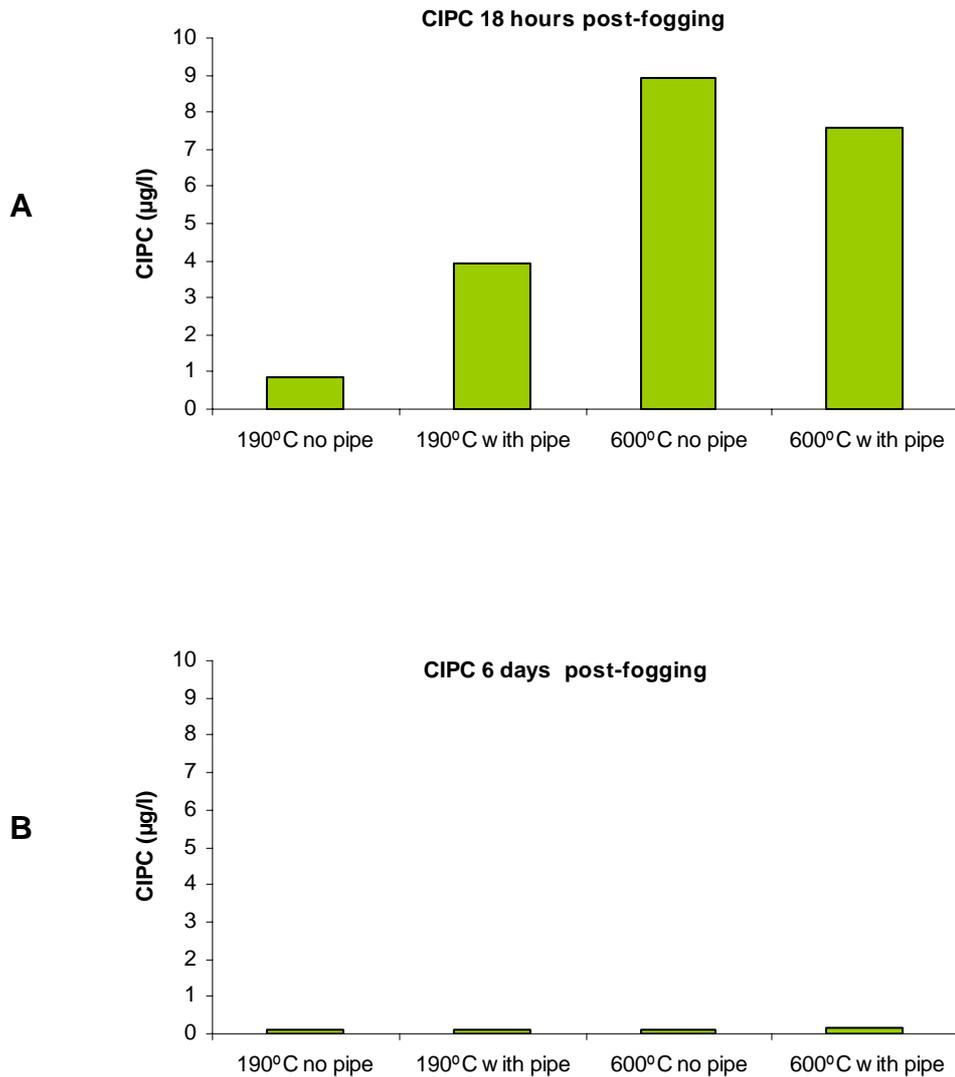


FIGURE 11: CIPC CONCENTRATIONS IN AIR SAMPLES COLLECTED ON TENAX A) 18 HOURS AND B) 6 DAYS POST-APPLICATION. NOTE THAT GRAPHS ARE ON THE SAME SCALE.

Discussion:

Samples collected in methanol traps immediately after application

CIPC: Significantly less CIPC was found in these samples than in the Tenax samples. This is likely to be a result of how and when they were collected. Fog will settle quickly from the top of the store, resulting in a loss of chemical from the part of store where sampling equipment was located. Sample collection took longer (up to 40 minutes) for this style of trap, during which time conditions in the store were constantly changing. The stated values represent an average of what was happening in

store over a period of time. Tenax sampling provides a better ‘snapshot’ of conditions at a particular point in time.

3CA: 3-chloroaniline was present in the samples collected in methanol immediately after application, which suggests it was produced during the application.

For both chemicals, the amount detected in the methanol sample was less than on the Tenax samples because of how the samples are collected, so in future work methanol samples will be collected to allow GC-MS analysis if necessary, but Tenax values will be considered a more accurate measure of fog concentration

Note on validation of the thermal desorption method:

The thermal desorption method was developed and validated at Glasgow [Boyd (1984)] and been used for determination of CIPC in air samples for over 20 years. In this particular study, the robustness of the original method was verified to show that 3CA and CIPC can be successfully separated and quantified, and to confirm that no thermal breakdown of CIPC occurs under analytical conditions.

The figure below shows the chromatograms obtained on analysis of three samples:

- A. A hexane standard containing only CIPC
- B. A hexane standard containing both 3CA and CIPC
- C. An air sample collected from a CIPC treated store

Note the absence of a peak at ~3.7 mins in Sample A (identified as 3-chloroaniline by GC-MS) showing that breakdown does not occur under analytical conditions. Further evidence of 3-chloroaniline’s origins in the store rather than in the analysis is provided by its presence in the methanol samples, which are not subjected to heat treatment.

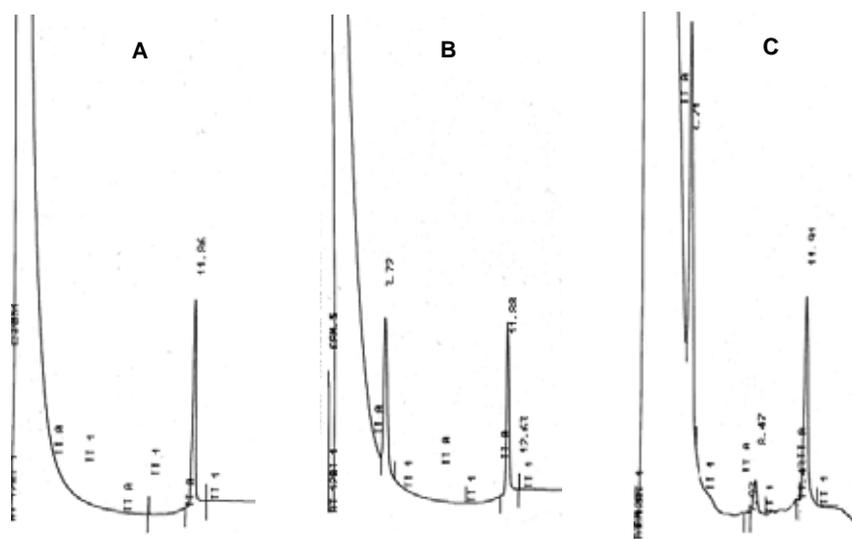


FIGURE 12: CHROMATOGRAMS RESULTING FROM THERMAL DESORPTION OF A RANGE OF SAMPLES FROM TENAX RESIN.

Samples collected on Tenax immediately after application:

3-chloroaniline was found to be present in samples taken from both stores that received a high burner temperature (600°C) application. The amount generated was more when the metal ducting pipe was used than when fog was applied into the store directly from the fog-head, in spite of the fact that less CIPC was actually added to that store.

No 3-chloroaniline was detected in fog samples from the two low-temperature stores.

These results suggest both direct thermal degradation as a result of high burner temperature and the catalytic effect of the metal pipe are responsible for the presence of 3-CA in the store. They do not, however, discount the possibility of further breakdown by biological processes during storage.

No values are shown for CIPC in the fog (i.e. immediately post-application). This is because the amount of CIPC relative to the amount of 3-chloroaniline is so high that the method of analysis could not measure CIPC accurately.

Samples collected on Tenax at 18 hours

3CA: (see figure 10B)

At 18 hours post-application, the levels of 3CA in the stores that received a high burner temperature application are higher than previously detected at 'equilibrium' in empty stores – the implication is that this chemical was generated as a result of the application and the conditions in store have not yet stabilised.

However, in low temperature stores, the very low levels (less than previous background values) suggest no chemical is produced during application. Flushing of the stores immediately prior to application is probably the reason for the unusually low values.

CIPC: (see Figure 11A) Previous to this work, we have worked in empty stores at SBEU and determined a 'background' level for CIPC vapour of ~0.1µg/l in contaminated stores under stable conditions at 10°C. In this work, CIPC levels in all stores at 18-hours post-application were significantly higher (10-80 times) than that. They are also significantly higher than levels determined by other workers in commercial stores several days/weeks post-application [e.g. Boyd (1984)]. In this study, sampling was carried out immediately after application while previously several weeks had passed since the last application. This result suggests that either the atmosphere is super-saturated with CIPC vapour, or the finest fog particles have not settled after 18 hours. This may affect the amount of chemical lost when the store is vented, which can be important in terms of both environmental pollution and the efficacy of treatment. The physical conditions (e.g. temperature, relative humidity) in these stores were not controlled in the aftermath of application (store controls remained off for the duration of the study) and variations in temperature and RH were not monitored.

Samples collected on Tenax at 6 days post-application (see Figures 10C and 11C)

After 6 days, the amount of CIPC in the atmosphere in each store is very similar both to each other and to the ballpark figure of 0.1µg/l at 10°C from previous work in empty stores. The levels of 3CA are again more similar among the stores, and more in keeping with background levels.

Summary

Fog samples collected immediately post-application show detectable quantities of 3CA in stores receiving 600°C application but none in the corresponding 190°C stores. Breakdown is higher where the metal pipe is used than when it is absent.

Vapour samples collected 18 hours post-application suggest that complete deposition of CIPC fog has not occurred by this time. Levels are elevated ~50 times compared to background at this point. In high (600°C) burner temperature stores, 3CA levels are also elevated relative to the background. This effect is not seen in low (190°C) burner temperature stores, where levels are reduced as a result of the flushing out of the store.

Vapour samples collected after 6 days show CIPC and 3CA concentrations have returned to background levels. There are no significant differences between any of the stores.

Conclusions

This trial has demonstrated that at least two aspects of the application process may be responsible for generating 3CA in store. We are interested in this process because any losses of CIPC from the store, whether through leakage, venting or breakdown, can have implications for the efficacy of the treatment.

We have demonstrated the potential for modifying the application process to minimise the production of 3CA and the associated loss of the active chemical CIPC:

- Lowering of burner temperature: at <200°C no thermal breakdown was observed. However, this will have implications for fog quality, since the production of a satisfactory dry, buoyant fog becomes more difficult as the temperature is reduced. It is important to stress that the high temperature treatment was carried out at temperatures in excess of usual operating conditions (600°C vs standard 475°C) so these results represent an exaggerated effect.
- Replacement of the metal ducting pipe to minimise the catalytic effect: contact with hot metal surfaces is known to increase the risk of chemical breakdown. For example, problems with breakdown of compounds during analysis led, in the past, to the development of all-glass flow paths for GC analysis. In this set of experiments, we eliminated the pipe completely but not without difficulty. In a commercial situation, this would not be possible. Development of a suitable pipe made of a non-metal material would be one way to solve this problem. In the long term, a flexible pipe will be required but for experimental purposes a rigid plastic would suffice, at least until we illustrate the principle.

- It is also possible that the rate at which the formulation passes through the fogger could influence the degree of CIPC decomposition. The solvent element of the formulation may have a cooling effect, and reduce the likelihood of breakdown.

Experiment 2: Effect of burner temperature and formulation flow rate

This trial looked at differences in the amount of 3-chloroaniline (3CA) as related to the burner temperature and also the rate at which the formulation passed through the fogger. For an SCC Unifog as used, standard operating conditions would be 475°C burner and 1 litre/minute formulation flow.

Applications were carried out on the 27th April 2004 using SCC Machine F and MSS CIPC 50M. Six stores at SBEU were used for two sets of three applications (one to investigate burner temperature; one to investigate flow rate), which were made as shown in Table 5 below:

TABLE 5: APPLICATION CONDITIONS IN STORES (APRIL 2004)

Store	Burner temperature (°C)	Formulation flow rate (l/min)	Application time (sec)	CIPC added to store (l)
1	600	0.5	15	0.11
2	500	0.5	15	0.11
3	400	0.5	15	0.18
4	600	0.25	30	0.09
5	600	0.5	15	0.12
6	600	1.0	8	0.13

Burner temperature ranged from 600°C to 400°C to cover the range above and below the standard operating conditions (475°C). Flow rates varied between 0.25 litre/min and 1.0 litre/min to give a range covering normal conditions while still ensuring a reasonable quality of fog. Flow rate did not seem to affect fog quality as much with this machine. In all cases, metal ducting pipe was used to carry fog into store as standard.

Sampling: Samples were collected immediately after application, and at 18 hours and 7 days post-fogging. Sampling was carried out as described previously using a combination of Tenax traps and methanol solvent traps.

Results:

Figures 13 and 14 show the concentrations of 3CA and CIPC determined in samples from store atmospheres and various times after application.

In the 3CA graphs, 'data missing' denotes a sample that was not quantified due to problems during analysis. CIPC concentrations were not determined immediately after application as they are too high to quantify under the sampling conditions.

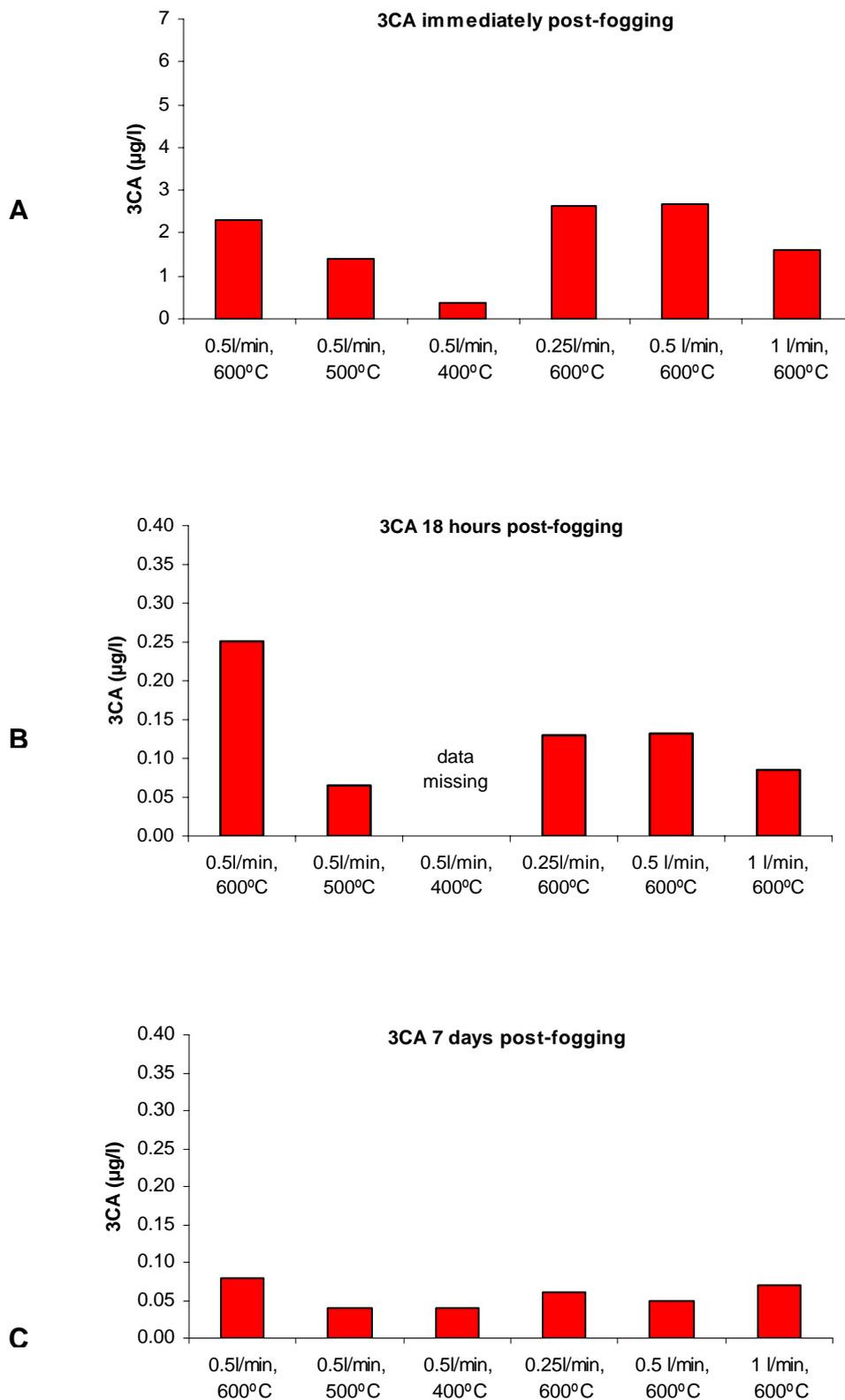


FIGURE 13: 3-CHLOROANILINE IN STORE ATMOSPHERES A) IMMEDIATELY B) 18 HOURS POST-FOGGING AND C) AT 7 DAYS POST-FOGGING AT DIFFERENT BURNER TEMPERATURES AND FORMULATION FLOW RATES

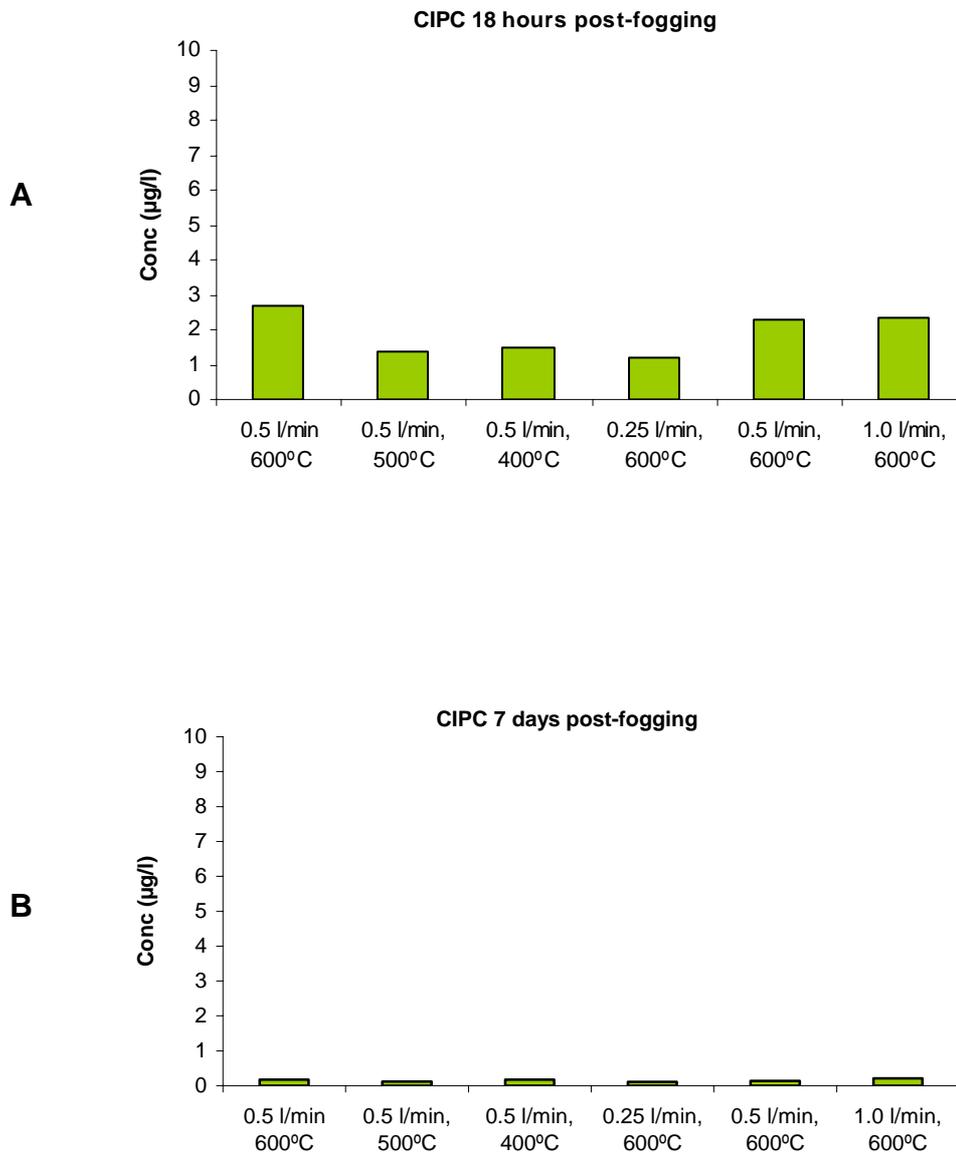


FIGURE 14: CIPC CONCENTRATIONS IN SAMPLES COLLECTED ON TENAX A) 18 HOURS AND B) 7 DAYS POST-APPLICATION.

Discussion:

Burner temperature seems to have a significant effect on the amount of 3CA produced – this confirms the results from the first set of experiments, where no 3CA was identified following application at 190°C but significant amounts were present at 600°C. In this case, the store in which the lowest concentration of 3CA was found was actually the one that received the largest CIPC dose, which further emphasises the effect of temperature.

The influence of flow rate (i.e. the cooling effect of the solvent) is not so clear. However, of the three stores in which flow rate was investigated, again the store that received the highest dose of CIPC showed the least 3CA. This is also the store in which the formulation flow rate is fastest, which might suggest an effect from the solvent cooling. The relatively small differences seen here make it difficult to tell conclusively, so a repeat would be necessary.

In this work, two stores received applications under the same conditions (600°C; 0.5 litre/min) because the study was constructed as two sets of three stores. The amounts of 3-chloroaniline produced in these two stores were very similar.

Comparison with previous study: One store received an application under the same conditions as in the previous study on burner temperature and metal pipe (600°C; 0.25 litre/min). This time, significantly less 3CA was present in store after application (~2µg/l as compared with ~7µg/l). It is not clear why this is, but possible explanations include:

- Formulation effect: different batches of MSS CIPC 50M were used.
- Machine effect: Machine F this time vs. Machine A previously
- Different amounts of loss from the store, resulting in less chemical remaining in store this time.
- Variation due to day-to-day differences in conditions (e.g. ambient temperature, humidity, wind speed and direction).

Of these factors, the last two cannot be controlled, but the first two can be investigated.

Experiment 3: Effect of machine, burner temperature and pipe material:

From the first two experiments, the clearest effects on production of 3CA appear to be burner temperature and the use of a metal pipe, with formulation flow rate less influential.

As such, it was decided that in the next piece of work, two different Unifog machines would be used for applications to remove i) day-to-day variation and ii) formulation effects. We also found a potentially suitable plastic pipe so decided to revisit the catalytic effect of the metal pipe.

The three variables investigated in this trial were 1) the burner temperature 2) which particular machine was used and 3) what the pipe was made of.

All trials to date had been carried out under extremes of physical conditions (in terms of burner temperature and flow rate) and it was considered important to carry out an application under standard conditions i.e. burner 475°C and formulation flow 1 litre/minute. In this trial, the flow rate of formulation was either 1 to 0.5-litre/min. Application time was altered in accordance, in order to get a similar amount of chemical into store.

A suitable alternative pipe for experimental purposes was found after a comprehensive search. The selection criteria included non-metal construction, flexibility, resistance to temperatures exceeding 300°C and ease of fitting onto the 4” diameter fog head.

In the end, a 4-metre length of Flexi-Sil ducting (4” diameter) was ordered from Flexible Hose Supplies Ltd (Northampton). Flexi-Sil ducting is constructed from a plated spring steel wire helix covered in silicone coated glass fibre. It is also lined with silicone coating on the inside to give a smooth bore. The temperature specification of the pipe is –60°C to 300°C, which should be suitable for this experiment since the duration of application is so short (8-15 seconds) although the burner temperature range was 475-600°C.

Three sets of physical conditions were investigated, using two different foggers to make a total of six treatments as detailed below

TABLE 6: APPLICATION CONDITIONS IN TREATED STORES (SEP 04)

	Machine	Burner temperature (°C)	Pipe material	Flow rate (litre/min)	CIPC added (litre)
1	A	475	Metal	1	0.16
2	F	475	Metal	1	0.39*
3	A	600	Metal	0.5	0.12
4	F	600	Metal	0.5	0.13
5	A	600	Plastic	0.5	0.20
6	F	600	Plastic	0.5	0.12

*The counter on the fogger was not reset to zero after running the machine for a short time to set the flow rate, so we don’t know how much chemical went in

Sampling:

Samples were collected immediately post-application (on Tenax and in methanol traps), at ~18 hours and 5 days later, as in the previous experiments.

In addition to the usual samples at T₀ and 18 hours, we sampled one store more closely to get an idea of what happens in the store in between. For CIPC, we previously found elevated levels at 18 hours, so sampling continued until the end of the week (Day 4 post-application). One store that received a standard application (Store 1 with Machine A) was sampled every 5 hours for four days (96 hours). In all other stores, only one sample was collected on each of Days 1 to 4.

Results

3CA in store atmospheres (15 - 96 hours post-application)

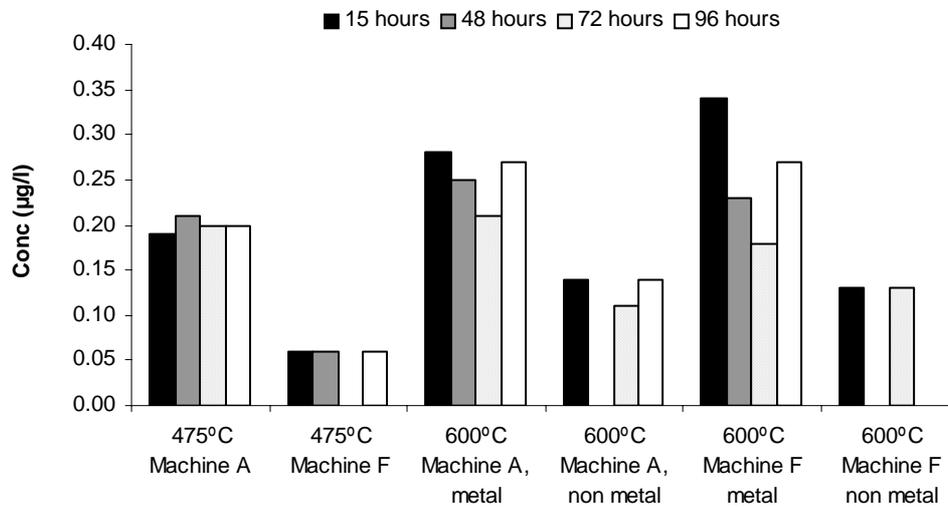


FIGURE 15: 3-CHLOROANILINE CONCENTRATIONS IN STORE ATMOSPHERES AT VARIOUS TIMES BETWEEN 15 AND 96 HOURS POST-APPLICATION

CIPC in store atmospheres (48 - 96 hours post-application)

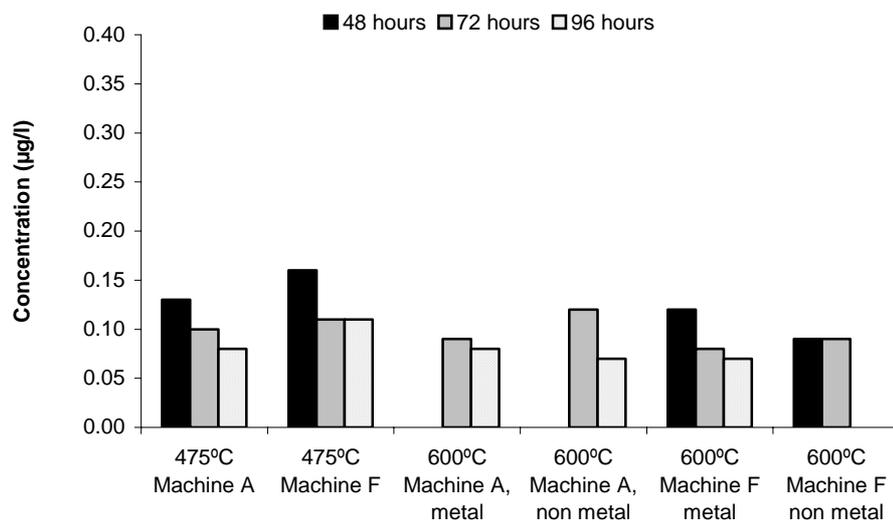


FIGURE 16: CIPC CONCENTRATIONS IN STORE ATMOSPHERES AT VARIOUS TIMES BETWEEN 15 AND 96 HOURS POST-APPLICATION

Note: In each figure, some values are missing due to problems during analysis.

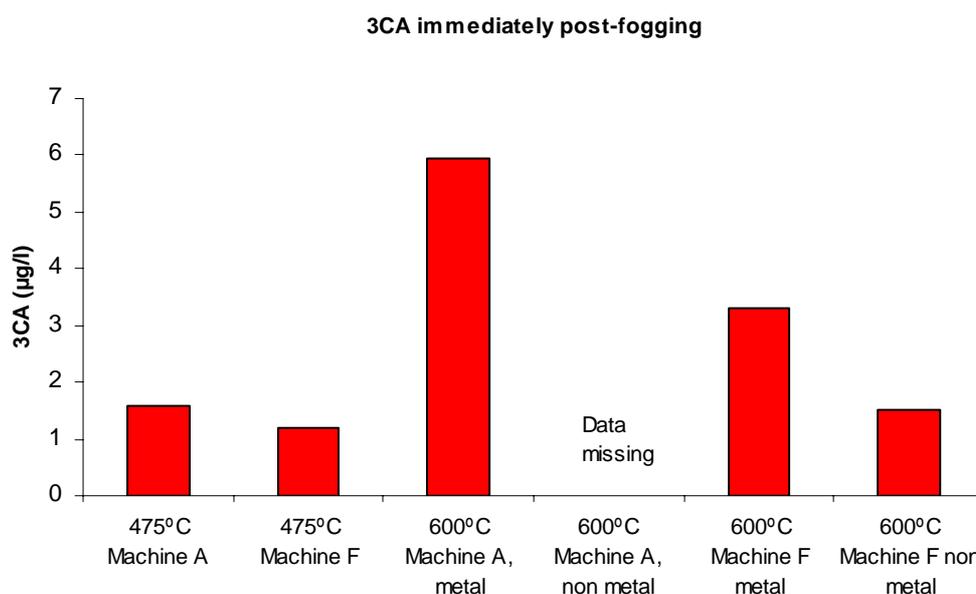


FIGURE 17: 3-CHLOROANILINE CONCENTRATIONS IN STORE ATMOSPHERES IMMEDIATELY POST-APPLICATION (SEPT 04)

Discussion of results of routine sampling:

- At 475°C, it appears Machine F produces less 3CA than Machine A. It may be that less chemical went into this store: the flow counter was not reset so we don't actually have a figure for this store. However, Machine A also produced more 3CA in Experiment 1 than Machine F did under the same running conditions in Experiment 2. Missing values make it difficult to draw any firm conclusion.
- Less 3CA was produced when plastic pipe was used instead of metal
- Less 3CA was produced at 475°C (ie under standard conditions) than at 600°C
- Levels at 600°C with plastic pipe are roughly equivalent to 475°C levels with metal pipe.
- No difference between CIPC concentrations in any store at 48 hours and any later – we can assume conditions in the store are stable by then and most likely well before. Also no significant difference between any of the stores.

Observations: The plastic pipe became a little more flexible when warm, but did not become brittle once cooled. Some blackening on the inside of the pipe suggests slight damage, but it remained functional throughout the trials. Whether it would withstand a continuous hour of application (e.g. a commercial application) remains to be seen.

An interesting next step would be to try standard burner temperature with the plastic pipe to see if it would reduce levels even more.

Rate of reduction in CIPC and 3-chloroaniline in atmosphere (intensive sampling)

Previous sections have shown that CIPC has not reduced to ‘vapour’ levels at 18 hours after application. This may mean that larger amounts of chemical are lost through venting in the early stages after application – it has been assumed that once fog can no longer be seen, the majority of chemical has settled out and only vapour remains. Values for CIPC in the atmosphere at 18 hours have been 50-80 times higher than this background level. This may present a problem in environmental terms, and may also impact on the efficacy of treatment if significant amounts of active ingredient are lost. It may also help us construct a mass balance for CIPC, since a large proportion of the chemical added to a store is often unaccounted for.

One of the stores that received a standard application (475°C burner with a metal pipe and flow rate 1 litre/minute) was sampled every 5 hours over the study period of 96 hours to investigate at what point the fog has fully settled.

Results:

CIPC headspace in Store 1 (Machine A, 475°C, metal pipe)

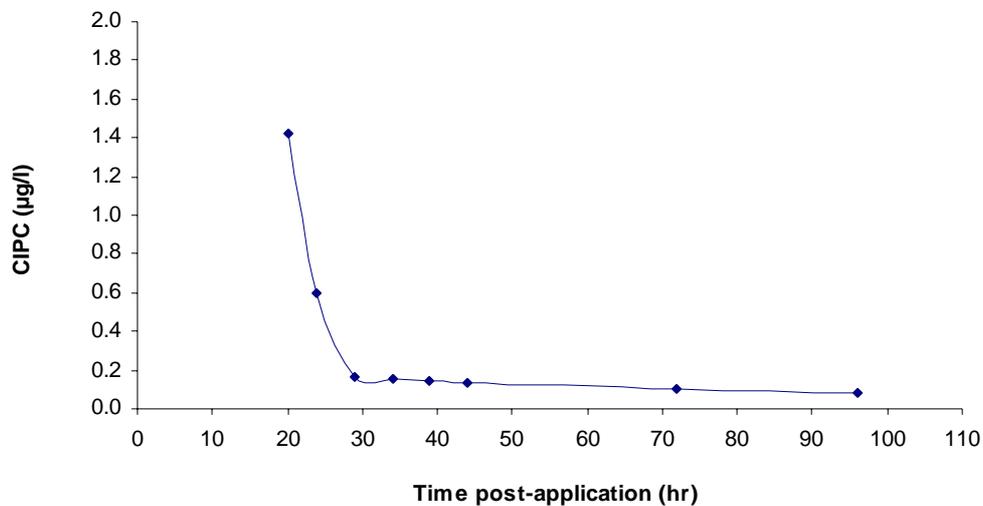


FIGURE 18: DECLINE IN CIPC CONCENTRATION WITH TIME (MACHINE A, STANDARD OPERATING CONDITIONS)

3CA concentration in Store 1 (Machine A, 475°C, metal pipe)

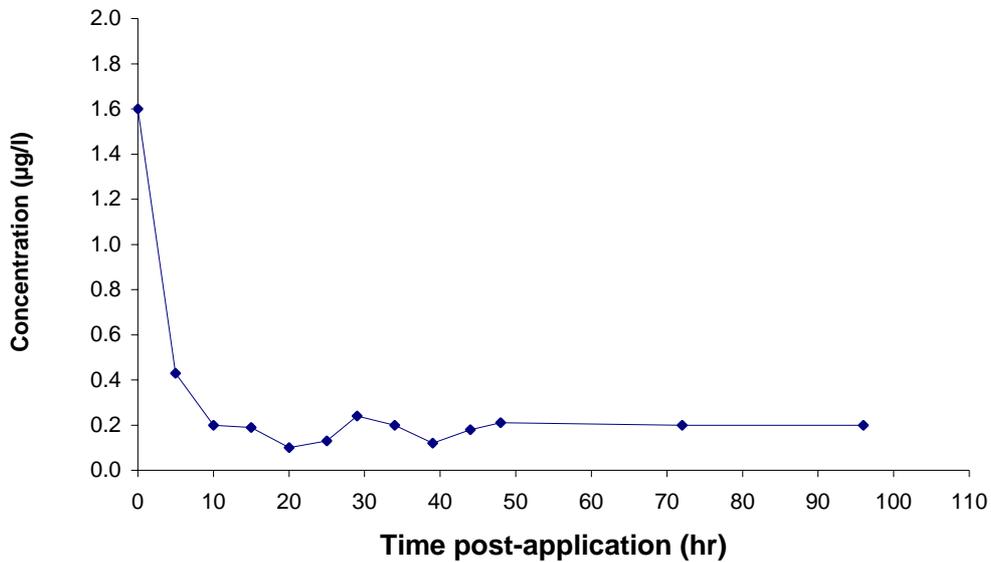


FIGURE 19: DECLINE IN 3-CHLOROANILINE CONCENTRATION WITH TIME (MACHINE A, STANDARD OPERATING CONDITIONS)

Discussion:

CIPC: It was difficult to quantify CIPC in the early hours post-application because there was too much CIPC to be accurately measured under the usual conditions of analysis. In future, reducing the sample volume (by reducing sampling time) would solve this problem. As a result, only values from 15 hours and later are included on the graph. Because the concentration varies by orders of magnitude as the fog particles settle out, it wouldn't be possible to show all values on the same graph anyway.

By ~30 hours post-application, levels are down to what we would consider to be vapour.

3CA: There is not the same large-scale variation in 3CA values, so all data from T_0 can be shown on the same graph – this is probably because 3CA is a vapour and will not undergo settlement in the same way as CIPC. Levels stabilise more quickly, although it is subject to small-scale fluctuations once down at 'normal' levels.

Washing water studies

4.1 Sampling of effluent from commercial washing operations

At the beginning of the study, a small survey was made of different commercial washing operations to determine the likely concentration of CIPC in effluent at various stages. This part of the work took in a variety of situations, from washing at a processing plant to examining water used to fill a hydro-cooler in a situation where untreated crop had been found to contain CIPC residues.

4.1.1 Pre-pack washing plant

Samples were collected on two occasions in the morning and evening from a pre-pack potato washing line. This study was carried out twice, in April and June 2003, when CIPC treated crop was running through the washer

Results:

TABLE 7: CIPC IN WASHING WATER AT PRE-PACK PLANT (TREATED CROP)

Sample	Tonnage washed	CIPC (ppm)
April, washer barrel, morning	12 tonnes*	5.35
April, washer barrel, evening	46 tonnes	9.20
June, washer barrel, morning	0 tonnes	0.33
June, washer barrel, evening	-	3.60

April: Initially, we were told that 12 tonnes had run through the washer before the first sample was taken. The CIPC level seemed too high for such a small amount of crop, and it later transpired that the washer had been filled and used for the night shift the day before. We therefore do not know the exact tonnage through at that point. All we do know is by the end of the day, 46 tonnes in total had been washed since the water was last replaced.

June: This time, the morning sample was collected before any crop was washed, and represents a background level of contamination in the washer, which may result from small amounts of contaminated soil left at the bottom of the barrel. In contrast, we do not know the total tonnage washed by the end of the day, but given the lower concentration it might be reasonable to suggest the total tonnage was less than in April, since most crop will have been removed from store by this point.

Samples were collected from various points in the effluent treatment process at a potato processing plant.

4.1.2 Hydrocooler at pre-pack plant

These samples were collected on a site where untreated potatoes have been found to contain CIPC residues after the washing process. It is possible that the use of recycled water to fill the washer and/or hydrocooler instead of mains water might be responsible (standard practice on site is to use mains water, so this would have been

an oversight if it happened). This work was carried out in July 2003, when new potatoes that had not been stored were being washed.

TABLE 8: CIPC IN WATER SAMPLES FROM DIFFERENT LOCATIONS AT PRE-PACK PLANT (UNTREATED CROP)

Location of sample	Tonnage washed	Treatment before reaching sampling point	CIPC concentration (ppm)
Recycled water outlet	-	Settlement of solids and carbon filtration	trace
Washer barrel	70	“	0.03
Hydrocooler	70	“	trace

Trace: a small response was found for CIPC (<0.01 mg/l)

The washer barrel is filled using the recycled supply, so to find a higher concentration in the barrel suggests that the washer itself contains residual contamination, perhaps in a small amount of soil material at the bottom. The low levels in the recycled water shows that settlement and carbon filtration has been effective at reducing CIPC residues to an acceptable level.

4.1.3 Mobile washer:

In contrast with the previous work that was carried out at large-scale plants, this study was carried out at a much smaller operation where crop removed from store was washed in a mobile washer. In such situations, effluent may be released into watercourses with only remedial or no treatment at all. It is therefore important to know the amounts of CIPC present at various points in the process. The study was carried out towards in June 2004, by which time the crop being washed had received several applications of CIPC, which accounts for the high concentrations in the washing water.

TABLE 9: CIPC CONCENTRATIONS IN WATER FROM MOBILE WASHER (TREATED CROP)

Location of sample	Tonnage washed	CIPC concentration (ppm)
Stone trap	0	2.32
Stone trap	250	4.48
Overflow tank	250	5.56
Spray bar (no flocculant)	84	5.04
Spray bar (with flocculant)	210	5.48
Spray bar (with flocculant)	250	9.48

All crop to be washed passes through the stone trap before reaching the barrel, along with any associated soil and stones. The spray bar rinses potatoes as they leave. The

overflow tank collects excess from the barrel, which builds up as a result of the addition of rinsing water throughout the day.

Chemical residues in the washing solution build up as more crop is washed. However, the addition of a flocculant part of the way through the day helps keep levels down, as demonstrated by the fact that the concentration after 210 tonnes and the addition of a flocculant is not significantly higher than after 84 tonnes and no flocculant.

Summary and conclusions:

Significant contamination of washing water can occur through the washing of CIPC treated crop. The levels in the liquid part of the effluent are likely to reach ~10 mg/litre during normal operation, but will depend on the throughput of crop. There may also be seasonal variation, relating to the number of treatments the crop has received. Washing effluent will require treatment to reach the EQS of 10µg/litre, although discharge consents granted by the Environment Agency are likely to take into account dilution factors.

Most of the CIPC removed during crop washing is likely to remain with the solid fraction of the effluent since CIPC is not very water-soluble and has a strong affinity for organic matter. Thus, effective settlement or removal of suspended solids can go a long way to reducing chemical residues. However, contaminated solids left in the bottom of the washer after the water is replaced can be a source of contamination for the fresh water added.

4.2 Breakdown of CIPC residues in soils following application of effluent to set-aside land

A small study was conducted in collaboration with a potato grower to investigate the levels of CIPC in effluent from a mobile washer following on-farm washing of potatoes. Effluent was then applied to set-aside land, with a view to following the decline in residues as the chemical migrated through the profile or was broken down.

Two fields were selected that had been set aside for the last couple of years. The influence of soil type and conditions was included in the study by selecting two sites with quite different properties:

- Field 1: Sandy and flat. Surface cover is grassy, and there are no nearby watercourses.
- Field 2: Heavy clay soil, with a slight slope (test plots located at the bottom). There is a small stream crossing the yard of the farm, and a water quality testing station nearby. Little surface cover.

The growers have been advised by the Environment Agency that liquid effluent can be spread on the set-aside land at a rate of up to 30m³ per hectare. This is on the understanding that effluent is not spread close to a watercourse. Sediment from the washer is collected in a skip and may also be spread back onto land, subject to the same restrictions as the liquid effluent.

Treatments: The plan was to apply doses of effluent regularly throughout the season, and follow the build up or decline of chemical in the soil. All treatments were replicated on the sandy and clay soils. Three plots, 5 metres by 5 metres, were staked out side by side in each field, allowing for three different treatments:

1. Plot 1 to receive one application of washing effluent in December 2003, at the full dose rate allowed by the Environment Agency ($30\text{m}^3/\text{ha}$)
2. Plot 2 to remain untreated until later in the season.
3. Plot 3 to receive regular applications at rates higher than recommended by the Environment Agency

The application rates and timings were decided by the grower, in agreement with Glasgow University and SBEU. Effluent spreading was done by personnel on foot using a watering can.

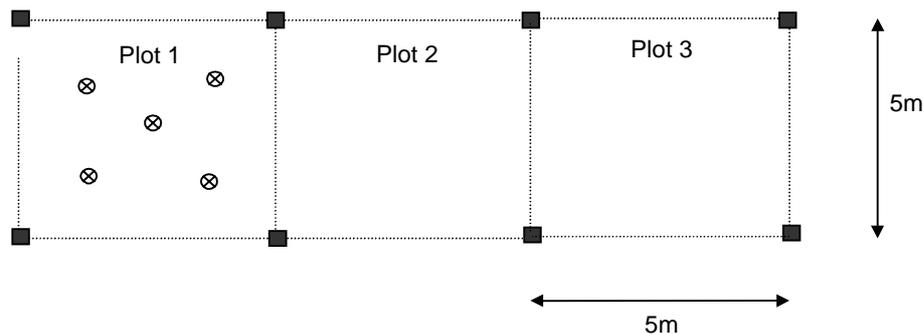


FIGURE 20: PLOT LAYOUT AND DIMENSIONS, AND MODEL SAMPLING PATTERN

Soil sampling: Samples of soil were collected from the surface of the plots. Profiles were not sampled to exact depths to investigate chemical migration in this initial part of the study. Approximately one bucket full of soil was collected from each plot using a spade. This was then sub-sampled, and a full sample bag was sent to Glasgow for analysis. The rest was then returned to the plot.

The sampling pattern was as shown above, and was selected to ensure that a representative sample of the plot is taken. The sides of the plot were avoided when collecting samples. This 'dice' pattern is also used when sampling plots for potato cyst nematode.

Control samples were taken from each plot on 2nd December 2003 before the first application of effluent was made. No CIPC contamination was found in any of them.

The sampling schedule for the rest of the study was as follows:

Plot 1: Within 3 days of the application being made; ~2 weeks post-application; ~8 weeks post-application

Plot 3: Within 3 days of application; then on the day of all subsequent applications (~monthly intervals) before the effluent application is made.

The timing of later samples remained subject to change, depending on the results obtained as the study progressed.

Washer sampling: The washer has a capacity of approximately 1,800 gallons (~8,100 litres) and can wash up to 1,400 tonnes of crop per day. The water in the barrel is usually replaced every second day, but the frequency of change can depend on crop condition i.e. if the water gets dirty but crop condition is good, only half the volume might be replaced at a time to reduce the suspended solid load but conserve water. Water is recycled in the system and only a small volume of additional fresh water is supplied during the day, via jets that rinse crop as it leaves the washer.

In our study, the effluent was sampled directly from the barrel at the end of the day. Two-litre volumes were sent to Glasgow in plastic bottles for analysis. It was also possible for samples of sediment and crop (before and after washing) to be analysed as agreed with all parties.

Results:

No detectable residues were found in any of the soil samples from the surface of plots.

Concentrations of CIPC in the washing water samples were higher than many previous samples at 50-60 mg/l.

Sediment sampled from the bottom of the washer contained approximately 80mg CIPC per kg.

Discussion:

Soil residues in the field: Although no detectable residues were found in the samples of soil following sample preparation and analysis in the lab, a visual assay suggests that CIPC did remain in the soil profile for a while. Bald patches appeared in the field as the trial progressed, as shown in the photograph below.



FIGURE 21: PHOTOGRAPH SHOWING THE HEAVY SOIL SITE (31ST MARCH 2004) 11 WEEKS AFTER A SINGLE APPLICATION OF CIPC CONTAMINATED EFFLUENT

The white fibreglass poles used to mark out the 5m by 5m plots can be clearly seen in the photo. Where CIPC was applied, plant cover did not grow. In particular, volunteer cereals were absent. The effect was greater the more CIPC was applied. The plot on the left of the photo received a single application of 60m³/ha, the middle plot got none, and the right hand plot received 30m³/ha.

This effect suggests that CIPC interfered with the germination of seeds, but not in the growth of the shoots, since to begin with there was little or no vegetation cover on this site. In contrast, this effect was not seen on the sandy soil, which had perennial grassy cover (i.e. germination had already occurred) when the trial began.

Environmental conditions may also affect the residence time of CIPC in the soil. In January 2004, there was a lot rain for a number of days both before and after the application was made. In the light soil, good drainage and a large volume of water could encourage the chemical to migrate down through the profile. If the heavy soil was waterlogged when the effluent was added, it may have run off down the slope rather than penetrating into the soil.

Washer effluent residues: Soil from the bottom of the washer contained significant amounts of CIPC. The 'liquid' part of the effluent also appears to contain a lot more CIPC than seen in previous water samples. However, this effect may be related to problems encountered during sample preparation. Suspended solid material is usually removed from the samples before chemical extraction, via a combination of centrifugation and filtration. In this case, the samples still appeared cloudy after both processes, and it proved difficult to pass the solution through the C18 extraction cartridge. This suggests that some very fine material still remained, and that CIPC associated with these particles is included in the result. CIPC is not particularly water soluble, and it seems unlikely that concentrations this high could be achieved purely in the aqueous phase.

Practicalities: Two applications of effluent were made during the season 2003-4. There was a long break between the first effluent application and the collection of the post-application soil sample, so the chemical could have broken down or migrated through the profile by this time. After the second application, only a few days elapsed between application and sampling (followed by a few days sample preparation in the lab) but still no residues were detected. This is now believed to be because only a small proportion of the plot surface was sampled, which was then 'diluted' by the inclusion of sub-surface material in the analysis. The amount of chemical present in the extracted was just too small to quantify. In future, sampling will concentrate on the top 2-3cm of the plot only, and a much larger proportion of the surface will be sampled and available for analysis. The surface area of the plot will also be much reduced to make sampling more practical and less time consuming.

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Research Report

Review and development of the CIPC application process and evaluation of environmental issues

Part 2

**Work undertaken between September 2004 and November
2005**

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Summary of work undertaken between September 2004 and November 2005

Crop contamination: A repeat of a study conducted in Year 1 investigated passive uptake of CIPC from a contaminated atmosphere onto untreated potatoes. Crop residues increased during 35 days of storage in a CIPC-contaminated atmosphere. CIPC-laden air was not actively moved through the crop, so only potatoes at the surface were contaminated.

Methods for reducing residues on the crop post-application: The amount of chemical on edible produce is an area of concern for the consumer, so small studies investigated methods by which the chemical could be removed from the potato at the end of storage. The addition of various compounds to washing solutions, and allowing the crop to 'air' for a period of time in a CIPC-free environment were both successful in reducing the measured concentration on the potato.

Application through multiple ports: An attempt was made to alter the movement of chemical during application by splitting the dose and applying it through two application ports at different points in the store. The aim was to reduce the tendency for fog to accumulate at particular locations in the store, and encourage movement of the chemical around the store. Potatoes were sampled 24 days post-application and analysed (unwashed) for CIPC deposit levels. Access to the crop was restricted by the layout of the boxes, but potatoes were sampled from both top and bottom of the 4-high stacks where possible.

Thermal degradation of CIPC and mass balance: following on from Year 1, in which several factors were identified as having a significant effect on the breakdown of CIPC during application, further trials were conducted under conditions more similar to commercial practice. Lowering the fogger burner temperature and using a plastic pipe to carry fog into store both had beneficial effects.

Washing water: Samples of washing effluent were collected from a number of washing operations, some at permanent installations, and some using on-farm mobile washers. The amount of CIPC (and one of its metabolites, 3-chloroaniline) in the water was quantified, and assessed relative to EQS and discharge consent levels.

CIPC in commercial store atmospheres Three stores were followed during season 2004-5 to investigate changes in the amount of CIPC in the store atmosphere. Both processing and pre-pack stores were selected because differences in their management are likely to affect the retention or release of CIPC. In addition to routine sampling throughout the season, store air was also sampled in the hours following application to determine how quickly the fog settles and store conditions return to normal.

Decontamination of store fabric: Isolating which materials in the store are most responsible for releasing CIPC into the air will provide information on how to reduce airborne chemical levels. A combination of the uptake vs release characteristics of the material must be considered. For example, a material like PU insulating foam will take up significant amounts of chemical (e.g. previously used as a trap for pesticide vapour in field studies) but will not release it easily (requires high temperature thermal desorption). This type of material, although it may be more contaminated, may be a lesser concern than something like concrete that does not 'hold on to' the chemical and will release it freely. Two types of approaches to decontamination can be adopted: 1) Destruction of residues (i.e. chemical treatment of fabric to destroy the

CIPC molecule) 2) Preventing the re-distribution into the atmosphere by ‘sealing in’ the chemical (i.e. removing the pathway of exposure – ie contamination source remains, but pathway by which it can reach the crop is blocked).

Summary of conclusions

Breakdown of the CIPC molecule occurs during thermal fogging by a) direct thermal degradation of the molecule and b) the catalytic effect of a metal pipe. Under exaggerated conditions (burner temperature c.600°C), 1-2% of the applied chemical is lost in this way. 3CA production by thermal degradation can be minimised to almost nil by operating at the lowest possible burner temperature (determined by the quality of fog produced). Replacing the metal ducting pipe with plastic reduces the catalytic breakdown, which occurs on contact with hot metal surfaces. Figures for the amount of chemical broken down in this way take no account of losses through leakage – the amount of chemical displaced from the store during application is estimated to be 20-40%.

Applying through more than one port appears to increase the efficiency of deposition since deposit levels are generally higher, although it did not, in this instance, improve the distribution. A number of factors control the behaviour and movement of fogs (e.g. temperature, headspace volume, store layout), and there is no clear explanation for observed differences between the ‘conventional’ and ‘multiport’ stores, which were as similar as possible. The high values in the multiport store occurred at the warmest points in the store, but this pattern was not seen in the conventional store. Although improvements may occur, the use of more than one port cannot address the major problem in box stores, that is, the tendency for chemical to accumulate at the top of the store in a way that restricting access to store headspace (e.g. by using an artificial plenum) might.

CIPC and/or its metabolites are present in washing water effluents. This year, we saw evidence that biological breakdown can reduce CIPC to trace levels in a few days. However, this ‘treatment’ will not affect other quality parameters (e.g. BOD and suspended solids), which are also regulated in discharge consents.

Washing CIPC treated potatoes in solutions other than water alone can help reduce crop residues – improved solubility (e.g. in methanol) and surfactant type action help transfer the chemical into the aqueous phase. The washing solution would still require treatment prior to discharge, but this may be preferable to high levels of chemical in edible produce. Although the principle of better removal of chemical through additions to the washing solution has been illustrated, more work would be required to find something that is commercially viable and acceptable for produce: using alcohol solutions is not a practicable suggestion. If treated potatoes are left to air in a CIPC-free atmosphere, crop residues were shown to decrease by c.80% after a period of around 12 weeks.

Sampling of air in commercial stores showed that fog settles within c.7 hours after application. Routine sampling throughout the season showed a reduction in vapour CIPC levels in-between applications, particularly in higher temperature stores that are regularly vented. When stores are empty and at ambient temperature over the summer, the higher concentration of chemical suggests release from contaminated fabrics.

Work carried out in experimental stores at Sutton Bridge Experimental Unit did not identify the main fabric responsible for supplying chemical to the atmosphere. Covering the floor with plastic, and washing and scrubbing the accessible surfaces in the store did not reduce the amount of chemical in the air. It may be that the entire building (stores are located within a larger hangar) is contaminated, and flushing the store with hangar air does not remove CIPC from the store to begin with (i.e. there is as much CIPC in the purging air as inside the store itself). Surfaces that are inaccessible in terms of cleaning may harbour CIPC (e.g. inside/behind the plenum and duct work). Use of ozone generators, in store, may help destroy the molecule in the air, but although considered promising, this approach could not be tested due to time constraints.

Experimental Section

Analysis

This section details the conditions under which samples collected in the reported studies were prepared and analysed

Tuber samples

Because of the low levels of CIPC expected in most cases, only the peel from each tuber was analysed (rather than a sub-sample of the whole tuber as in MRL protocol).

Peel was diced and weighed, then Soxhlet extracted with hexane for 2 hours following the method of Khan (1999).

GC conditions were as follows:

Temperatures:		Gas flow rates:	
Oven	180°C	Nitrogen carrier	30ml/minute
Injector	220°C	Flame hydrogen	30ml/minute
Detector	250°C	Flame air	180ml/minute

Under these conditions CIPC has a retention time on the column of ~3 minutes.

Air samples collected on Tenax

Air samples were collected onto Tenax resin using an SKC Aircheck personal air sampling pump (model number 224-PCXR8) at flow rates of around 0.1 litre/min. Generally, a sample volume of at least 5 litres was required, although a larger volume was necessary when very low concentrations of CIPC were expected. Resin traps were analysed by thermal desorption using a modification of the method developed by Boyd (1984) onto the same GC column with the same gas flows as above. However, air samples require a different oven temperature programme to allow an effective separation of the volatiles present in the atmosphere. A programme devised in previous work is as follows:

130°C for 6 minutes
12°C per minute to 190°C
Hold for 4 minutes

Under these conditions, CIPC has a retention time of approximately 11 minutes and its metabolite 3-chloroaniline around 3 minutes.

Air samples collected in methanol traps

Air samples collected in methanol were analysed by gas chromatography on a Hewlett-Packard Model HP5890, equipped with a 15m megabore column (DB1) and flame ionisation detector.

Temperatures:		Gas flow rates:	
Injector	220°C	Helium carrier	2 ml/minute
Detector	250°C	Nitrogen make-up gas	30ml/minute
Oven program	40°C for 2 minutes	Flame hydrogen	30ml/minute
	55°C/minute to 190°C	Flame air	180ml/minute
	Hold for 7 minutes		

Under these conditions, CIPC has a retention time of ~10.4 minutes

Washing water samples

250ml of the sample was centrifuged at 4,200rpm for 10 minutes, and then filtered through a GF/C filter paper to remove suspended solids. The solution was then passed through a 500mg C-18 solid phase extraction (BondElut) cartridge at a rate of ~2ml per minute. Once all the solution had been passed through, the cartridge was vacuum dried for one hour to remove residual water.

CIPC was eluted from the column in 2ml acetone, which was then analysed by either packed column or capillary GC under the conditions described above for potato and air samples.

Samples were eluted immediately where practical, but chlorpropham extracted from water onto solid-phase extraction columns have been stored for up to 7 weeks with no degradation [Liška and Bíliková 1998)].

Contamination of untreated crop held in 12-tonne stores previously treated with CIPC – Year 2

Background

This section details the repeat of a study originally carried out in July 2004 and reported in Part 1 of this report.

The aim was to investigate CIPC uptake from a contaminated atmosphere onto untreated potatoes over a five-week storage period. The previous work had shown that significant residues (in excess of 2 mg/kg in some cases) could be accumulated during this time through passive uptake from the atmosphere. This study aimed to validate those findings.

Store details

The reported trial was conducted in November 2004 in two 12-tonne experimental stores at SBEU. Each store had a history of frequent CIPC treatment and CIPC-treated boxes were used as an extra source of contamination.

Several factors believed to influence chemical uptake were investigated, including:

1. Cultivar: Three cultivars were used to examine whether differences between them (e.g. in skin type and tuber shape) influence the amount of CIPC taken up. Cultivars were Saturna, Russet Burbank (processing) and Maris Piper (ware).

2. Store temperature: The study was conducted at 4°C and 10°C to compare ‘packing’ and ‘processing’ storage conditions

3. Degree of exposure to the atmosphere: Potatoes were held as a single layer on trays (~10kg) and also in full one-tonne boxes. In Year 1 the boxes and trays were in separate stores, but in Year 2 they were in the same store. This modification was necessary to allow the results of the trial to be used in another study.

Air was not drawn deliberately through the potatoes, but was circulated within the store to maintain the desired air temperature.

Sampling

Samples of crop and store air were removed at intervals to investigate residue levels.

Air: Air samples were collected on the same day as potatoes to minimise disruption to the stores at all other times. A sample of ~10 litres was drawn through Tenax resin and analysed as previously described.

Crop: Potatoes were removed from stores at Day 1, 4, 7, 14, 28 and 35 of the storage period. Three tubers were removed from each tray on each occasion. In the boxes, three potatoes were taken from the surface of the pile (avoiding the edges) and also from a depth of ~10cm.

For Russet Burbank, potatoes were only taken from one half of the box during the trial, leaving the other half untouched. At the end of the study, potatoes from various depths were taken from the undisturbed half as the box was unloaded. This allowed

differences related to a tuber's position in the box to be investigated at the end of the 5-week storage period.

At this time, samples were taken from two locations in the undisturbed portion of the box.

- touching the side of the wooden box
- in the centre of the box, as far as possible from the sides and edges

Potatoes were also selected from five depths within the box

- at the surface
- sub-surface (~10cm depth)
- middle (midway between top and bottom of box)
- middle-bottom (midway between middle and bottom of box)
- bottom (touching the wooden base)

The position in the box will limit a potato's contact with the atmosphere or other potential sources of contamination, for example, the floor

Results:

The graph overleaf (Figure 1) show how the CIPC content of potatoes increases with time in the store held at 4°C. Values shown are the mean of three replicate analyses – error bars are not given so that the trends can be seen more clearly.

Figure 2 shows the same information for the second store, held at 10°C.

The concentration of CIPC in the store atmospheres at various stages during the 5-week storage period are shown in Figure 3 on the following page.

Finally, the effect of a potato's position in the one-tonne box on the amount of CIPC that reaches it is illustrated in Figure 4.

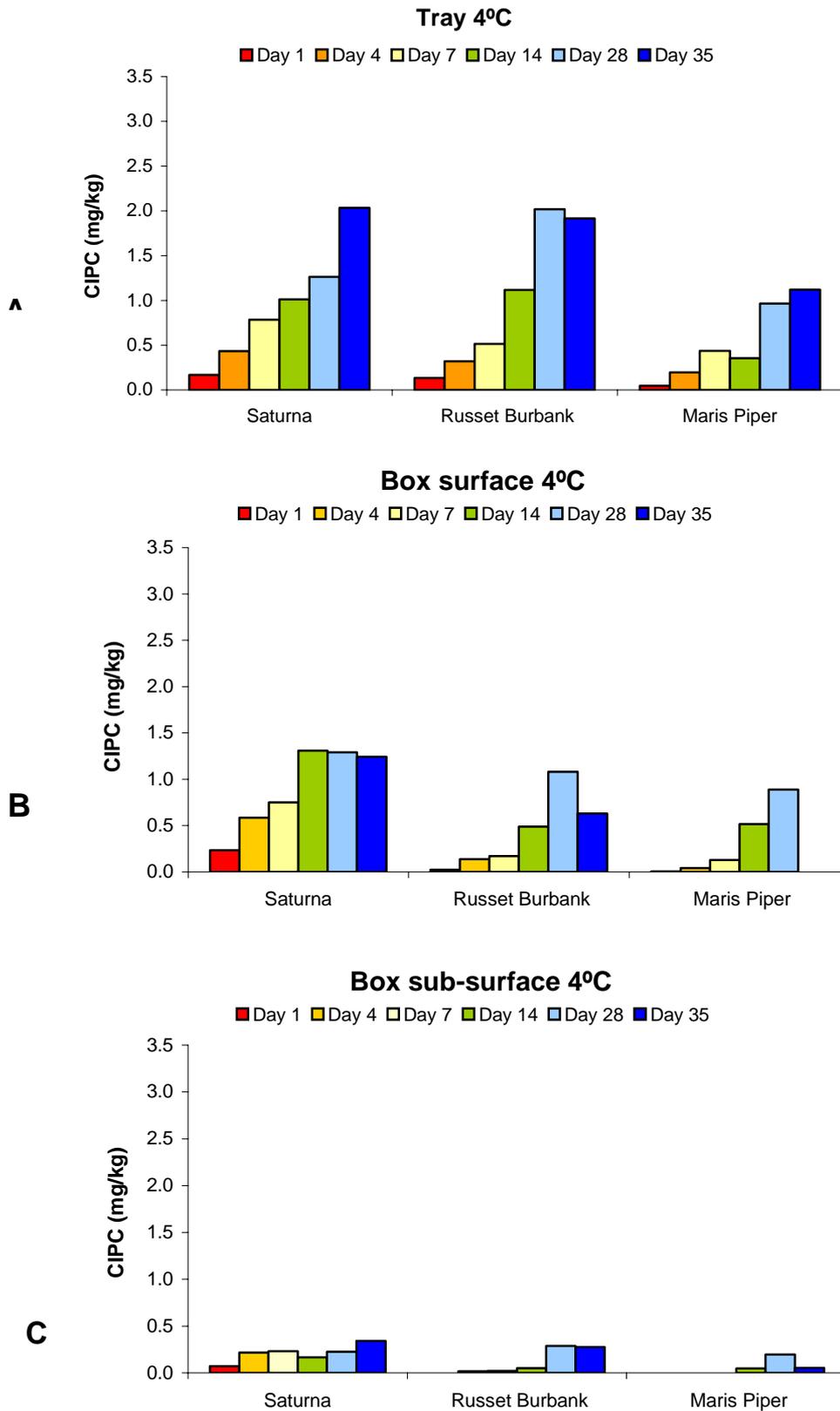


FIGURE 1 INCREASE IN TUBER RESIDUES OVER 35 DAY STORAGE PERIOD AT 4°C A) IN TRAYS B) AT THE SURFACE OF BOXES AND C) IN THE SUB-SURFACE (C.20CM DEPTH)

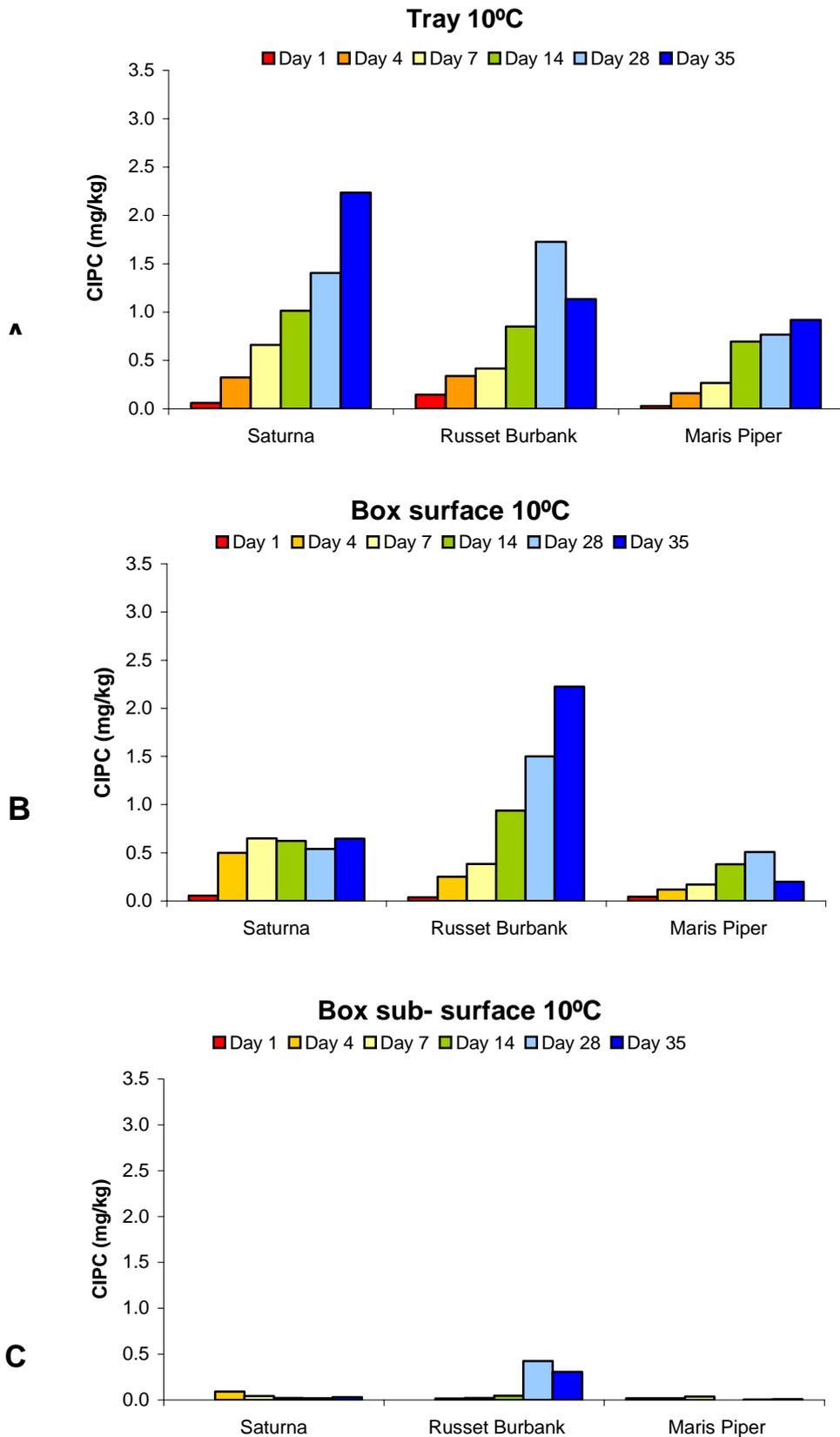


FIGURE 2 INCREASE IN TUBER RESIDUES OVER 35 DAY STORAGE PERIOD AT 10°C A) IN TRAYS B) AT THE SURFACE OF BOXES AND C) IN THE SUB-SURFACE (C.20CM DEPTH)

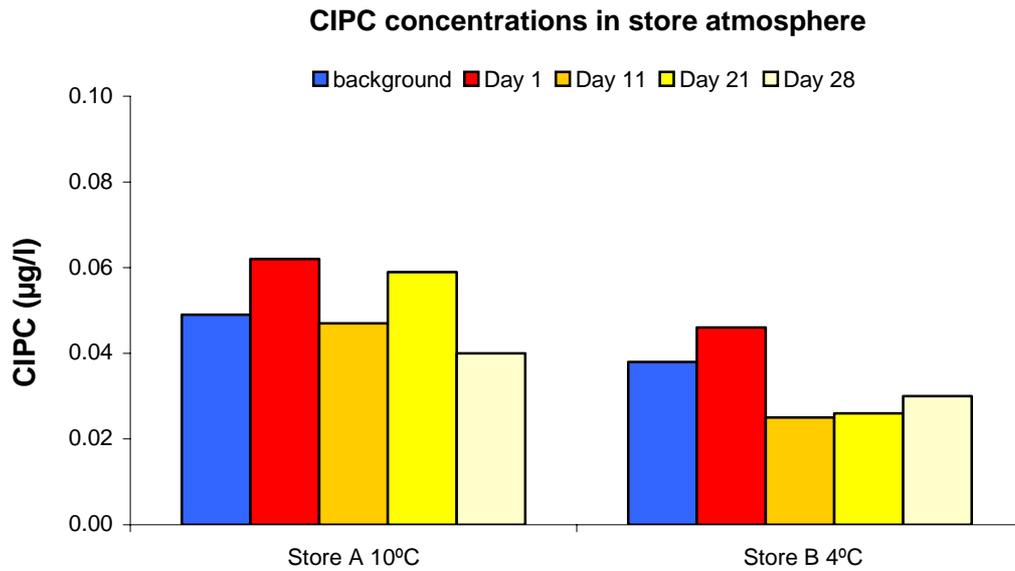


FIGURE 3 CONCENTRATIONS OF CIPC IN STORE ATMOSPHERES AT VARIOUS STAGES DURING THE 35-DAY STORAGE PERIOD.

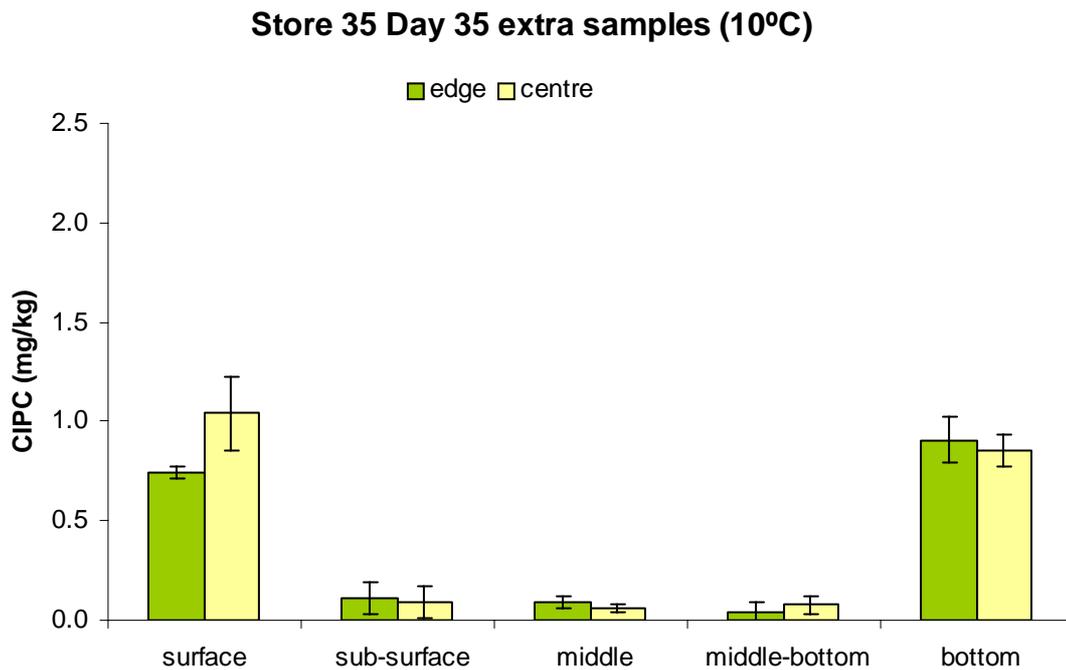


FIGURE 4 MEAN CIPC CONCENTRATION ON POTATOES FROM DIFFERENT DEPTHS IN A ONE-TONNE BOX AFTER 35 DAYS STORAGE IN A CIPC CONTAMINATED STORE

Discussion:

Air samples: The concentration in the 10°C store at the start of the trial was lower than might be expected considering previous results [Park (2004)], which resulted in there being little difference between it and the 4°C store. The reason for this is not clear, but it may be explained in part by the time of year at which this work was done, since not many applications had been made since the store was last cleaned. As the trial progressed, a difference did appear to develop between the two stores, with the 4°C store stabilising at ~0.025µg/l and the 10°C store at ~0.04µg/l. This will happen as the stores at different temperatures equilibrate to the presence of crop inside.

Crop samples:

As seen in Year 1, there was no consistent, significant difference between the cultivars when held under the same conditions. However, Russet Burbank at 10°C at the surface of the box had a much higher concentration than in Year 1 – there is no obvious explanation for this effect although annual variation in crop, chemical treatment (ethylene) and changes in skin properties at different times of year may have an effect. In general, it looks like residues built up a bit more quickly in Year 2, although Maris Piper exhibited generally lower levels than last year. This cultivar varied more in terms of tuber size distribution than the other two.

Potatoes held in trays had a higher CIPC content (on mg/kg fresh weight basis) than those at the surface of the one-tonne boxes. This effect could arise due to a combination of factors: the entire surface of the potatoes in trays is open to the contaminated atmosphere, while surface potatoes have only their top halves exposed. There may also be a ‘dilution’ effect in the box because there is a much larger surface area over which the contamination can be spread. However, this effect is not always statistically significant.

The most significant effect is the position of potatoes in the box. Virtually no CIPC was found to penetrate to ~10cm depth in a box. Since air was not directed down through the box, transfer of residues would only occur as a result of passive air movement into the box. In reality, the predominant direction of air movement will be upwards out of the box, because of the convection of warm air produced by the respiring crop, so CIPC is unlikely to penetrate to any depth.

Potatoes held at 4°C did not contain smaller residues than crop held at 10°C. This suggests that the amount of CIPC in the air at any one time is not a limiting factor governing chemical uptake.

Position in a box: Residue levels depend on the position of the tuber in the box. There is a clear gradient in both directions in the box, with levels highest at the top and bottom of the box, decreasing towards the middle. At the surface, potatoes are in direct contact with the contaminated atmosphere. Bottom potatoes are closest to the floor, which is believed to be a significant source of the chemical residue in the atmosphere – transfer of heat means that air will move through the box from bottom to top, pulling in air from below.

Conclusions:

This study has shown the residue picked up by the potato to be:

- proportional to the storage time (the longer in store, the higher the residue level)
- dependent the position of the tuber in a box (surface vs sub-surface)

but not significantly and consistently affected by

- cultivar
- air temperature

Comparison with Year 1

Given the potential for variability as a result of a number of processes, this data set is considered to be a good repeat of the results from Year 1. All the same patterns of accumulation are present, although some cultivars behaved differently in Year 2, taking up slightly more or slightly less chemical. Annual differences in the properties of the crop, related to growing conditions, make it impossible to obtain exactly the same results two seasons in a row.

Conclusions

The levels of contamination found in this trial are significant, considering the Maximum Residue Level (MRL) of 10 mg/kg, particularly because these potatoes received no direct application of CIPC. In addition, this was a relatively short storage period (5 weeks) when compared with up to 10 months in commercial stores. However, levels like these are not expected to accrue in commercial crops for the reasons described in the discussion of the previous experiment (see Part 1 of the report).

Recommendations for future work

The next stage is to direct air movement through a pile of potatoes and show how this affects the uptake of CIPC vapour onto crop. In practice, a small-scale trial was carried out with 40kg of potatoes inside a pipe in which a fan was used to draw CIPC-contaminated air from the bottom to the top of the pile. A fairly even distribution of chemical was achieved through a pile of potatoes ~1m high when contaminated air was drawn through from bottom to top at a range of airflow rates from 0.07 – 0.46 m/s (0.1-0.8m³/sec/tonne) for a 19-day period.

Methods for reducing residues on CIPC treated potatoes

Background and aims

This study investigated two approaches to reducing the levels of CIPC in fogged and vapour treated potatoes. The way in which chemical is applied may affect the wash-off rate, since particles sitting on the surface of the potato after fogging might be easily removed by washing while vapour application may result in a stronger attachment to the potato (ie chemical held within the skin).

Firstly, treated potatoes were washed in a range of solutions: the theory being that if the solubility of CIPC in the washing solution is higher than in water alone (89mg/l), more CIPC could be removed from the crop.

Secondly, the effect of airing CIPC-treated potatoes was investigated. Crop residues were determined at the beginning of a period of storage, and again 11-13 weeks later. The conditions of treatment and storage will be fully described in the relevant section.

Reducing residues through washing

A range of solutions was tested including water, dilutions of alcohol and a proprietary vegetable wash (Veggi-Wash, FoodSafe Ltd). The ingredients of the wash are all vegetable-derived and include sucrose esters, cocoyl glutamate (from coconut, sweetcorn and palm kernel oils), trisodium citrate and glycerine. The label makes the following statement: "...the surface of fresh vegetables and fruit can be contaminated with pesticides ... they do not wash away with water. The patented product will neutralise harmful chemicals and rapidly assist in the removal of toxic grime and insects." The produce is washed or soaked for two minutes in 5 litres of water to which 1-2 capfuls of solution has been added. This product claims to remove 93.4% of chlorpropham residue on potatoes, compared with 6.7% reduction on washing with water alone. No information is provided on the conditions under which this study was carried out, so this claim could not be verified.

This product acts as a surfactant, or wetting agent. There are a number of these on the market (e.g. 'Fit Fruit and Vegetable Wash', 'Environée Fruit and Vegetable Wash', 'Simply Clean Fruit and Vegetable Wash') and all work on similar principles. Claims made for what some of the products can do, compared to water alone, have not been supported by results of some other studies [eg., Krieger *et al* (2003)].

The effectiveness of some products may be explained by the presence of alcohols in their formulation that improve the solubility of chemical, in particular that which has penetrated cuticular waxes of plants. The surfactant molecules (e.g. sucrose esters) will also encourage the removal of lipid-soluble compounds, like some pesticides, which have limited water solubility.

Materials and methods:

The potatoes used in this work had been treated with CIPC vapour in another experiment (were subsequently referred to as the ‘pipe trial’) and then held in an incubator at 15°C for 28 days for the lab-scale efficacy work also discussed there.

Six tubers were washed per sample in 5 litres of washing solution. Potatoes were added to the solution in a bucket, which was shaken by hand for two minutes. After washing, tubers were removed and air-dried prior to extraction and analysis.

Potato peel was extracted in hexane, and the extracts analysed by gas chromatography.

In the first phase of this work, vapour treated potatoes were washed in water, VeggiWash (diluted as instructed on product label) and neat methanol. The unwashed values obtained at this time were compared with the concentrations found in potatoes analysed immediately after the end of the pipe trial (i.e. no 15°C storage).

Phase 1 results are shown in Figure 5 below

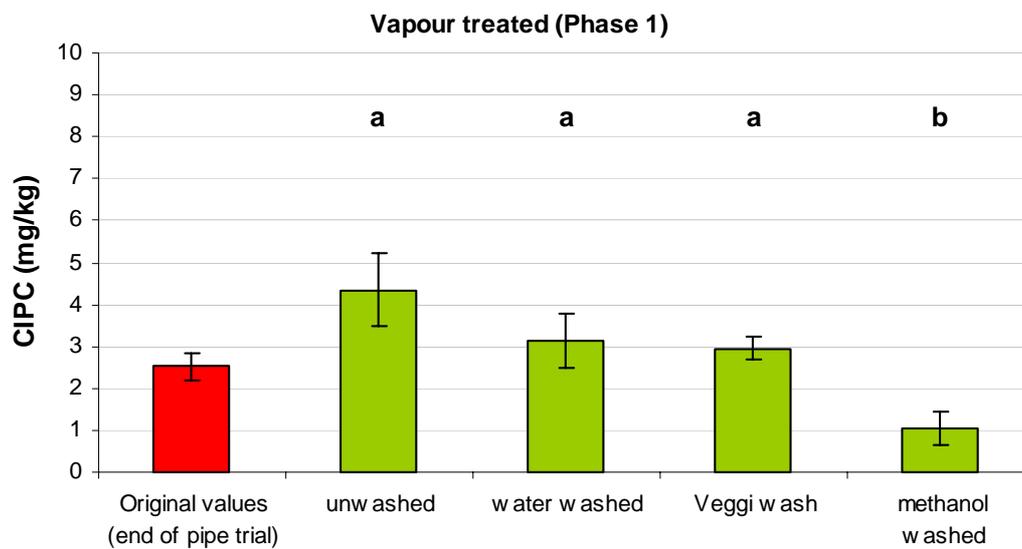


FIGURE 5 CIPC CONCENTRATIONS IN VAPOUR TREATED POTATOES WASHED IN A RANGE OF SOLUTIONS (PHASE 1)

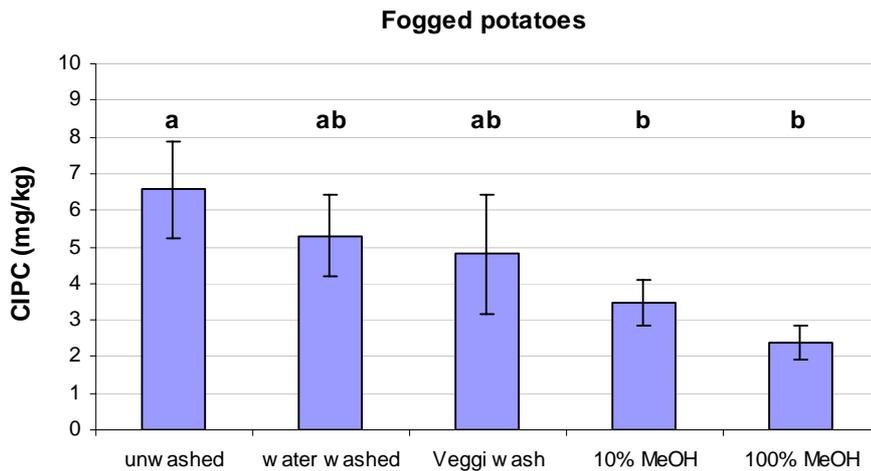


FIGURE 6 MEAN CIPC CONTENTS OF FOG TREATED POTATOES WASHED IN A RANGE OF SOLUTIONS (PHASE 2)

The first thing to note is that the concentration in the unwashed potatoes is about 70% higher after the 28 days storage than at the end of the pipe trial. This does not imply, as first appears, that more CIPC has been taken up onto the potatoes during storage. During the efficacy work the humidity in the chamber was only ~20%, so tubers lost water and shrank. The results show a relative increase in the **concentration** of CIPC expressed as ‘mg per kg of potato’ because the weight of potato has reduced.

Statistically significant differences were determined using Fisher’s LSD test. On the graphs, the different initial letters indicate statistically significant differences between treatments. It was not considered appropriate to compare the ‘original’ values to any of the treatments.

Washing in any solution decreased the mean content of CIPC in the potatoes. When washed with water, the mean reduction was 28%, although this was not a statistically significant effect due to the variability among values. VeggiWash reduced the mean residue by 33%, which is less than claimed on the cited website, and not significantly different to either water washed or unwashed values. After washing in methanol, the CIPC content of the potatoes reduced by almost 80%. Although this is a good result, it is not practical to suggest washing food crops in pure alcohols because of potential damage to the potatoes and guidelines on what treatments are acceptable for foodstuffs.

After Phase 1 was complete, a second phase of the experiment was carried out to investigate the effect of washing on potatoes that were treated with CIPC in different ways (fogged vs vapour treated) and also the effectiveness of a more dilute (10%) alcohol solution. Washing was carried out following the previous procedure.

Phase 2 results:

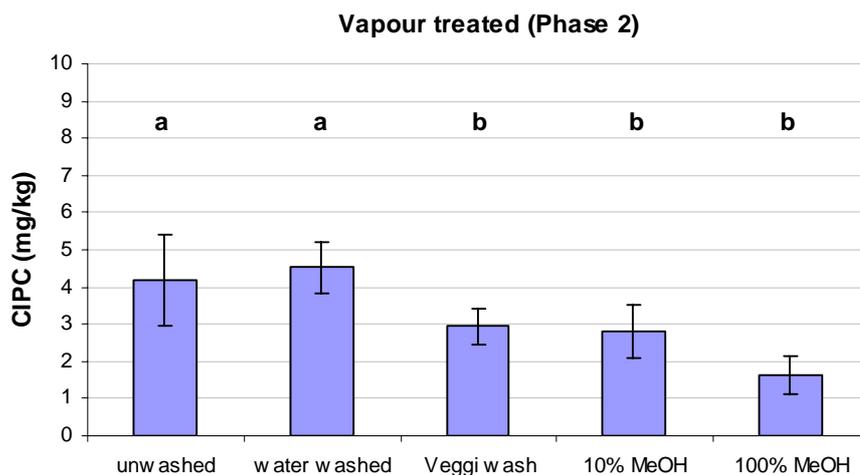


FIGURE 7 MEAN CIPC CONTENTS OF VAPOUR TREATED POTATOES WASHED IN A RANGE OF SOLUTIONS (PHASE 2)

TABLE 2 PERCENTAGE REDUCTIONS IN MEAN CIPC CONTENT AFTER WASHING IN A RANGE OF SOLUTIONS

Washing solution	% reduction in mean CIPC content after washing	
	Fogged	Vapour treated
Unwashed	-	-
Water	19	-8*
VeggiWash	27	30
10% methanol	47	33
100% methanol	64	61

Unwashed, fog treated potatoes have higher and more variable chemical levels than vapour treated, which makes significant effects more difficult to determine. The presence of particles of CIPC on the potato is responsible for both effects.

In general, CIPC levels were reduced by around 60% by washing for two minutes in 100% methanol and by around 30% when washed in VeggiWash. Both solutions performed similarly on fog and vapour treated potatoes. The dilute methanol removed more CIPC from the fog treated (~50%) than the vapour treated (~30%), but there was no significant difference between it and the VeggiWash in either case. Both treatments were better than washing in water alone.

Summary: Washing in water alone cannot be counted on to significantly reduce residue levels, but modifying water with ‘additives’ does increase ability of washing to reduce residue levels. Washing potatoes did reduce the mean residue level

* Mean concentration was 8% **higher** after washing – reflection of the degree of variability

regardless of a) the composition of the washing solution and b) whether they were fog or vapour treated, although the reductions were not always statistically significant (particularly for washing alone). Water washing removed about 20% of the chemical, and VeggiWash around 30%. In contrast, the cited website claims a wash-off rate of 6.7% and 93.4% for water and VeggiWash respectively. The addition of methanol makes the washing process more effective at removing CIPC held on or in the waxes of the skin. Adding 10% methanol removes 35-50% of the chemical, while washing in 100% methanol reduced crop levels by between 60-80%.

Part 2: Reduction of residues during storage

Crop history: Potatoes used in this trial were first vapour treated in an experimental store by exposure to contaminated atmosphere for 19 or 11 days. After this time, individual tubers from near the front and back of the pile were re-located to a CIPC-free store, where they were laid out on a wire rack. This store was maintained at 10°C and ambient RH for 11 weeks, then the temperature was increased to 15°C (as part of another trial) for a final two weeks of storage. The store was sealed for the entire storage period with no ambient ventilation i.e. fresh air was not introduced to the store, except when the doors were open for sampling.

Sprouting was also assessed in this store. There was more sprouting activity in potatoes originally at 850mm depth (“back”) than Layer 3 (“front”), which would fit with observations that residue levels were highest near the front of the pipe in most cases. In pipes where air was circulated, the sprouting index (SI) of crop was 1-2 at the bottom of the pile, and 2-3 at the top. For comparison, the commercially acceptable limit is SI = 3. Potatoes from pipes where air was not circulated had SI of 4-5 at the bottom and >12 at the top of the pile. Where there was no air movement, more sprouting occurred at the top of the pipe, where crop temperature would be higher due to upward movement of warm air produced by the respiring crop.

The number of sites of sprouting per tuber declined towards the end of the 13-week observation period. Dead sprouts (e.g. those that blackened and died back to nodes as a result of calcium deficiency) were not included in the sprouting assessment, which helps explain why sprouting did not appear to progress.

Results:

Figures 8 and 9 show the residues in potatoes exposed to vapour for 19 and 11 days respectively. Values are shown a) immediately after exposure and b) following approximately 12 weeks subsequent storage in a CIPC-free environment during an efficacy study.

Potatoes were sampled from the front and back of four pipes, each of which experienced a different speed of air movement during the initial 19-day vapour application period.

- 1) No air movement
- 2) Very low flow, air moving at ~0.03m/s
- 3) Low flow, air moving at ~0.07 m/s
- 4) Medium flow, air moving at 0.27 m/s

[Descriptions are relative to speeds from an original experiment where there was also a fast flow of 0.46 m/s].

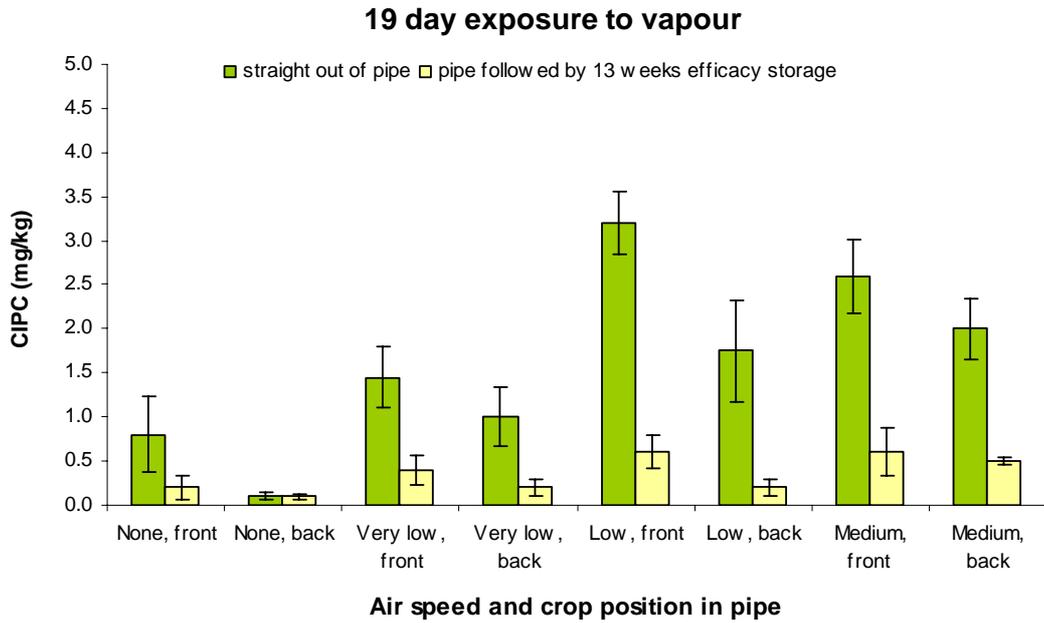


FIGURE 8 CROP RESIDUES IN POTATOES EXPOSED TO CIPC VAPOUR FOR 19 DAYS BEFORE AND AFTER 13 WEEKS EFFICACY STORAGE AT 10°C.

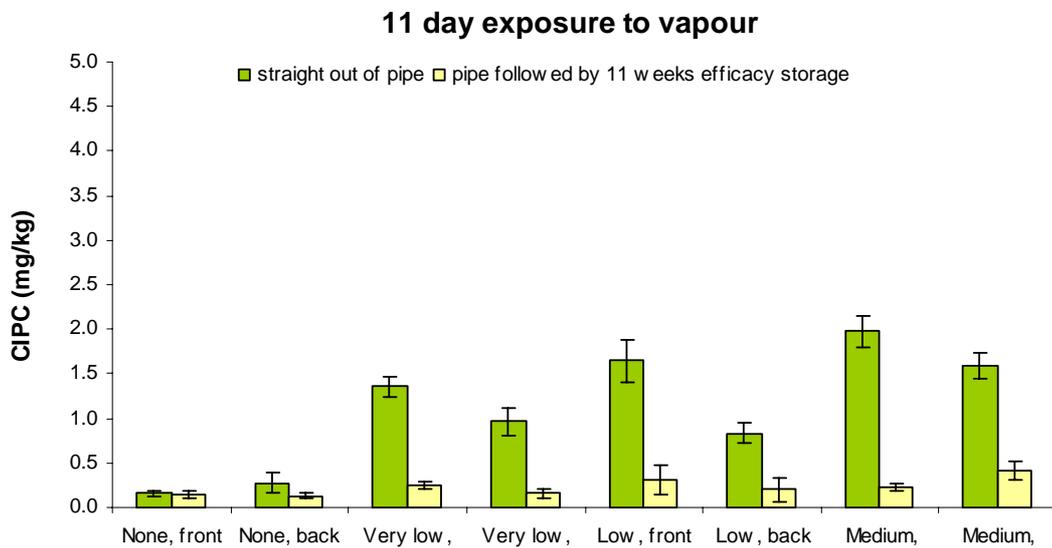


FIGURE 9 CROP RESIDUES IN POTATOES EXPOSED TO CIPC VAPOUR FOR 11 DAYS BEFORE AND AFTER 13 WEEKS EFFICACY STORAGE AT 10°C.

Descriptions of air speed are relative to speeds from an original experiment where there was also a fast flow of 0.46 m/s.

After around twelve weeks of storage, the chemical residue on the potato reduced by around 80%. This effect was consistent across all locations within a pipe; within all pipes in a particular study (except the no flow example) and regardless of whether exposure time was 11 or 19 days.

The extent of re-volatilisation of chemical applied to potatoes has been subject to debate, and a number of contradictory studies have been published in the literature. For example, Hajšlová and Davidek (1986) and Tsumura-Hasegawa *et al* (1992) attributed decreasing levels of CIPC during storage to evaporation of chemical from the surface of the potatoes. However, Coxon and Filmer (1985) cautioned that rates of evaporation might be less than expected from vapour pressure data alone. They measured vapour pressure when absorbed onto filter paper, and found it was fifteen times higher than when held on the skin of a potato. This effect was attributed to interactions between the chemical and the surface of the skin. Trace levels of CIPC metabolites have been identified in samples of treated potato [e.g. Heikes (1985), Worobey and Sun (1987)], but the very small amounts suggest that crop metabolism is a relatively insignificant cause of residue decline.

The decrease of ~80% seen in this trial after 11-13 weeks of airing could represent a positive attribute of vapour treatment. Residues are low and evenly distributed immediately after the end of the vapour treatment, and can be further reduced during storage. Volatilisation may also improve evenness of residues through redistribution. Efficacy is probably related to the residue level, so as chemical levels decline sprout control wears off. This may allow for start-stop treatment as required to i) maintain acceptable crop residue and ii) maintain sprout control. Relatively little chemical has to be added to the store per season compared with the amount applied during thermal fogging.

Changing the distribution of CIPC in a box store by applying through multiple ports.

Introduction

In box stores, following conventional fogging through a single port, there is a tendency for chemical to accumulate on top boxes of a stack and at the opposite end of the store from the application port. Conventional application produces a fast-flowing current of hot air that rises, causing fog to accumulate in certain places. The main aim of this experiment was to change the pattern of air movement, and thus fog deposition, around the store.

Boyd (1988) and Khan (1999) described the characteristic pattern of deposits in box stores. Burfoot *et al* (1996) and Xu and Burfoot (2000) used mathematical modelling to describe the movement of fog around a box store, and attributed the high levels near the top of the store to the settling out of larger particles on the surface of the potatoes.

In this trial, the application was made through two ports: the original port and a second one added at right angles at the same end of the store. The multi-port application was also pulsed since the application was split into four doses, with a 10-minute break after each while the fogger was moved into position at the other port. This pause should also help introduce turbulence to the store and break the pattern of constant addition.

Stores and treatments

A pair of box processing stores was used in this study, both containing potatoes *cv* Saturna at a holding temperature of 9°C. The stores had been loaded before they were selected for this trial, so box layout could not be modified to suit its purpose. The stores were two of a block of four, and were joined end-to-end, with only limited access to walls. Ideally, the dose would have been split into quarters and applied through four ports (one on each wall), but this wasn't practical in this case. As a result, the multi-port application was carried out through two ports in Store A with Store B acting as a 'conventional application' control.

A plan of the site showing the location of the stores relative to each other and the position of the application ports is shown below.

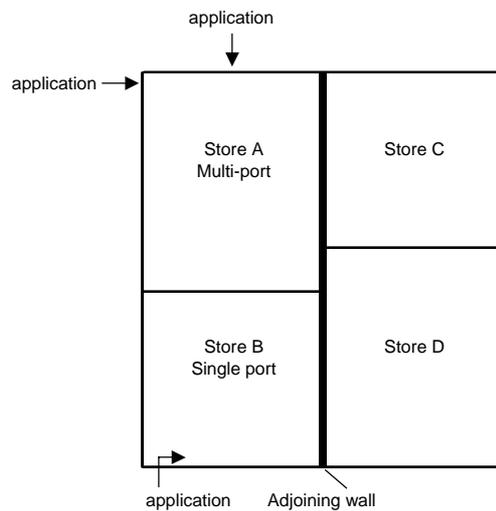


FIGURE 10 PLAN VIEW OF STORES LOCATION

Applications were carried out on 5th November 2004 using a Superfog machine and MSS CIPC 50M at a dose rate of 28ml/tonne. These were the first applications of the season, and were carried out while store temperature was ~12°C on the way to a holding temperature of 9°C.

Sampling and analysis

Timing: Samples were collected on 29th November (24 days post-application – different to previous work in Study 197, sampled at 24 hours) from both stores.

Locations: Samples were taken from the surface of top boxes (stacks were four boxes high) and also from the surface of bottom boxes although access was limited to boxes along the central corridor. Store plans and sample locations are shown overleaf in Figures 11 and 12 (not to scale).

Sample preparation and analysis: Analysis was carried out on unwashed potatoes to give the best indication of how the chemical is distributed around the store (i.e. deposit values). Three single potatoes were analysed from each location to illustrate the variability among tubers. Potatoes were extracted with hexane and analysed by GC-FID, following the method of Khan (1999) as detailed in the analysis section of this report.

Store A – Application through multiple ports ('multiport')

The total volume of 36 litres was split into four doses and applied through the two ports as follows:

- 9 litres through new port, followed by 10 minute delay
- 9.2 litres through original port, followed by 10 minute delay
- 8.8 litres through new port, followed by 10 minute delay
- 9 litres through original port

There were around 1,200 tonnes in the store at the time of application.

Samples were taken from the surface of top boxes at positions B2, B6, C13, H2, H9, H13, M2, M6, M13, T2, T9 and T13 as shown in the diagram overleaf. These positions were selected to provide coverage of the entire store while taking a realistic number of samples. Sampling positions for bottom boxes were restricted by the stacking pattern of the store, and were limited to locations adjacent to the alleyway – B6, H9, M6 and T9 to correspond to top box samples.

The position of the second port was also restricted by the stacking pattern of the store, and also the layout of the four-store complex – there was only one outer wall running the length of the store. The port was positioned at the same end as the original port to reduce the tendency for fog to accumulate at one end of the store.

Store B – single port application

A total volume of 22.5 litres was applied through the single port in the end wall, where the pipe entered through personnel door at one side (rather than larger access door). The pipe was turned to 90° inside the store because the main stack of potatoes was straight ahead. (i.e. the application was not made down a central corridor). There was not a lot of clearance room in either store, which dictated how and from where the chemical could be applied.

There were around 850 tonnes in store at the time of application.

Results

Figures 11 and 12 on the following pages show the layout of the stores, and the mean CIPC concentrations on potatoes at locations from the top and bottom of the stores.

Figure 13 shows the data in boxplot form, which also illustrates the variability among the individual tubers at each location. This allows easy visual comparison of the results from each store.

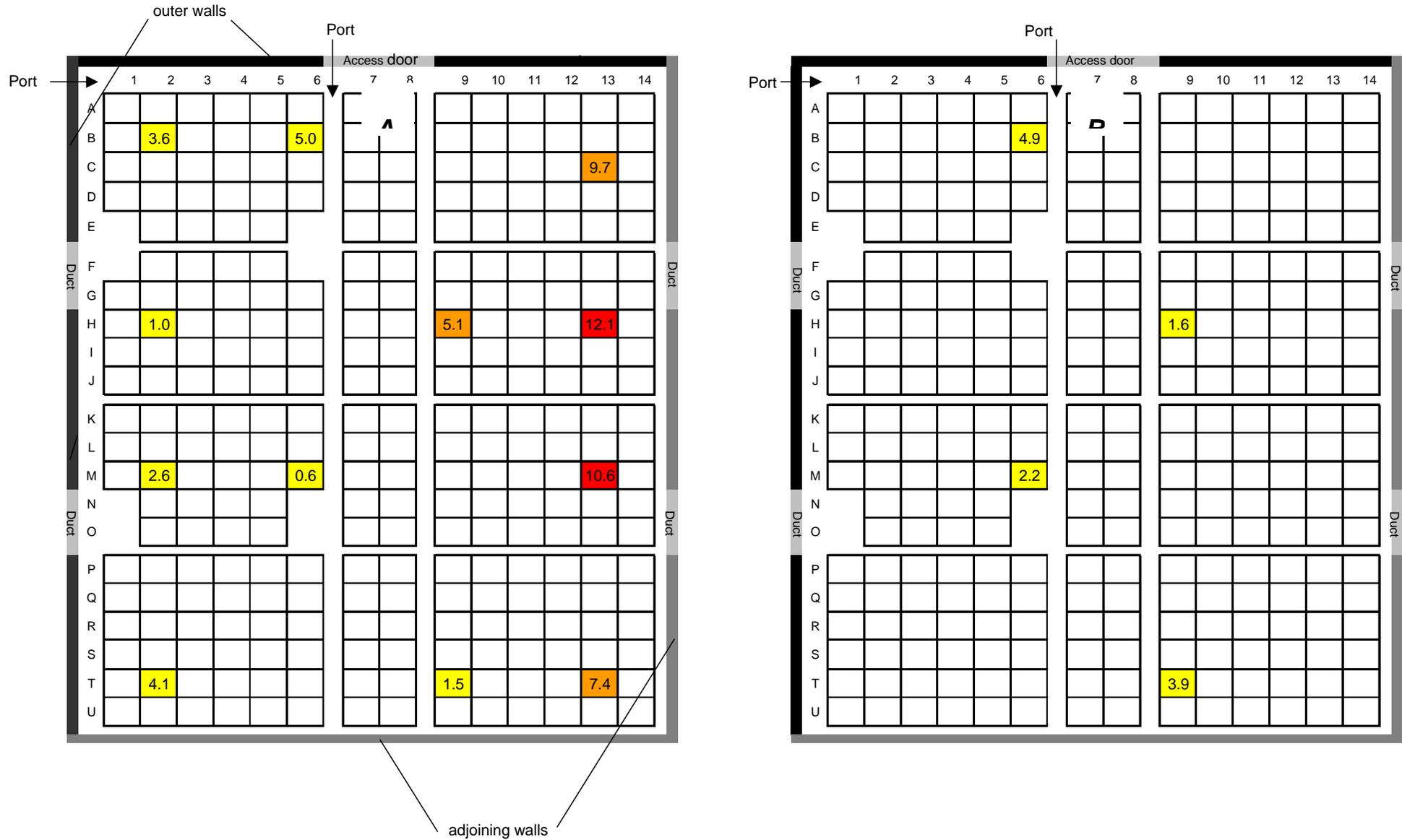
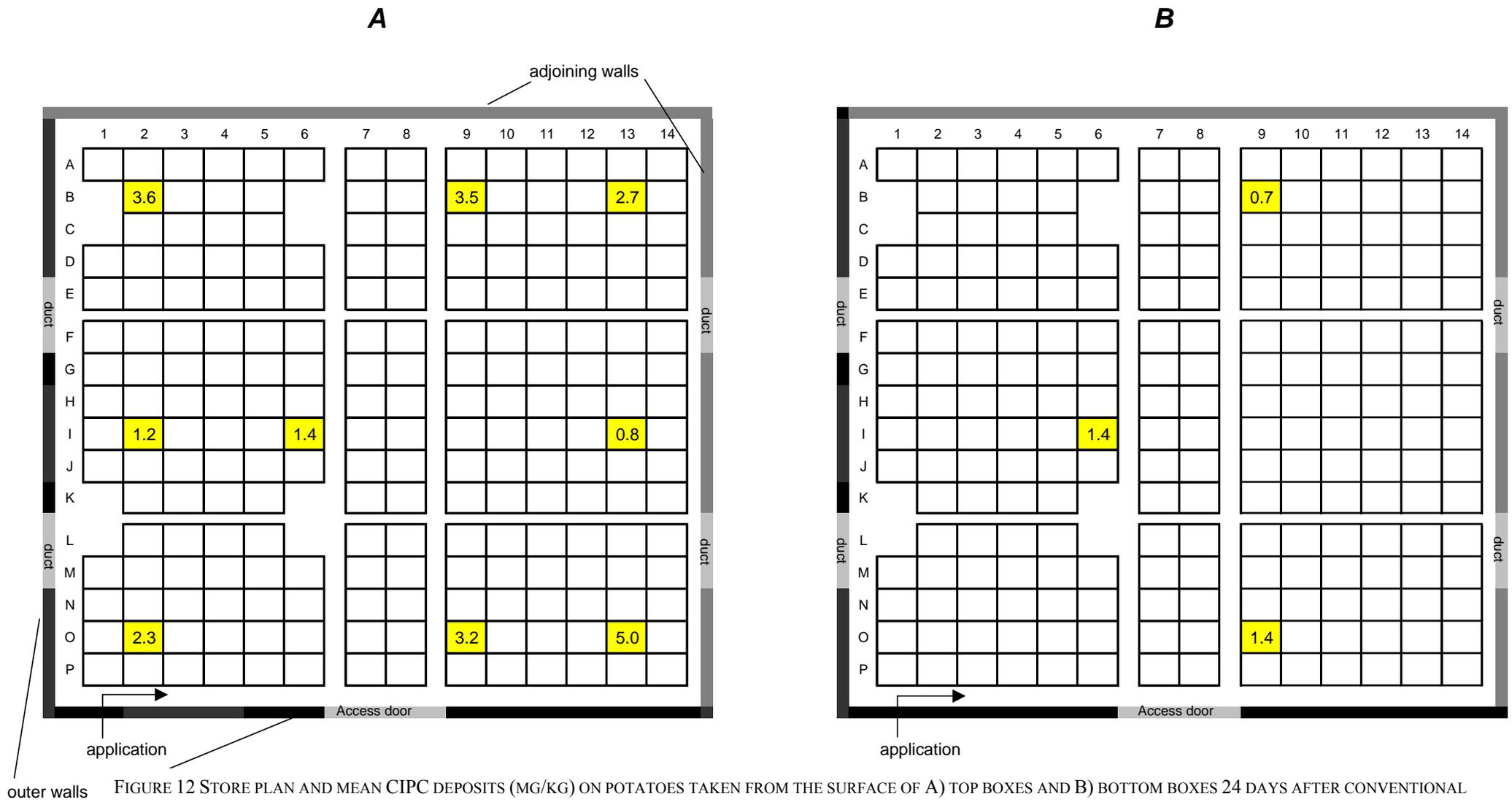


FIGURE 11 MEAN CIPC DEPOSITS (MG/KG) ON POTATOES TAKEN FROM THE SURFACE OF A) TOP BOXES AND B) BOTTOM BOXES 24 DAYS AFTER MULTI-PORT APPLICATION



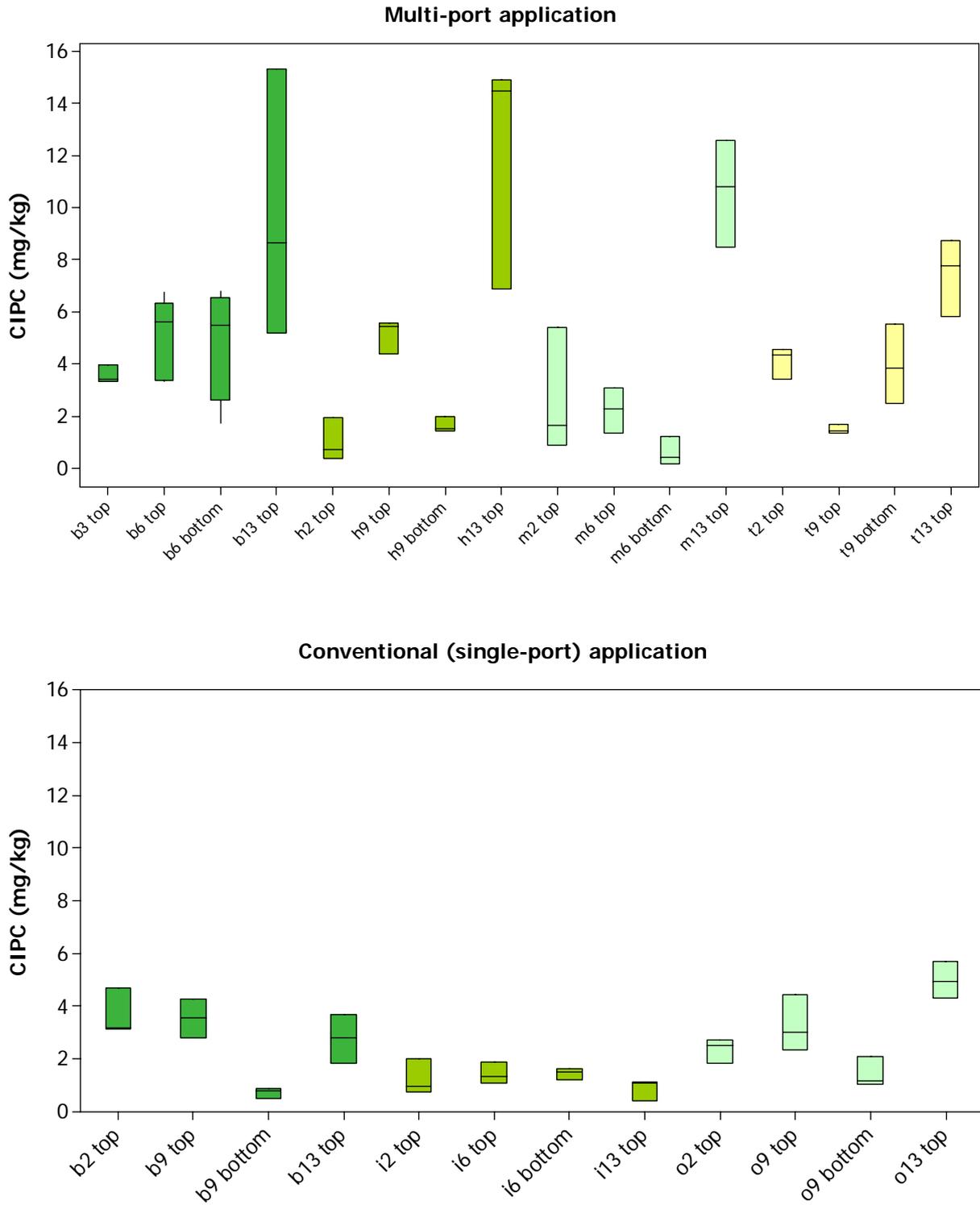


FIGURE 13 BOXPLOTS SHOWING THE VARIABILITY AMONG REPLICATES FROM A SINGLE LOCATION, AND AMONG LOCATIONS IN EACH STORE
 N.B. Graphs are on the same scale. The longer the boxes, the more variable the three results from that location.

Comments

In general terms, the results from both stores are good in the sense that values are lower than seen in previous studies, particularly on top boxes. Considering these are unwashed values, there is not likely to be any problem meeting an MRL of 10mg/kg. These samples were collected 24 days post-application, so there may have been re-distribution of residues during this time. In contrast, potatoes were sampled just 24 hours post-application in previous distribution work from (eg., BPC Project 197). Any re-distribution of residues in the 24 days since application should apply equally in both stores.

Distribution patterns were obviously different in the two stores. The stacking pattern was as similar as it could be, although the size of the stores were different, which meant there was an extra stack (6 by 6 boxes) in the larger multi-port store. The direction from which fog was introduced relative to the layout of the boxes was also different.

Overall, there is no obvious reason for the observed differences in the pattern of distribution. The control store performed surprisingly well. There may be an element of experience coming into play – conventional applications are carried out regularly and the store laid out accordingly. In contrast, boxes in the multiport store was not stacked with this application in mind, and access to walls was limited, meaning we could not get either the number or location of ports we would have liked in an ideal world. It has had an effect on how the chemical has moved around the store, although not necessarily as anticipated.

Differences between the top and bottom boxes appear less in the multi-port store. In some locations bottom box values are higher than the top. The very limited number of bottom box sites makes it difficult to be sure of any significant effect.

Because the stores were end-to-end, rather than back-to-back, any differences in ceiling height should also apply to both stores, as would any effect of wind direction. Applications were made on the same day to both stores so environmental conditions should not have any influence.

Multiporting appears to have increased application efficiency ie overall mean is higher than in conventional store, but at the expense of an even distribution which was more evident in the conventional store. The high levels in the multiport store are where we would predict them ie roughly opposite the ports. (The highest level in the conventional store is also opposite the port). In both stores though there are also samples with very low levels – which is a concern, as it will presumably trigger re-application.

Regardless of the number of ports used, hot-fogging of box stores will give rise to higher deposit values on top boxes, where fog is allowed to enter the roof-space. Multiporting is unlikely to have much more than a small influence on this, and, on our evidence, influence may be negative. Significant changes/improvements in distribution of the chemical are more likely where applied fog is prevented from entering the roofspace and reducing the sedimentation component of residue levels.

Conclusion

There was evidence of a **difference** in the way chemical moved around the store, although this difference was not an **improvement** in terms of even distribution. It is important to bear in mind that this was only a single study in a single store and was not carried out under ideal conditions because of restrictions caused by the physical layout of the stores.

Investigation of CIPC breakdown during thermal fogging – Year 2

Background

In previously reported studies [e.g. Park (2004)], a second compound was often found during routine monitoring of CIPC in the atmosphere of treated stores. Following investigation, this compound was identified as 3-chloroaniline (3CA), which is a well-known product of the microbial and thermal breakdown of CIPC [Kaufman and Kearney (1965), Nagayama and Kikugawa (1992)]. Prior to the development of all-glass flow paths for GC, direct GC analysis of CIPC was not possible because pyrolysis of the molecule occurred on contact with metal surfaces at temperatures >200°C [Romagnoli and Bailey (1966)]. In modern systems, contact with metal surfaces has been removed allowing straightforward analysis of the CIPC molecule.

3CA may be present in potato stores as a result of two processes: microbial breakdown during the storage season, or thermal degradation during application. In this study, the store atmosphere was sampled immediately after the application was complete, so any 3CA found was assumed to be a result of thermal breakdown.

3-chloroaniline may also be present in the CIPC formulation, but in very small, and strictly controlled, amounts. The EU monograph for CIPC states the FAO specification for CIPC as a maximum of 0.025% 3-chloroaniline by weight [European Commission (2003)].

Year 1

In Year 1, the relationship between various aspects of the thermal fogging process and the production of 3-chloroaniline from CIPC was investigated. These factors included burner temperature, pipe material and formulation flow rate. From this work, the most influential factors were shown to be temperature and pipe material. In Year 2 of the study, a further two experiments were carried out under conditions more similar to conventional fogging, with the particular aim of examining the influence of the pipe material at lower burner temperatures (475°C and less).

Stores and treatments

All applications were carried out using a Unifog machine and MSS CIPC 50M. Unpredictable differences between machines arose in Year 1 so the reported work was carried out using only the fogger that gave the more consistent results in Year 1.

August 2005: Six applications investigating the combined effect of burner temperature (conventional 475°C vs ‘high’ 600°C) and pipe material (metal vs plastic).

October 2005: Six applications looking at the effect of the pipe material (metal vs plastic) at lower temperature (conventional 475°C vs ‘low’ 350°C).

In both sets of experiments, the plastic pipe was a 4m length of Flexi-Sil ducting (4” diameter) from Flexible Hose Supplies Ltd (Northampton). It consists of a plated spring steel wire helix covered in silicone coated glass fibre, and is silicone lined on

the inside to give a smooth bore. In constant use, it can withstand temperatures of – 60°C to 300°C, which is suitable for this short-duration experiment although burner temperature ranges from 600°C to 350°C.

Sampling

All stores were purged on the morning of the study by opening the doors while the fans were running to remove any background 3-chloroaniline in the stores. Re-sealing of stores was left until immediately prior to application to minimise the accumulation of chemicals in the air.

Samples were collected on Tenax resin at two times post-application to investigate the chemicals present in the atmosphere:

- A. Immediately after application finished, duplicate samples of atmosphere were collected at 100ml/min for 1 minute
- B. 18 hours post-application, duplicate samples collected at 100ml/min for 60 minutes.

Experiment 1: Comparing CIPC breakdown under ‘conventional’ application conditions with a) high burner temperature and b) plastic pipe material

Applications were made to six twelve-tonne experimental stores at SBEU on the 4th August 2005, using MSS CIPC 50M and SCC Machine A. Using only one machine allowed two applications to be made on the same day with the same machine to demonstrate reproducibility for the first time.

Three combinations of factors were selected as detailed in Table 2 below.

TABLE 3 STORE TREATMENTS 4TH AUGUST

Store	Burner temperature (°C)	Formulation flow rate (l/min)	<i>Pipe material</i>	Volume added to store (l)
31	475	1.0	Metal	0.21
32	475	1.0	Metal	0.17
33	600	0.5	Metal	0.14
34	600	0.5	Metal	0.13
35	600	0.5	Plastic	0.14
36	600	0.5	Plastic	0.18

Ideally, the formulation flow rate would be the same in all treatments. However, the 475°C application was carried out as a ‘standard’ commercial application, in which the flow rate would be ~1 litre/minute. The high temperature flow rate was kept at 0.5 litre/min for consistency with previous work.

The volume of formulation added to each store varied depending on the exact flow rate and time of application, both of which are difficult to control accurately.

3.5 Results

Table 4 below shows the concentrations of 3-chloroaniline in air samples collected a) immediately and b) at ~18 hours post-application. The data is also shown in Figures 14 and 15 on the following page, where the means of duplicate analyses are given.

TABLE 4 CONCENTRATIONS OF 3-CHLOROANILINE IN STORE ATMOSPHERES 4TH – 5TH AUGUST

Store conditions	3CA Concentration (µg/l)	
	Post-application	<i>At 18 hours</i>
475°C metal pipe (1)	0.67	0.16
475°C metal pipe (2)	0.89	0.15
600°C metal pipe (1)	2.75	0.23
600°C metal pipe (2)	3.07	0.14
600°C plastic pipe (1)	1.15	0.10
600°C plastic pipe (2)	1.76	0.15

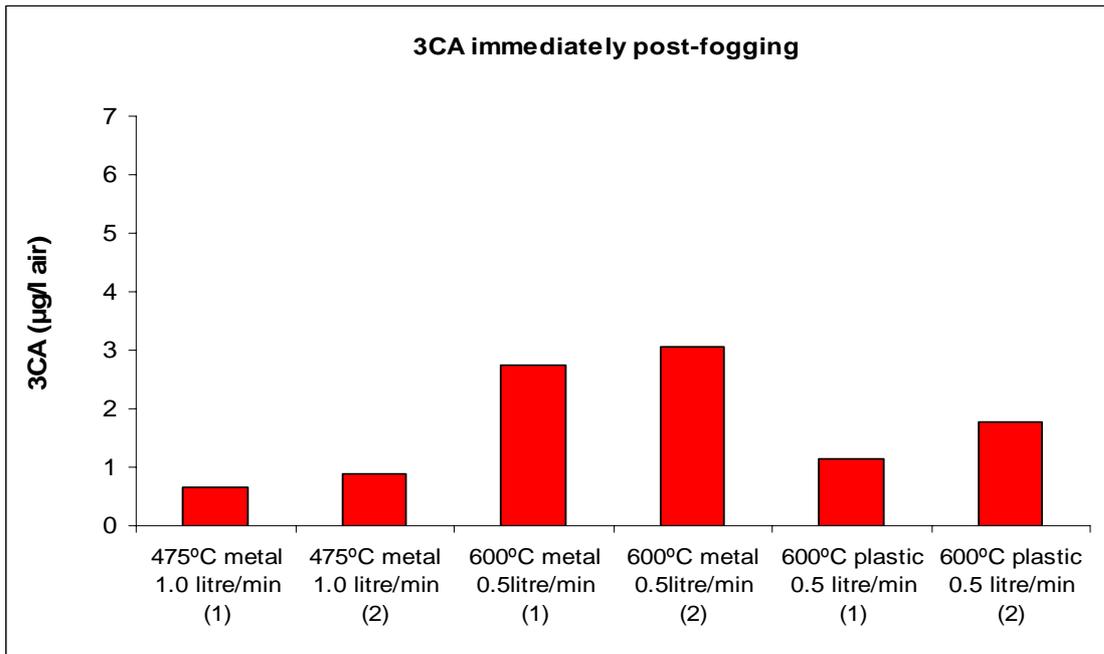


FIGURE 14: 3CA CONCENTRATIONS IMMEDIATELY POST-APPLICATION

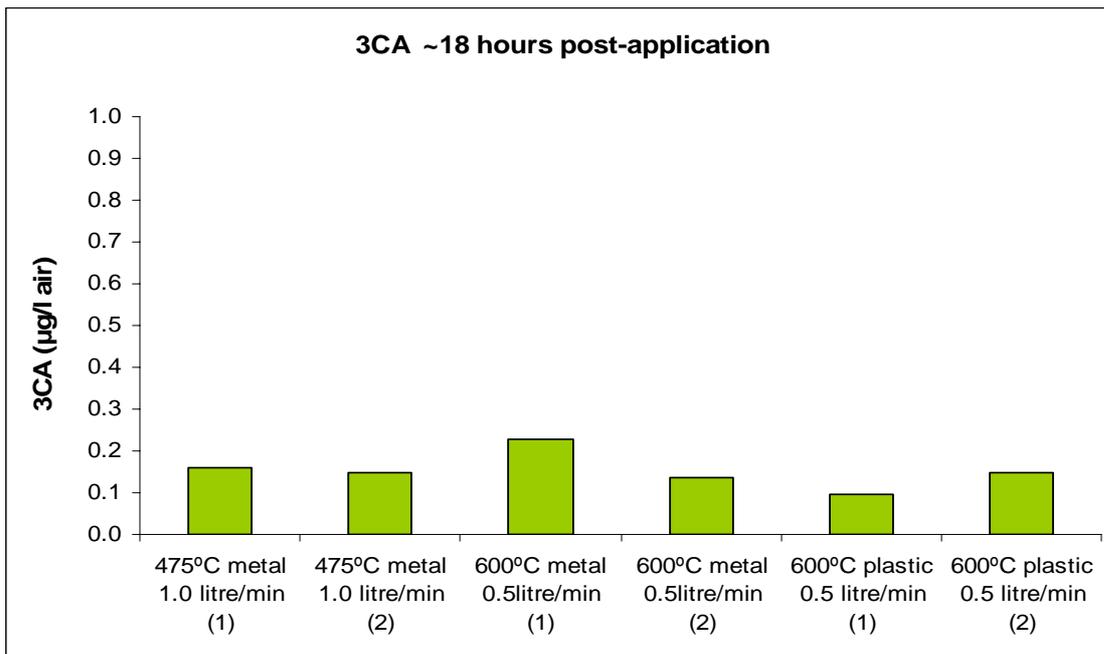


FIGURE 15: 3CA CONCENTRATIONS AT 18 HOURS POST-APPLICATION

Note that the graphs are on different scales (0-7µg/l and 0-1µg/l respectively)

The CIPC concentration immediately post-application was not determined because CIPC and 3CA are present in such different quantities (up to three orders of magnitude difference) that it is not possible to quantify them both in the same sample. The analysis of Tenax samples is destructive so the samples cannot be re-run under different conditions to allow quantification of both.

Statistical comparisons of treatments were not appropriate because of problems arising during analysis, which meant that some samples were lost.

Discussion:

Differences in the amount of 3CA in the air were apparent immediately post-application whereas at 18 hours, all stores are very similar. This effect is due to equilibrium being achieved in the sealed stores by this point.

Comparisons with Year 1: The concentrations of 3CA are very similar to those under comparable conditions in Year 1. Concentrations of c.3µg/l after fogging at 600°C are seen in both sets of experiments. Higher values of 5-7µg/l were obtained under one specific set of conditions in Year 1. The achievement of equilibrium concentrations of c.0.15µg/l after 18 hours is also comparable with previous results.

In general, the use of a plastic pipe instead of metal reduces the amount of 3-chloroaniline produced to around half. Levels are more similar to those obtained at the lower temperature, so the use of a plastic pipe might offset some breakdown at higher temperatures (475°C is taken as standard operating conditions for this machine, but applications can be made in the range 350-550°C).

Differences in the volume of formulation added or in the amount of air leaked out of the stores could affect the concentration greatly, so having very similar concentrations of 3CA in stores that received the same treatment demonstrates good reproducibility under difficult conditions.

Experiment 2: Assessing the breakdown of CIPC at lower burner temperatures with metal and plastic pipes

In previous studies, the plastic pipe was only used at temperatures of 600°C (higher than commercial practice), so this trial investigated the effect of using it at the standard burner temperature of 475°C and below. 350°C was selected as the lowest temperature at which a good quality fog could still be produced at ‘commercial’ formulation flow rates of c.1 litre/min.

Applications were made to six twelve-tonne experimental stores at SBEU on the 5th October 2005, using MSS CIPC 50M. Each application lasted for 8 seconds, and all stores were empty during the study. Stores were vented prior to application to remove any background interferences.

Three sets of conditions were selected as detailed in Table 5 below. Duplicate applications were made under the each set of conditions.

In addition to the two samples collected for 3CA analysis immediately post-application, a third was taken to allow determination of CIPC at this time.

TABLE 5 STORE TREATMENTS 5TH OCTOBER

Store	Burner temperature (°C)	Formulation flow rate (l/min)	<i>Pipe material</i>	Volume added to store (l)
31	475	1.0	Metal	0.13
32	475	1.0	Metal	0.13
33	475	1.0	Plastic	0.14
34	475	1.0	Plastic	0.14
35	350	1.0	Plastic	0.13
36	350	1.0	Plastic	0.14

Results:

TABLE 6 CONCENTRATIONS OF 3CA IN STORE ATMOSPHERES 5TH-6TH OCTOBER

Store conditions	3CA concentration (µg/litre)	
	Immediately post-application	At 18 hours
475°C metal pipe (1)	1.43	0.18
475°C metal pipe (2)	1.22	0.13
475°C plastic pipe (1)	0.61	0.28
475°C plastic pipe (2)	0.72	-*
350°C plastic pipe (1)	<LOQ	0.21
350°C plastic pipe (2)	<LOQ	0.19

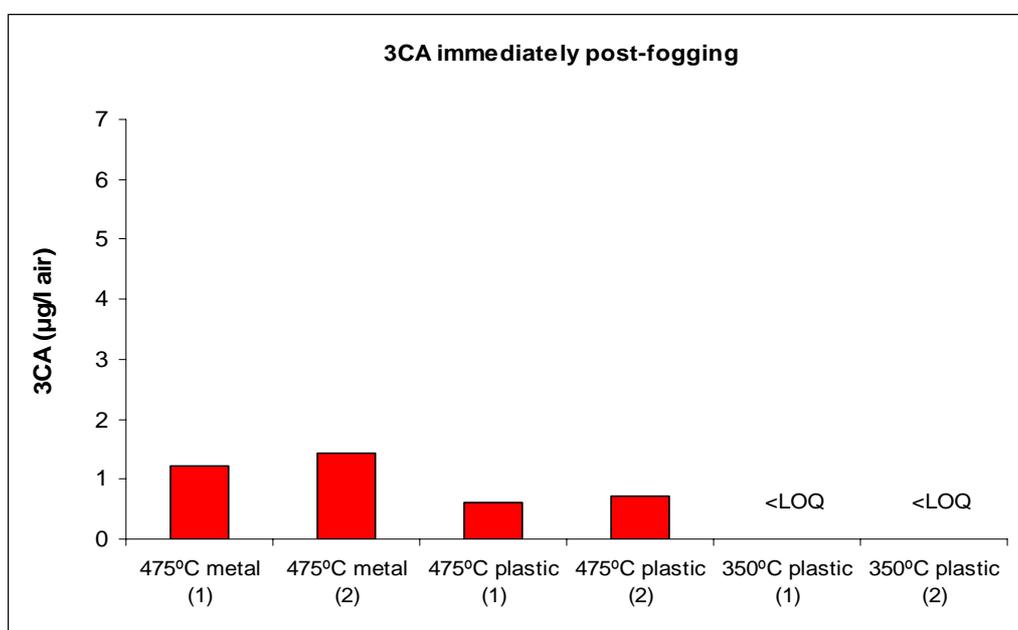


FIGURE 16: 3CA CONCENTRATIONS IMMEDIATELY POST-APPLICATION

NB: Limit of quantification (LOQ) in these samples corresponds to c.0.4µg/l

* Problems during analysis mean no value was obtained

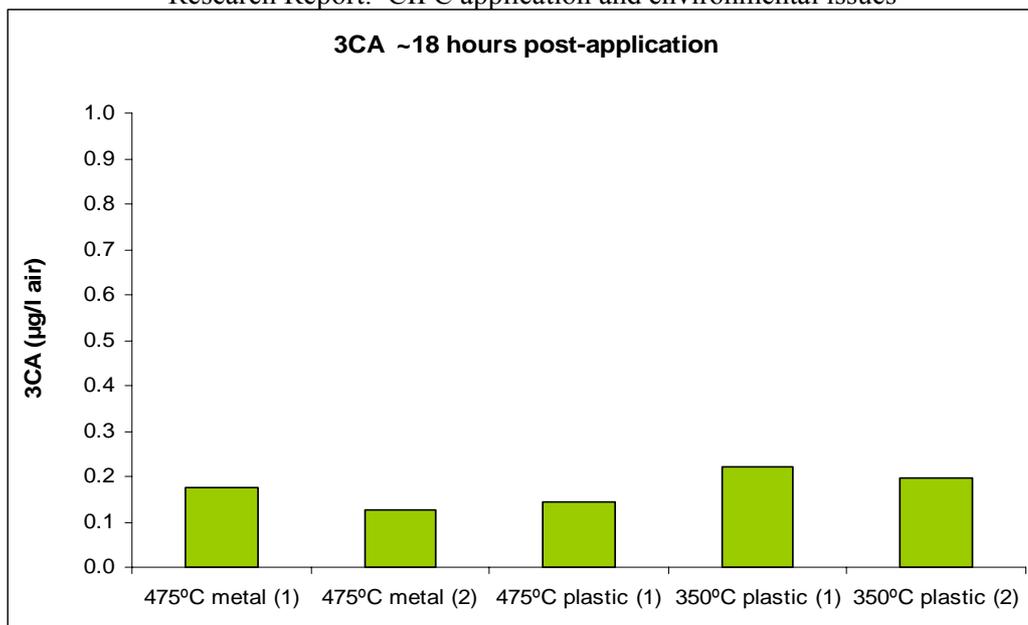


FIGURE 17: 3CA CONCENTRATIONS AT 18 HOURS POST-APPLICATION

No value is given for the second store with 475°C and a plastic pipe at 18 hours because, on analysis of the two samples, the 3CA peak was not fully resolved from another large peak on the chromatogram. This suggests the presence of an unidentified volatile compound in the air in this store – this peak is usually present in samples, but it was bigger for some reason and interfered with the 3CA peak, where normally they are fully resolved. It is worth noting that a response was seen, so the 3CA was present. There is no suggestion that it would be any different the values shown, which are all very similar to each other and to previous results.

At temperature of 475°C and a plastic pipe, the amount of 3CA generated was close to the limit of quantification of the analytical method. With a metal pipe, it was c.1µg/l as in the previous experiment. At burner temperature 350°C with a plastic pipe, the amount of 3CA was too small to quantify. It is not clear what would happen at low burner temperature with a metal pipe –there may well be some 3CA but less than the amount at 475°C.

CIPC determination and estimation of loss: The extra sample collected immediately post-application was analysed by a different method (collection on Tenax, elution into hexane then GC analysis by direct injection) to allow the concentration of CIPC to be determined. This allows an estimate to be made of the amount of CIPC lost due to leakage from the store during the 8-second application. The concentrations of CIPC in the store air, and the estimated percentage loss for each store are shown in Table 6 below. The estimates were made using the following calculation:

Concentration (µg/l) * volume of the store (l) = weight of CIPC in store (µg).

Subtract weight remaining in store (g) from the weight added (volume of formulation * concentration) = weight of chemical lost from the store. This can then be expressed as a percentage of chemical added.

A sample calculation is shown below using the result from the first store with 475°C and metal pipe:

12-tonne store dimensions 5.13m * 3.46m * 4.49m = 77.697m³ or 77, 697 litres.

Air concentration = 648µg/l * 77,697 = 50,348mg (50.35g) remains in store

Applied to store = 0.13 litres * 500g/litre = 65g.

% lost = (65-50.35)/65 * 100 = **22.5%**

TABLE 7 CIPC CONCENTRATIONS IN STORE AIR AND ESTIMATES OF LOSS THROUGH LEAKAGE

Application	CIPC concentration (µg/litre)	Loss from store (%)
475°C metal pipe (1)	648	22.5
475°C metal pipe (2)	633	22.4
475°C plastic pipe (1)	724	17.6
475°C plastic pipe (2)	696	20.8
350°C plastic pipe (1)	488	40.2
350°C plastic pipe (2)	578	34.2

Estimating loss of CIPC through thermal degradation: In order to make a fair comparison between applications in which different amounts of chemical are added to the store, the concentration of 3-chloroaniline can be expressed as the percentage of the applied CIPC broken down to produce this amount of 3CA. This figure does not take account of any chemical that has left the store through leakage, so is likely to be an underestimate.

The calculation was carried out as follows:

- 3CA concentration (µg/l) * volume of the store (79,700 litres) = total weight of 3CA in the store
- Multiply 3CA weight by 1.68 = weight of CIPC needed to produce this amount of 3-chloroaniline (CIPC = 214g and 3CA = 127g so CIPC/3CA = 1.68)
- This weight of CIPC / the total weight added to the store * 100 = percentage breakdown.

Table 8 overleaf shows the estimates for chemical breakdown in each store

TABLE 8 ESTIMATES OF THE PERCENTAGE OF APPLIED CIPC LOST THROUGH BREAKDOWN

Application	3CA concentration ($\mu\text{g/l}$)	Corresponding CIPC broken down (g)	% breakdown
475°C metal pipe (1)	1.43	0.192	0.30
475°C metal pipe (2)	1.22	0.163	0.23
475°C plastic pipe (1)	0.61	0.082	0.13
475°C plastic pipe (2)	0.72	0.096	0.14
350°C plastic pipe (1)	<0.4	<0.049	<0.07
350°C plastic pipe (2)	<0.4	<0.049	<0.07

Discussion

The concentration of 3CA after application is similar in both sets of experiments run in Year 2 under the same conditions (475°C, metal pipe). The use of a plastic pipe instead of metal at burner temperature 475°C reduces 3CA concentration by half. At a burner temperature of 350°C using a plastic pipe, the amount of 3CA produced is less than the limit of quantification for the analytical method. It is worth noting that the LOQ is determined as the smallest weight of CIPC that can be quantified by the GC. In practical terms, the larger the volume of the air sample, the lower the LOQ (i.e. the more sensitive the method is) in terms of air concentration. The volume of sample collected at 18 hours is higher (40 minute sampling time) than immediately post-application (1 minute 'snapshot' of conditions) so the LOQ is much less.

Loss through leakage: these values agree well with previous estimates of loss from commercial stores. Leakage during application was estimated to remove 13-33% of the applied chemical from the store [Park (2004)]. Leakage losses are larger in the 375°C application (c.35% compared with c.22% at 475°C) but there is no obvious explanation for this. Since experimental conditions are difficult and all results are within the range previously estimated, this may not be a significant effect.

The maximum proportion of 3CA as an impurity in CIPC is 0.025%. The <0.07% value in the low temperature applications is getting near to this value, so no significant degradation is likely to have taken place. This amount is insignificant when we consider that >1% breakdown was observed in some of the 600°C applications in previous work.

0.3% loss of CIPC may not sound like much (only 3g for every kg added) but during a one hour application 30kg CIPC will be added to a store, and around 90g of CIPC might be lost, producing c.50g 3CA. By reducing the burner temperature, production of 3CA is reduced.

Summary of 3-chloroaniline work

The observed rates of thermal degradation of CIPC are not likely to have any effect on efficacy. They are useful in terms of mass balance, as are estimates of leakage, which is a more significant loss pathway.

Under conditions close to 'conventional' applications, less than 1% of the CIPC is estimated to be degraded. This proportion will increase with burner temperature, but replacing the metal pipe with a plastic one can offset this effect. Thus there is evidence of both direct thermal degradation and a catalytic effect of hot metal surfaces.

By combining reduction in burner temperature and use of a plastic pipe, production of 3CA is reduced to virtually nil. At its highest in any of the experiments carried out in Year 1 and Year 2, CIPC breakdown rate was c.1.5% based on what was left in store (no account of anything lost through leakage – estimates of loss would be around 1/3). This would represent 450g (590g including loss) of CIPC lost, or 270g (350g including loss) of 3CA produced per hour of application time.

This work has concentrated on the presence of 3-chloroaniline in terms of mass balance of CIPC. However, some workers have reported low levels of CIPC metabolites in potatoes [Heikes (1985)], including 3-chloroaniline [Worobey and Sun (1987)]. In these cases, 3CA may be present because the potatoes metabolise CIPC during storage, or 3CA may have been present as an impurity in the formulation, or it may be a result of thermal degradation at the time of application.

Studies on potato washing water effluent

Aims

In Year 1, a number of samples of washing effluent were collected and analysed. In Year 2 more samples were collected from washing operations (some mobile, some at permanent installations) in order to provide a more detailed picture of the levels of CIPC present in effluent. Samples were collected in early Summer 2005.

The CIPC content of the liquid fraction of the effluent was determined after the solids had been removed. The method of analysis also allowed 3-chloroaniline (3CA), a product of microbial breakdown of CIPC, to be quantified. In legislative terms, 3CA is not considered a problem, as there is no EQS or statutory EA/SEPA working standard for it. It is not of toxicological concern to the regulatory authorities since it can be broken down relatively quickly in the environment.

Sampling and analysis

One-litre samples of water were collected in plastic bottles and sent to Glasgow for analysis. Once received, samples were centrifuged (at 4,200 rpm for 10 minutes) to remove most of the solids, and then filtered through GF/C filter paper to remove the finer material. An aliquot of the solution (250ml) was then passed through a C-18 solid-phase extraction (SPE) cartridge, followed by a small volume of clean water to remove any impurities held on the column. After vacuum drying for one hour, the cartridge was eluted with 2ml acetone and the extract analysed by GC-FID.

Site A

Samples were collected from a mobile washer on 19th May 2005 after a) 100 tonnes and b) 185 tonnes of CIPC treated potatoes had been washed. Potatoes were crisping crop (cv Saturna) and had received several treatments of CIPC.

Samples were received at Glasgow on 25th May 2005 by which time the samples were black in colour and had an offensive smell, indicative of anaerobic breakdown. It was difficult to prepare these solutions for analysis, with filtration proving a particular problem.

TABLE 9 CIPC AND 3CA CONCENTRATIONS IN SAMPLES FROM SITE A (MAY 05)

Tonnage washed	Effluent concentration (mg/l)	
	3-chloroaniline	CIPC
100 tonnes	3.5	0.2 (5.9)
185 tonnes	5.1	trace (8.6)

[NB the values in parentheses represent the original concentration of CIPC required to produce this amount of 3CA– see later discussion for details on calculation]

Site B

Samples were collected on 1st June 2005 after a) 75 tonnes and b) 135 tonnes of CIPC treated potatoes had been washed. The capacity of the washer was ~6,000 litres, and the potatoes had received 5 applications of CIPC in season 2004-5. The washer was filled with fresh water on the morning of the study. On this site, all effluent and yard drainage is collected and pumped into willow coppice wood.

Samples were received at Glasgow on 3rd June 2005 and were light brown in colour with no offensive odour. Centrifugation and filtration easily produced a fairly clear solution, with very little solid material in any of the samples.

TABLE 10 CIPC AND 3CA CONCENTRATIONS IN SAMPLES FROM SITE B (JUNE 05)

Tonnage washed	Effluent concentration (mg/l)	
	3-chloroaniline	CIPC
75 tonnes	6.3	1.5 (10.6)
135 tonnes	6.5	trace (10.9)

Site C

Samples were collected on 1st June 2005 after a) 110 tonnes and b) 200 tonnes of CIPC treated crop had been washed. Crop being washed came from two stores, had received 5 applications of CIPC in season 2004-5. In the morning, the potatoes being washed had considerable levels of rotting but by the time the second sample was collected, better quality crop (from a different field) was going through the system. The volume of the washer was ~8,000 litres. On this site, the effluent is collected and spread back on land, which may represent a potential disease problem.

Samples were received at Glasgow on 3rd June and contained an unusually large amount of solid material – this meant that the liquid fraction of the 100ml aliquot was considerably less than 100ml by the time all the solids were removed. There was no hissing or offensive smell when the bottles were opened. The liquid fraction was still quite cloudy after centrifuging and filtering but it passed through the C-18 cartridge easily.

TABLE 11 CIPC AND 3CA CONCENTRATIONS IN SAMPLES FROM SITE C (JUNE 05)

Tonnage washed	Effluent concentration (mg/l)	
	3-chloroaniline	CIPC
110 tonnes	3.4	0.3 (5.7)
200 tonnes	2.7	trace (4.5)

Site D

These samples were collected in early June 2005 from four points around a site where wastewater is cleaned and recycled. Duplicate samples were taken at each point, but the values shown in the table represent the means of the replicate analyses. No details were received regarding the tonnages washed, but crop is known to have come from two separate box stores; one of which was treated 5 times and the other 4 times in 2004-5.

Samples were received at Glasgow on 10th June and all samples were ‘normal’ e.g. no offensive odour, light brown in colour rather than black.

On this site, water is used to re-fill the washer after on-site treatment (sedimentation in a lagoon). During the day, additional fresh water is added at the spray bar, so the washer is never completely filled with clean, fresh water.

Results

TABLE 12 CIPC AND 3CA CONCENTRATIONS IN SAMPLES FROM SITE D (JUNE 05)

Location	Effluent concentration (mg/l)	
	3-chloroaniline	CIPC
Entering system after on-site clean up	3.5	0.05 (5.9)
From drain at bottom of washer	3.3	trace (5.5)
Overflow from washer	3.7	trace (6.2)
Pumped from settlement pond (en route to soakaway)	3.7	trace (6.2)

Discussion of results

In previous work (eg., Part 1 of this report) CIPC was identified in washing water. The amount will vary depending on a number of factors including the treatment history of crop, throughput, how frequently the washer is filled with fresh water. Trace levels of CIPC were detected and reported in this second year of the study, along with some 3CA. In previous work, 3CA may have been present but was not quantified.

Standard solutions of CIPC in water were run through the system to confirm the satisfactory performance of the analytical method, so the absence of CIPC can be attributed to the condition of the samples themselves. The limit of quantification for the analytical method corresponds to 0.04 mg/l in the original effluent (it will vary depending on the volume of effluent extracted, in this case 250ml).

It is suggested that the washer may contain a microbial population that is quickly degrading CIPC to 3CA. Where a viable population is well adapted to using CIPC as a substrate, the lag period reported in soil studies may not be present. In any future work, the addition of a microbial inhibitor (e.g. sodium azide) immediately after collection would help prevent breakdown during sample transport and storage. Another option would be to carry out sample preparation and extraction on site before samples are sent to the lab. Once extracted onto the SPE columns, CIPC is stable for at least 7 weeks [Liška and Bilikova (1998)] because the diameter of pores in the cartridge is small enough (58-87Å) to exclude the micro-organisms responsible for breakdown. However, the addition of a microbial inhibitor (such as sodium azide) is a more practical option than carrying out sample clean-up on site.

Where 3-chloroaniline is present, an estimate of the original concentration of CIPC can be made using the relative molecular weights of the CIPC (213g) and 3CA

(127g). Multiplying the 3CA concentration by 1.68 (213/127) provides an estimate of the original amount of CIPC. These values are shown in parentheses in the tables, but may still underestimate the original CIPC content since any degradation that has proceeded past the 3CA stage will not be taken into account. When the 'original' CIPC content is estimated in this way, the values are similar to those found under comparable conditions in previous years. The reason for the particularly quick degradation this year is not clear.

In terms of discharge consents and EQS for CIPC, the rapid breakdown of the CIPC is a good thing, and well-adapted microorganisms can completely mineralise phenolic compounds leaving only innocuous products. However, consideration must be given to the nature and stability of intermediates in order to demonstrate responsible management of effluent.

Degradation of CIPC in the environment

A number of classes of organisms have been shown to be capable of degrading CIPC in the environment including

- ectomycorrhizal fungi in soils [Rouillon et al (1989)]
- soil bacteria including *Pseudomonas striata* [Moe (1970)], *Achromobacter sp.* and *Flavobacterium sp.* [Kaufman and Kearney (1965)]
- soil fungi including *Aspergillus fumigatus* [Wolfe, Zepp and Paris (1978)] and *Fusarium oxysporum* Schlecht [Fletcher and Kaufman (1979)]
- blue-green algae, specifically *Anacystis nidulans* [Wright and Maule (1982)].

Rate constants are two orders of magnitude higher for bacteria than fungi [Wolf *et al* (1978)], so they will be responsible for most CIPC biolysis in the environment.

The organism responsible for bacterial soft rot of potatoes, *Erwinia carotovora*, may contribute to the degradation of chlorpropham if it is present on soil removed during the washing process or on rotting potatoes – the organism is a facultative anaerobe and will utilise organic molecules as energy sources in the absence of oxygen (e.g. in a sealed bottle). The smell and black colour of some samples analysed one week after collection suggested anaerobic breakdown had taken place.

It is assumed that the 3CA present in the water originates from CIPC that has broken down during the washing process, rather than during the storage of the potatoes. Other workers reporting on the metabolites of CIPC in treated potatoes describe only very low (mostly ppb) levels, so crop metabolism appears to be negligible in relation to biodegradation in water.

Treatment of washing effluent

Biobeds can be useful for low-volume, high-concentration waste e.g. rinsate and vehicle washdown [Torstensson (2000), Environment Agency (2003), Basford (2003)]. However, washing water is a high-volume, low-concentration waste that may not be suited to this type of approach. The volume of waste, the concentration and nature of the pollutant and the capacity and residence time in the system are all factors that would need to be investigated for this to be a viable option.

Reed beds are employed on some sites, although the size required dictates whether this is a practical option. For example, on a site where large volumes of crop are washed every day, this may not be a practical option because the size of bed needed to treat the effluent would be too large to accommodate on site. At smaller installations, or where washing is more sporadic, a realistic size of bed may be an option. Such operations are still subject to EA regulation and discharge consents, but the sites we are aware of have had no problems meeting them. Where plants are to be used for effluent clean-up, consideration should be given to the toxicity of CIPC (which is a herbicide) when selecting the species to be used.

Coppiced willow is also being used on another site where regular crop washing is carried out –an area of around 60 hectares of coppice is available. All yard drainage, vehicle-cleaning waste and washdown from the site is collected together and disposed of in this way. None of the constituents of the effluent has any negative effect on the growth of the willow, which is burned to heat an office building in the winter.

Spreading back on set-aside land is also an option, with application rates subject to Environment Agency consent. In this situation, biological breakdown will occur in the soil and/or the chemical will be adsorbed onto soil particles, so contamination of ground or surface waters should not occur. As an example, one site we have worked on has agreed limits of 30m³ per hectare per year. The EA regularly sample surface waters near this site, and have not reported any problems with residues to date.

When properly maintained and regulated, washing effluent does not appear to cause environmental problems. The reason mobile washing operations are of interest to the Environment Agency is mainly because they are unregulated and difficult to police, rather than because they present a significant risk to the environment.

Conclusions

In previous work, a fairly consistent concentration of c.10mg/litre was found in samples from washers at the end of a busy day. There is no clear explanation for why only trace levels of CIPC were present in most samples collected this year.

The presence of 3CA suggests that CIPC is quickly breaking down to produce 3-chloroaniline (by hydrolysis of the ester linkage). The amounts of 3CA found correlate well with CIPC concentrations found in previous work.

The results from Year 2 suggest that allowing washing waste to sit around for a few days prior to discharge can be a form of treatment in itself, by allow the microbes to

act on the chemical residues. However, this form of 'treatment' will not address any other factors that may be covered in the discharge consent (e.g. suspended solids, BOD).

Changes in CIPC levels in the atmosphere of treated stores 1) during storage and 2) immediately post-application

During season 2004-5, a program of air sampling was conducted in three stores where CIPC was being used. The aim was to investigate how concentrations CIPC vapour change throughout the season.

Samples were collected at intervals during the storage period, and included both before and after application as well as in the intervening weeks. Both processing/chipping stores (high temperature, vented daily) and packing stores (low temperature with little air exchange) were included in the study.

Sampling was also conducted in the hours immediately after application in a small number of stores to determine how quickly the fog settles.

Details on store management and the timing of CIPC applications were obtained from the store managers and help to complete the picture of what is happening in the stores. Each store and its results will be discussed separately since there were significant differences between them.

Sampling and analysis:

In the early stages of the study, air samples were collected from close to the crop (pump located on the edge of a box, and the resin trap resting on top of the potatoes) as well as from the free headspace in the store to investigate any difference in conditions closer to the potatoes. Once no difference was found, air samples were only taken within the boxes, which were easier to access since headspace sampling required access to the top of the stack, which is difficult under Health and Safety Executive 'Working at Height' regulations.

Samples were collected on Tenax resin and analysed by thermal desorption and GC-FID as described previously. During routine sampling, in some cases both CIPC and its metabolite 3-chloroaniline (which is present in trace amounts in the store as a result of thermal fogging) were identified on the chromatogram. The amount of 3CA was very small, and it was not quantified. It decreased as the season progressed, since there was only a small amount present to begin with.

Part 1: Changes in CIPC concentration during the storage season

Store A:

A box store (capacity 1300 tonnes) with a holding temperature of 2.5°C. The store was fully loaded by 13th October 2004. Ethylene (sprout suppressant) was used from November until the end of January. Two applications of CIPC were made on 11th February and 12th May. The last load was removed on 27th July 2005. The store was then cleaned and disinfected with Jet 5 (a solution containing 5% peracetic acid, 27% hydrogen peroxide and 8% acetic acid) on 16th August then shut down in preparation for the following season. Unlike the other two, this store was not CIPC treated in the previous season (2003-4).

The concentrations of CIPC found in the store air are shown in Figure 18 below. Note that only the points on the graph are actual air concentrations measured on specific days – the line is included to illustrate the general trend in the values, but does not represent the actual concentration at any other time.

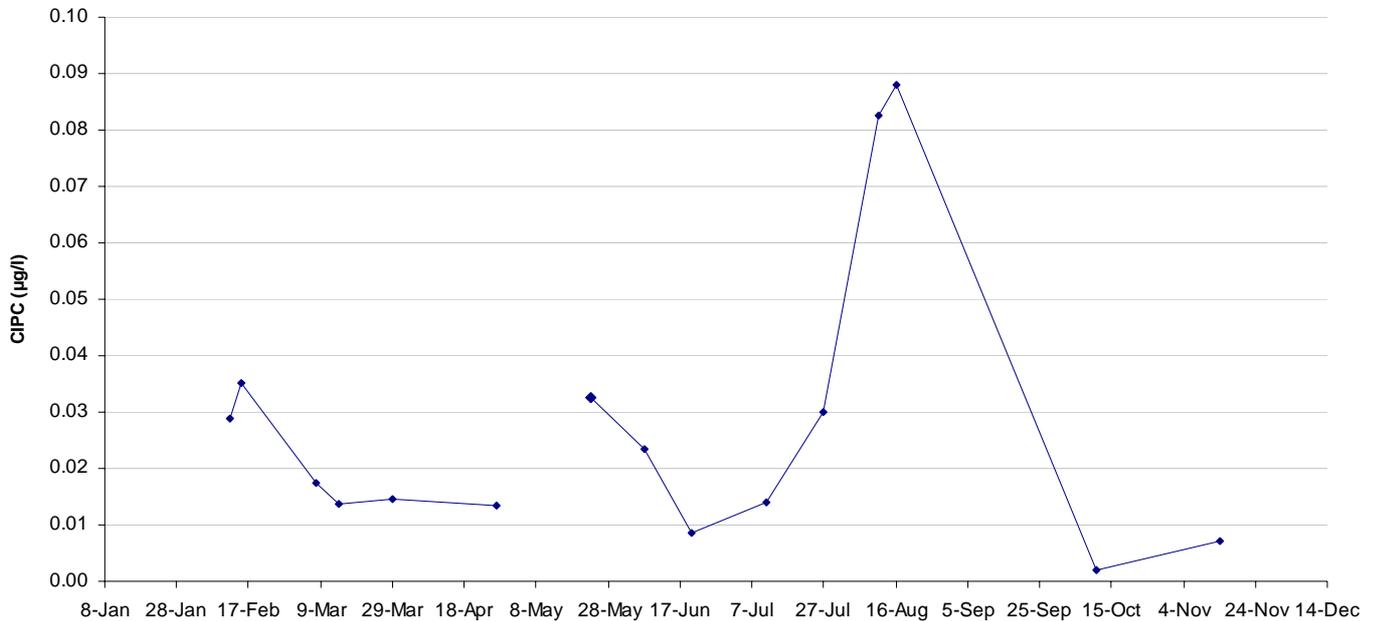


FIGURE 18 CONCENTRATIONS OF CIPC IN THE ATMOSPHERE OF STORE A BETWEEN FEBRUARY AND NOVEMBER 2005

The highest levels of CIPC in the atmosphere are present shortly after fogging. Levels then decrease with time, and stabilise at $\sim 0.015 \mu\text{g/l}$. Once the store was emptied and the temperature increased from 2.5°C to ambient, the concentration increased to $c.0.09 \mu\text{g/l}$. Jet 5 cleaning had no discernible effect on the concentration of chemical in the air. This suggests that there is still a pool of available CIPC in the store, and that increasing the temperature when the store is empty and purging the atmosphere may help reduce the availability of CIPC vapour by the start of the following season. By the time the store was filled again (October 2005), air concentration was low ($0.005 \mu\text{g/l}$) considering a relatively high temperature of $\sim 11^\circ\text{C}$.

Store B:

A box store (capacity 1147 tonnes) with a holding temperature of $8-8.5^\circ\text{C}$. Throughout the season, the store was ventilated for 12 minutes every 7 hours. The crop was loaded on 28th September 2005. Three applications of CIPC were made, on 20th October, 18th November and 27th January – in each case, the reason for re-application was new sprout growth. This store was only added to the study following the third application in January. After the removal of all crop, the store was vacuumed and swept out on 5th July 2005. It was then treated with FarmFluid on 14th July (only sprayed on concrete and metalwork as it stains insulating foam). FarmFluid is a blend of organic acids, surfactants (which help to break up biofilms and expose organisms to disinfection) and high and low molecular weight biocides used as a disinfectant for control of pathogens including viruses, bacteria and fungi (<http://www.antecint.co.uk/main/ffs.htm>).

The concentrations of CIPC determined in the air between January and November 2005 are shown in Figure 19.

Prior to the third application of CIPC on 27th January, the air concentration was ~0.02µg/l. This increased to ~0.043µg/l post-application. In contrast with Store A where the CIPC content of the air appeared to stabilise in between treatments, the concentration in this store decreased gradually to almost undetectable levels by the time the store was emptied in July.

The higher air temperature (8.5°C) and frequent venting in this store means that more CIPC will have been lost during the season than in Store A, where the air temperature was 2.5°C (air holds more CIPC the warmer it is) and the store was not vented. Once the store was at ambient temperature, the increase in CIPC concentration was not nearly as marked as in Store A – only increased to ~0.03µg/l compared with ~0.09µg/l. This suggests a reduction in available CIPC as the season progressed.

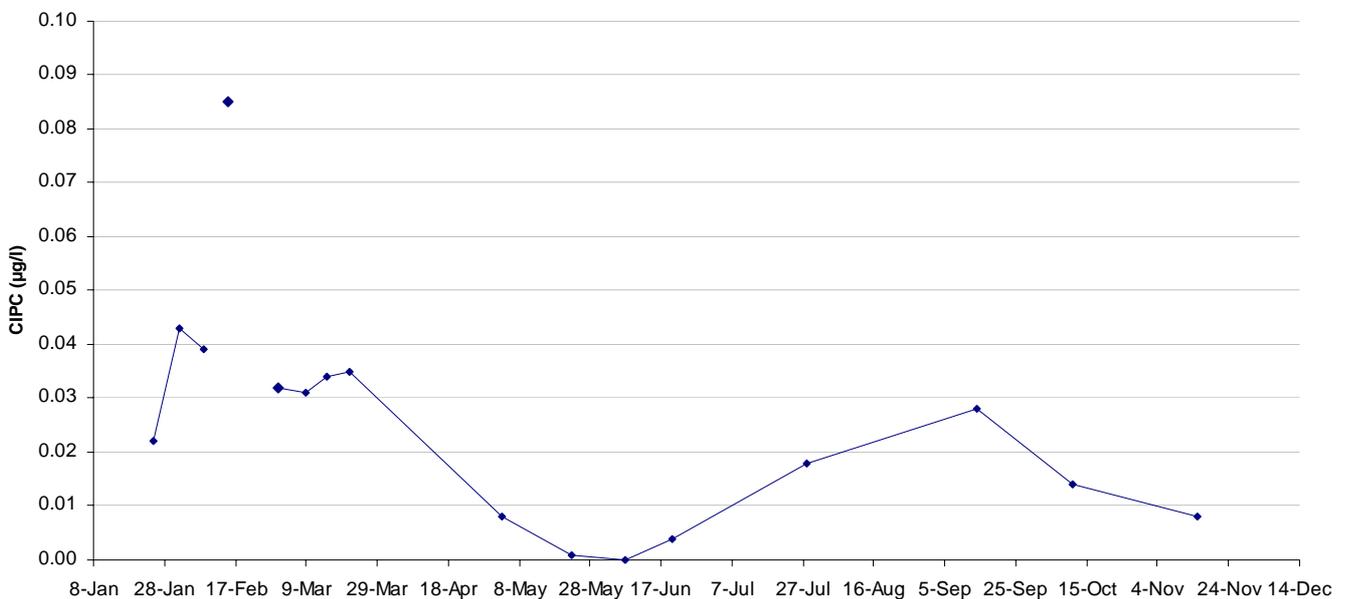


FIGURE 19 CONCENTRATIONS OF CIPC IN THE ATMOSPHERE OF STORE B BETWEEN JANUARY AND NOVEMBER 2005

Store C:

A box store (capacity 1155 tonnes) with a holding temperature of 2.5°C. The store was loaded on 7th September 2004 and emptied by late June 2005. It received one application of CIPC on 24th March 2005. The store was vacuumed and cleaned on 28th June and treated with FarmFluid on 8th August. The store was left at ambient temperature over the summer months.

The concentrations of CIPC determined between March and August 2005 are shown in Figure 20.

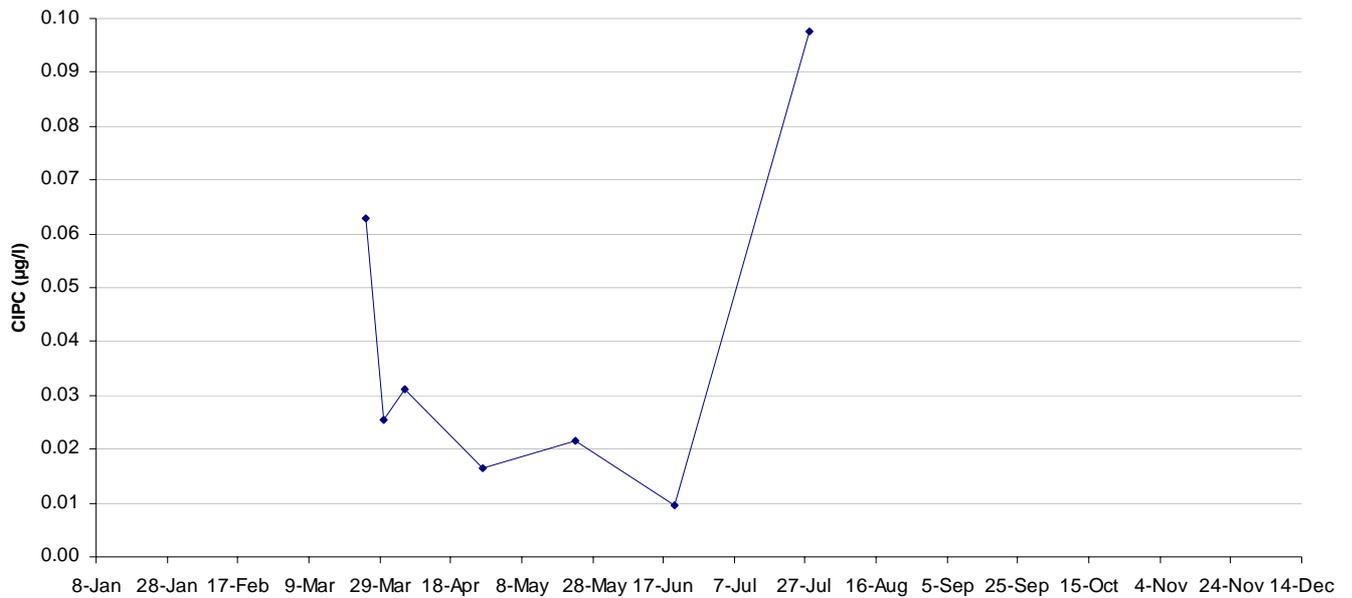


FIGURE 20 CONCENTRATIONS OF CIPC IN THE ATMOSPHERE OF STORE C BETWEEN MARCH AND AUGUST 2005

This store shows a similar increase as Store A to $\sim 0.1\mu\text{g/l}$ once the store was empty and at ambient temperature. This appears to be a ‘cold store’ effect; perhaps a result of a lot of available CIPC remaining in the store fabric because of reduced volatilisation as a result of low storage temperatures and limited air exchange.

Results:

Values in commercial stores have always been lower than under equivalent conditions in empty experimental stores. Once the stores were emptied and the temperature increased to ambient, CIPC vapour levels in all stores increased. The increase was most dramatic in cold stores because i) the temperature differential is biggest and ii) there is probably more CIPC left in these stores because losses are less due to lower air temperature and little air exchange.

Cleaning (vacuuming, brushing, disinfecting) had no significant effect on reducing chemical residues in the air. The increase in cold stores once empty is much higher (to $0.1\mu\text{g/l}$) than in processing store (to $0.03\mu\text{g/l}$). The high temperature, venting and flushing during the season may have removed more of the reservoir of contamination in the store.

Part 2: CIPC concentrations in store atmosphere in the hours following application.

In this part of the study, samples were collected from three stores in the hours immediately after application to investigate how quickly the fog settles and CIPC levels return to ‘background’ vapour levels (around $0.1\mu\text{g/l}$ at 10°C). Each sample was collected over a period of 30 minutes, so the value shown is a mean over this period although conditions are constantly changing. All stores were box stores.

Store 1: This store was followed for 24 hours post-application. Samples were collected for 30 minutes at two hourly intervals. Personnel were present onsite to take samples and switch over the pumps, which allowed this intensive sampling to be completed. This store was very leaky, and fog could clearly be seen exiting from the back of the store shortly after the application commenced. Losses from this store are expected to be more than usual, so conditions may stabilise quicker than expected. Note in this store that samples were withdrawn from the top and bottom of the store at each time to illustrate the differential settling of fog from the top of the store (immediately post-application, higher levels are expected at the top because fog rises due to heat).

Store 2: This is a Store A from the previous part of the study. Personnel were not onsite, so the number of samples was restricted by the number of sampling pumps available (four). The most interesting time in terms of fog deposition is the first few hours following application, so pumps were set to start sampling at 1, 2, 3 and 4 hours post-application.

Store 3: This is Store C from the previous part of the study. Sampling was also automated on this site, so sample numbers were limited to 4 samples over a 4 hour period.

Presentation of results:

Results for each store are plotted together on Figure 21. The differences in the amount of CIPC in the atmosphere are so great over the sampling period (reduction of several orders of magnitude from fog to vapour levels) that results cannot be plotted on a linear scale. A \log_{10} scale is used in Figure 21 to allow all data to be plotted on the same graph. A straight line is obtained in each case, suggesting exponential settling of the fog.

Samples were collected over a 30-minute period and represent a mean of conditions during that time. For the purposes of plotting the graph they are shown at half way through the sampling time i.e. the sample collected from 0-30 minutes post-application is shown at 15 minutes. True vapour concentration of CIPC is estimated to be around $0.1\mu\text{g}/\text{l}$, which corresponds to a value of -1 on the \log_{10} scale. Extrapolation of trend lines to reach this point was used to estimate when the fog had settled. Results from each store are also shown in Tables 13 and 14, expressed as $\mu\text{g}/\text{l}$ of air.

TABLE 13 MEAN CONCENTRATIONS OF CIPC IN STORE 1 ATMOSPHERE 0-20 HOURS POST-APPLICATION

Start time post-application (hr)	CIPC concentration ($\mu\text{g/l}$ air)	
	Top of store	Bottom of store
0	1331.36	892.59
2	19.75	14.92
4	0.28	0.20
6	0.11	0.10
8	0.08	0.04
10	0.11	0.10
12	0.08	0.09
14	0.14	0.11
16	0.10	0.08
18	0.11	0.07
20	0.09	0.09

Only the 0, 2 and 4-hour post-application samples are significantly higher than vapour levels. This suggests that the fog has settled within the first 6 hours after application. This store was very leaky, and we might expect it to take a little longer in more modern, better-designed stores. Differentials between the top and bottom of the store are seen as expected at 0 and 2 hours post-application. After this time, values are very similar, which suggests that the rising and settling of the fog is complete by this time.

TABLE 14 CIPC CONCENTRATIONS 1-4 HOURS POST-APPLICATION IN STORES 2 AND 3

Start time post-application (hr)	CIPC concentration ($\mu\text{g/l}$ air)	
	Store 2	Store 3
1	133.92	171.40
2	15.97	40.40
3	6.73	7.49
4	2.88	1.64

Results were very similar in these two stores. Neither store was considered excessively leaky, and after 4 hours CIPC levels were still high relative to Store 1.

Figure 21 overleaf shows the results for each store plotted together for comparison. Using extrapolation of the trend lines to estimate when the fog had settled suggests that in Store 1 this point was reached after 4.5-5 hours, but in Stores 2 and 3 it took 6-7 hours for equilibrium to establish. This is in line with previous observations.

Stores are now commonly vented around 8 hours post-application to remove ethylene (introduced to the store as an undesirable component of fogger exhaust), which can damage fry colour. It has been suggested that loss of chemical from the store may be increased through early ventilation before the fog has fully settled. These results

suggest that excessive loss of fog would not occur through venting at this time, compared with 24 hours used traditionally.

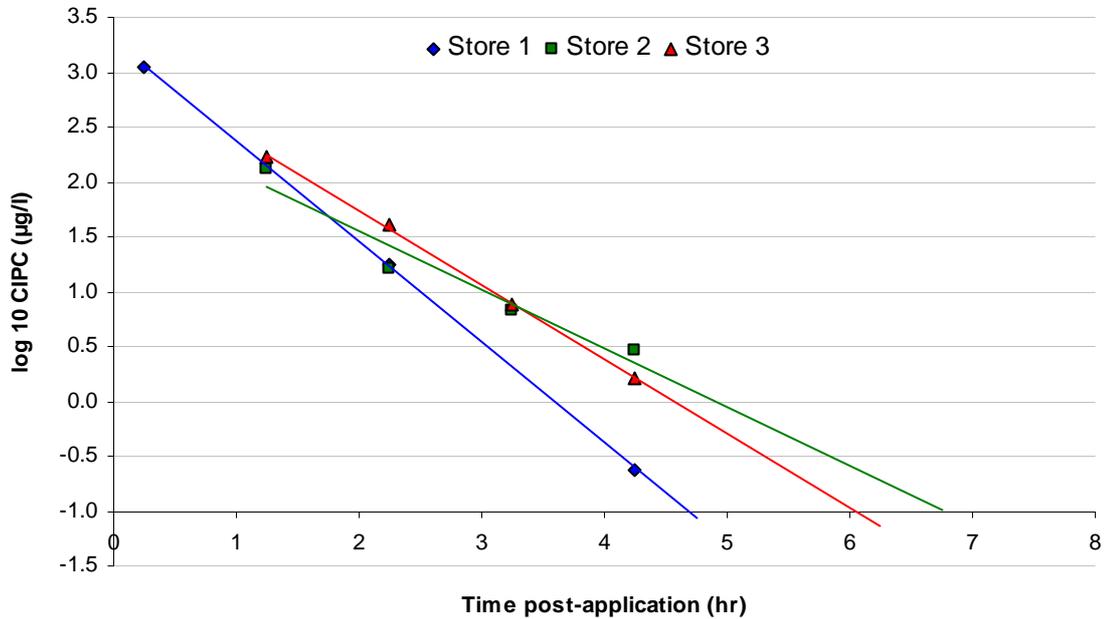


FIGURE 21 CIPC CONCENTRATIONS IN STORES AT 0-4 HOURS POST-APPLICATION

By extrapolating the trend lines backwards, the initial concentration in all three stores can be estimated to be of the order of 10^3 µg/l (or mg/l), as expected in a fog containing particulate CIPC.

Conclusions from commercial store work:

In general, CIPC vapour levels are highest in the days immediately after an application. In processing stores, which are vented on a daily basis, the concentration in air decreases as more and more chemical is lost from the store. It appears that levels in cold stores are more stable. This is likely to occur because air is not replaced regularly, and the low air temperature also will result in a lower rate of volatilisation.

As a result of the described differences in store conditions, more CIPC is retained in cold stores at the end of the season than in processing stores. A combination of high air temperature and frequent venting contributes to the loss from warmer stores. Increasing temperature and flushing when the store is empty (e.g. over the summer) may help reduce the pool of available CIPC and lessen the degree of contamination in the store.

Conventional store cleaning methods (brushing, Jet 5 and FarmFluid disinfection) did little to reduce the CIPC vapour concentration. These methods may be effective

against CIPC on the very surface of the store fabric (contact action), but are not expected to degrade anything more deeply held within the materials.

In the hours following application, store conditions return to normal, in terms of the amount of CIPC in the air. Early venting, therefore (around 8 hours), should have little effect on the amount of CIPC lost, with limited impact in terms of loss of efficacy and environmental burden.

Vapour build-up and decontamination of experimental stores

Background

This work was carried out as a series of trials in 12-tonne stores at Sutton Bridge Experimental Unit, where each store had a long history of CIPC use. The aim was to investigate how quickly the concentration of CIPC in a contaminated store recovered after a period of venting, during which the air was assumed to be purged of all chemical. Later trials attempted to isolate the major source of contamination in the store: all the surfaces in the store may be contaminated as a result of previous CIPC applications, but the contribution each makes to the amount of airborne chemical may differ (surface area, tendency to re-volatilise). Once the source of contamination has been identified, strategies can be employed to minimise the release of CIPC from the material, which will reduce the airborne concentration and the potential for crop contamination in the store.

Previous work on CIPC vapour conducted in 2001-2 in contaminated stores (part of BPC Study 197) found re-equilibration of airborne concentration after a change in store air temperature within a couple of hours [Park (2004)]. However, how quickly the CIPC vapour builds up from a starting point of zero was not investigated in that study.

Stores and treatments

Studies were carried out in Stores 36, 33 and 35 at SBEU. Store 36 was used originally, but was not available for the later parts of the work. Store 33 was used in the second set of experiments, but had very low concentrations of CIPC in its atmosphere, which made it difficult to determine differences. As a result, the final set of experiments was conducted in Store 35.

The rate of vapour build-up was investigated in each store before any treatment was carried out. In each case, the quick accumulation of chemical after a period of purging the store atmosphere implied a large, freely available reservoir of CIPC was present in the contaminated store fabrics. An obvious candidate is the floor, because particles fall onto it every time a fog is applied and it will release chemical from on or within it back into the air fairly freely.

A number of approaches were considered for preventing accumulation of CIPC in the air. Working in a second store (Store 33), the first attempted method of decontamination was covering the floor with a layer of plastic to 'seal in' the chemical and prevent vapour accumulating in the air.

Results with floor covered were inconclusive, so this trial was repeated in reverse i.e. a background sample was collected with the floor covered, then the plastic was taken off and timed samples collected from then. The CIPC concentration in this store was very low anyway, so it was difficult to detect any significant differences.

In a third store (Store 36), physical methods of cleaning were investigated for their effect on airborne CIPC. The store was steam cleaned and scrubbed in an attempt to

remove the freely available chemical from the fabrics. Efforts concentrated on the floor, although the whole store was pressure washed.

August 2004: Establishing how quickly vapour builds up

Initial samples were taken in Store 36 while the store was sealed and at equilibrium i.e. to establish the ‘usual’ level of CIPC in the air. After this sample was taken, the store was vented by running the fans with the doors open for c.15 minutes. The store was then re-sealed and sampling began immediately. A relatively long sample collection period of 100 minutes was used because the rate of build up was unknown. Samples were collected throughout the day, and the pumps were also timed to run during the night and collect samples and one final sample was collected at c.24 hours the following morning.

Because of constraints on time and resources, only one sample was taken at each time. Results showed that the concentration built up to ‘background’ levels very quickly – the sample in the first 100 minutes was slightly lower than the others, but there were no distinguishable difference thereafter.

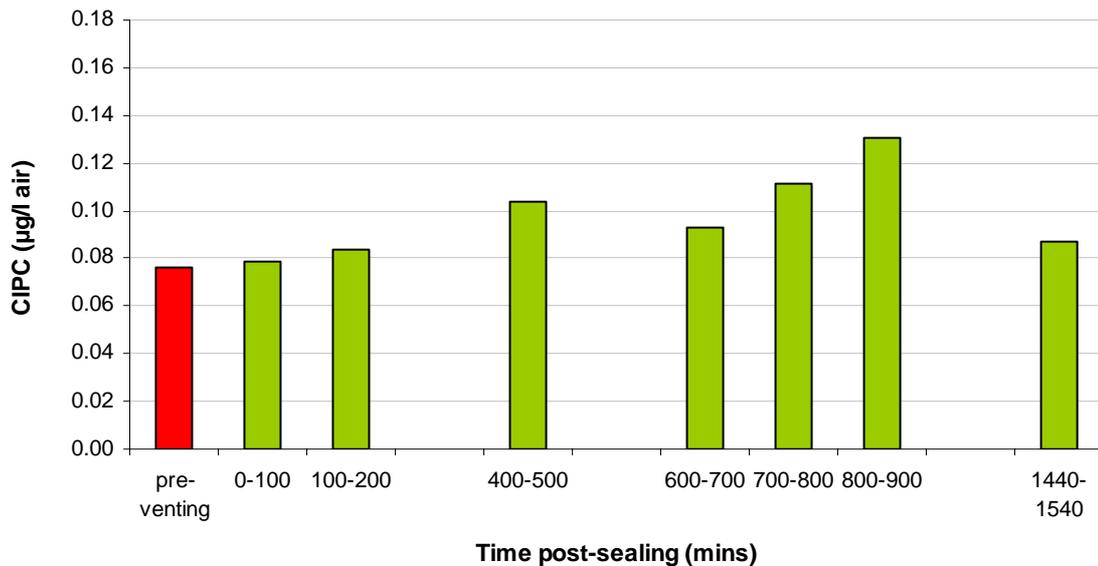


FIGURE 22 CIPC CONCENTRATIONS IN STORE 36 PRE-VENTING AND DURING 24 HOURS POST-VENTING

Given the relatively large amounts of chemical present even shortly after venting, in future work sampling time was reduced to 60 minutes to allow shorter intervals to be looked at – the shorter the sampling time, the better a ‘snapshot’ of store conditions is obtained.

April 2005: Effect of covering the floor to prevent vapour release

This second set of experiments began to consider the source of the contamination in the store, with a view to isolating it and prevent crop contamination. The concrete floor is a likely candidate since i) fog settles out onto it and ii) it is porous so may act as a reservoir for the chemical. Working in a third store (Store 35), a background sample was collected, then the store was opened and the floor covered with plastic sheeting. Store fans were run with the main door open for c.40 minutes to purge the store. Doors were closed and samples taken at 60-minute intervals. The results for the floor covering work are shown in Figure 23 overleaf. Both the pre-vent and 0-60 minute samples were lost because of difficulties during analysis, so the starting conditions in the store are not known. After this, values were relatively low ($0.02\mu\text{g}/\text{l}$) but stable until 24 hours ($0.16\mu\text{g}/\text{l}$). This high value is likely an anomaly (eg., dust/particles of CIPC), because later samples at 48 hours and 5 days later were similar to the lower values. These results are inconclusive, and a repeat of the work was scheduled for May/June. The vapour build up part of the trial was also repeated. The work was moved to another store because, in general, levels in Store 35 were very low compared to previous values in empty stores under equivalent conditions (10°C , ambient RH usually produces around $0.1\mu\text{g}/\text{l}$ compared with $\leq 0.05\mu\text{g}/\text{l}$ in this store).

Because the floor covering effect was not clear, the trial was repeated in reverse, that is, the starting condition was with the floor covered. The starting concentration sample was collected, then the doors opened and the plastic sheeting removed. After a period of purging the atmosphere, the doors were closed and samples were collected at hourly intervals to compare conditions with the floor uncovered.

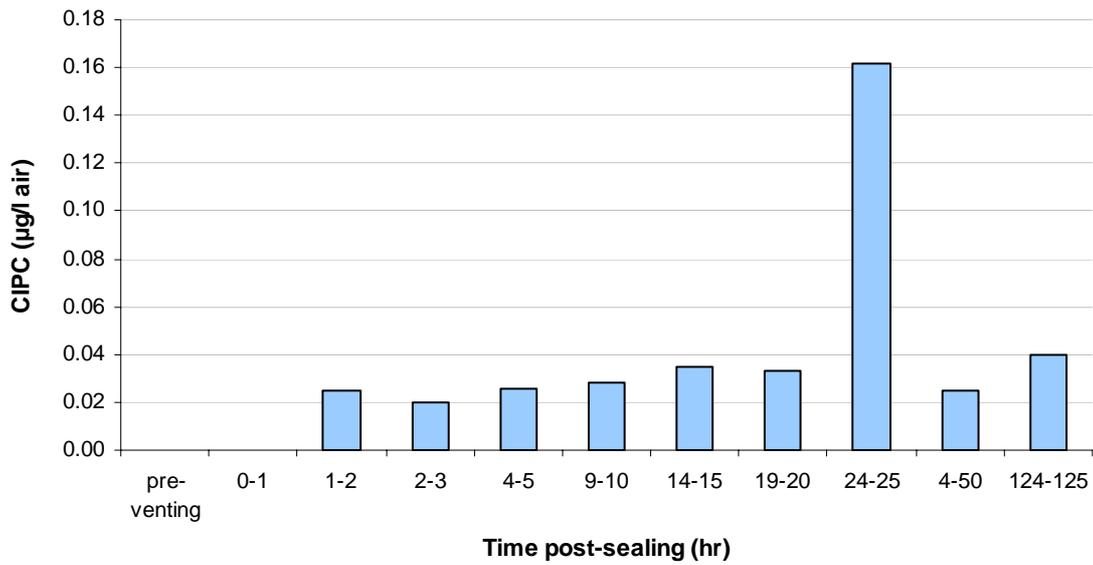


FIGURE 23 CIPC CONCENTRATIONS IN STORE 35 WITH THE FLOOR COVERED (PLASTIC SHEETING)

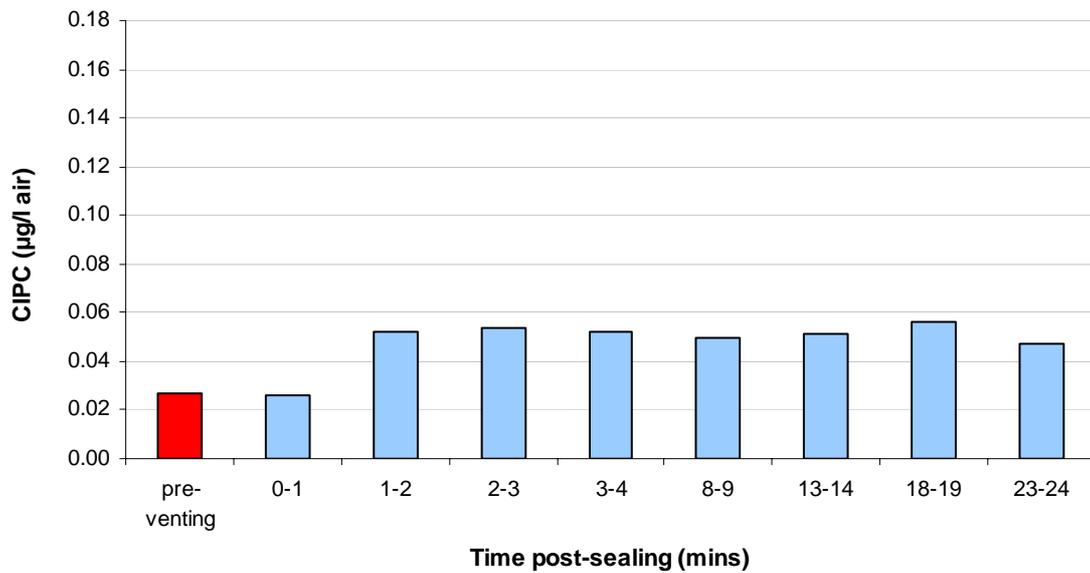


FIGURE 24 CIPC CONCENTRATIONS IN STORE 35 DURING 24 HOURS FOLLOWING REMOVAL OF FLOOR COVER

May-June 2005: Working in Store 33. Levels much more similar to expected (0.1µg/l ballpark) so a better store to work in – more chance of seeing a reduction/build up effect.

Vapour build-up 31st May (repeated because work was being done in a new store): Store closed and set for 10°C and ambient RH then left over the weekend to equilibrate. On Monday morning, both front and back doors were opened and fans run

to purge the atmosphere. A pre-venting sample was taken, and then hourly sampling (for 60 mins) until 7-8 hours, then 11-12 and 23-24 hours post-sealing. Again, values had recovered to 70% of the starting value within 2 hours of store closing, and to 90% of original values by 7-8 hours.

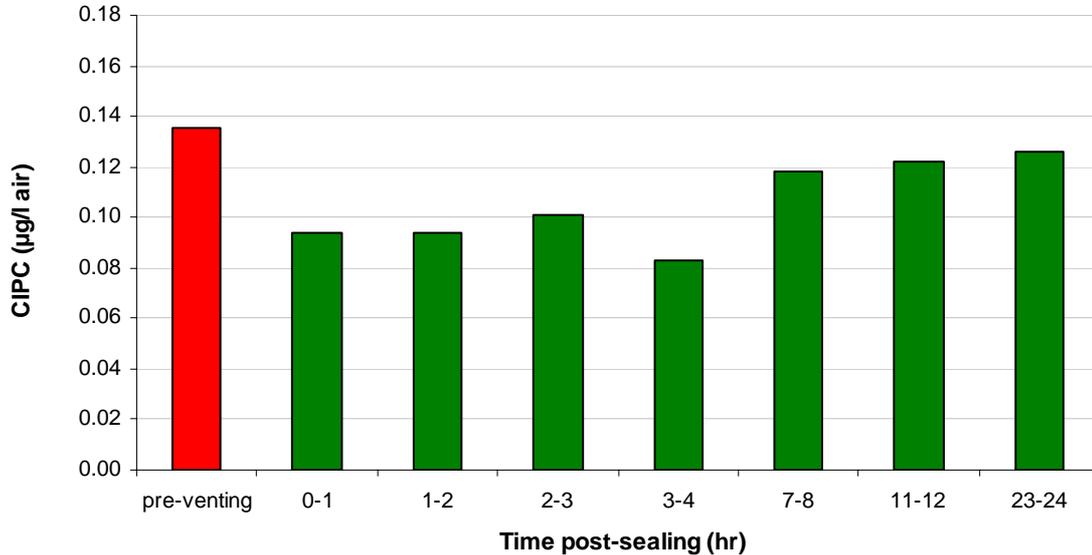


FIGURE 25 CIPC CONCENTRATIONS IN STORE 33 IN THE 24 HOURS POST PURGING BY VENTING

Floor covering 1st June: Front and back door opened and floor covered with plastic sheeting. Store fans were run with the doors open for c.40 minutes to purge the atmosphere. Extractor fans in the main hangar were also run during this period. Samples were collected at hourly intervals (from 0 hours up to 8 hours) then from 11-12 hours during the night and 23-24 hours the following morning.

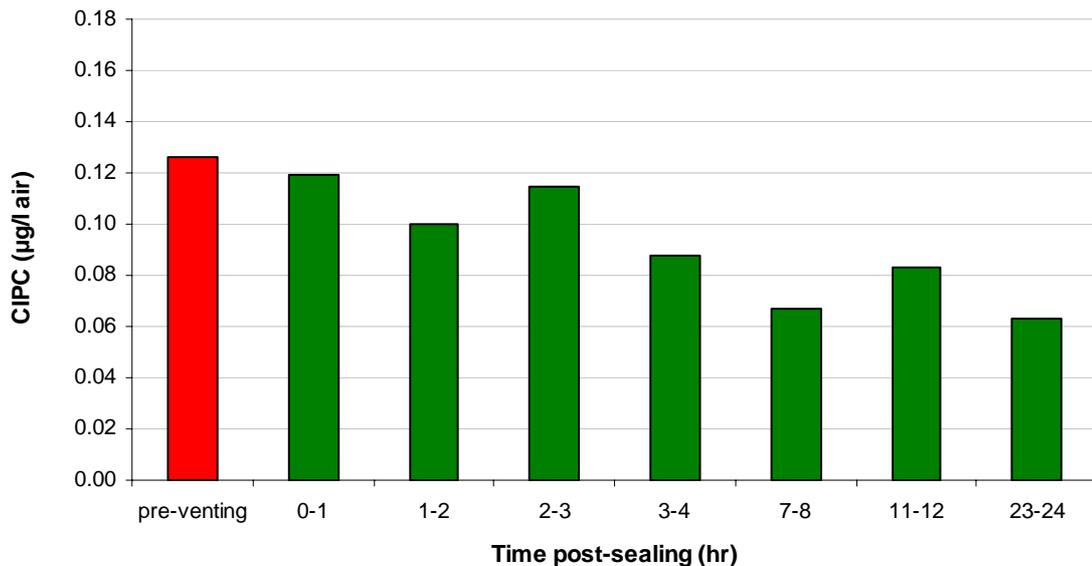


FIGURE 26 CIPC CONCENTRATIONS IN STORE 33 IN THE 24 HOURS AFTER THE FLOOR WAS COVERED

Store cleaning 2nd – 3rd June: The whole store was vacuumed, and then pressure washed at c.90°C with particular attention paid to the floor. The washing water was swept down the drain, and the wet floor vacuumed. A floor scrubber with abrasive pads was used on floor, then a repeat pressure washing at 90°C. The store was left to dry overnight with the doors open but no fans running. The following morning, the store was switched on for 10°C and ambient RH. Although no sample was taken, the starting level is assumed to be similar to those in the floor covering work on 1st June.

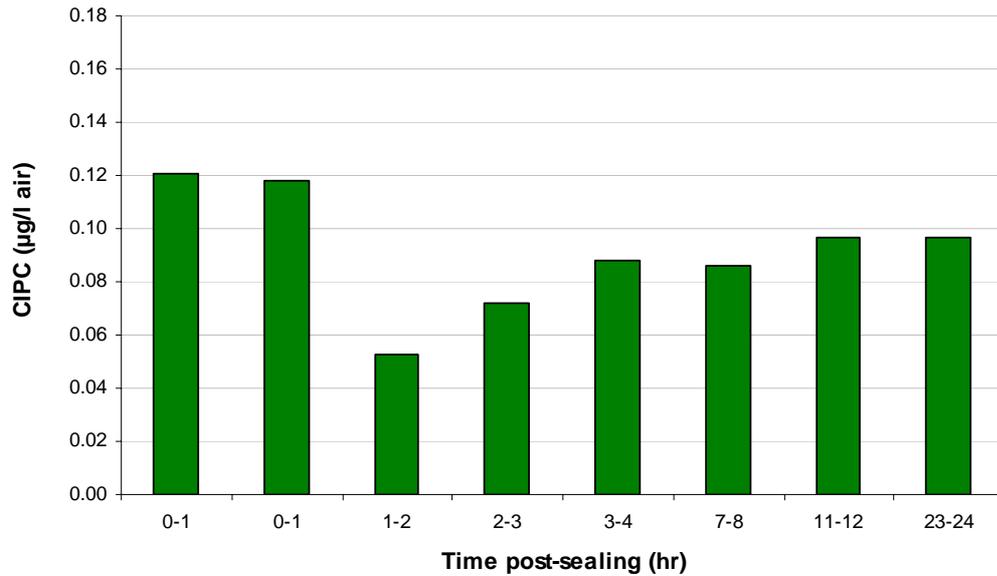


FIGURE 27 CIPC CONCENTRATIONS IN STORE 33 IN THE 24 HOURS FOLLOWING STORE CLEANING

The CIPC concentration in the duplicate samples collected between 0-1 hours of closing the doors is as high as usually seen in these stores. The low value at 1-2 hours is thought to be an anomaly, rather than a significant effect. Cleaning and covering the floor do not reduce vapour levels significantly, which suggests there is some other source of contamination in the store. Possible contenders would be the ceiling (fog rises so particular contamination of this surface is possible) and the plenum chamber (metal surfaces with difficult access for cleaning).

After the store was cleaned, the floor was re-covered – pressure washing at 90°C was assumed to have been relatively effective at removal of contamination from the walls (pvc film coated, mild steel faced, composite panels) of the store.

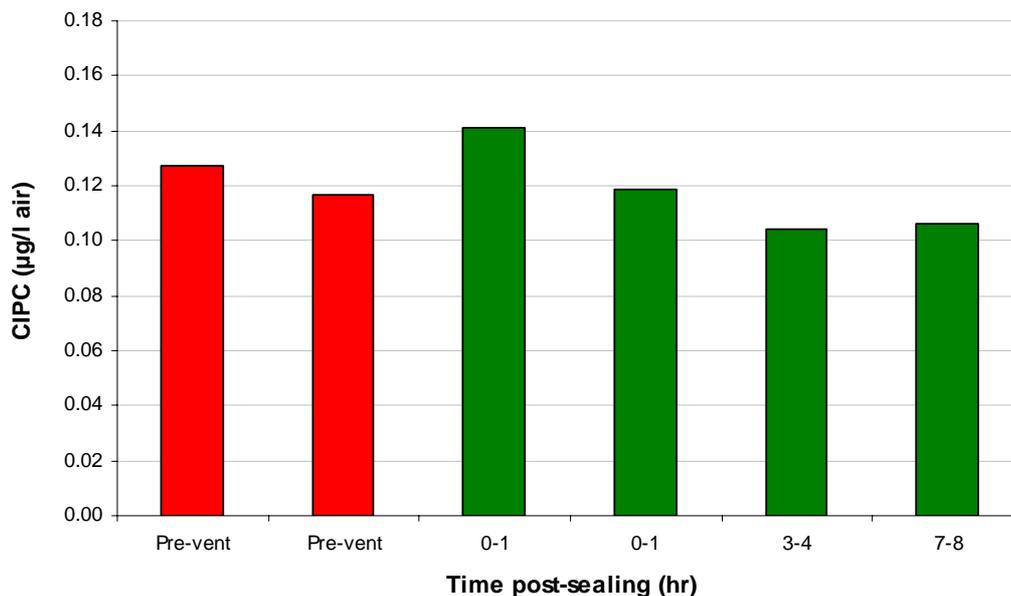


FIGURE 28 CIPC CONCENTRATIONS IN STORE 33 AFTER STORE HAS BEEN CLEANED AND FLOOR RE-COVERED

As shown in Figure 28, there was no difference between the pre-venting and post-sealing samples, even at 0-1 hours.

Conclusion:

It was not possible to identify which store fabrics are most responsible for the residue in the air. Floor covering made little difference, which suggests that significant amounts of chemical are elsewhere in the store or that the CIPC is mobile through the plastic. Steam cleaning, pressure washing and scrubbing of surfaces also had little effect. After the cleaning, re-covering the floor still did not reduce the amount of CIPC vapour in the atmosphere.

When the fans were run, air from the hangar was used to purge the store, rather than outside air. If the air in the building is also contaminated, it is possible that this process of purging did not reduce chemical levels in the store.

Planned experiments were designed to investigate the relative contribution of a range of surfaces by bonding the open end of a plastic sampling bag over an area of surface (floor, wall, plenum, ceiling etc) and inflating the bag with fresh air. Samples were removed from the bag after a period of equilibration. The set-up is shown below, which could easily be adapted to isolate surfaces other than the floor. Due to restrictions on store availability, this work could not be completed.

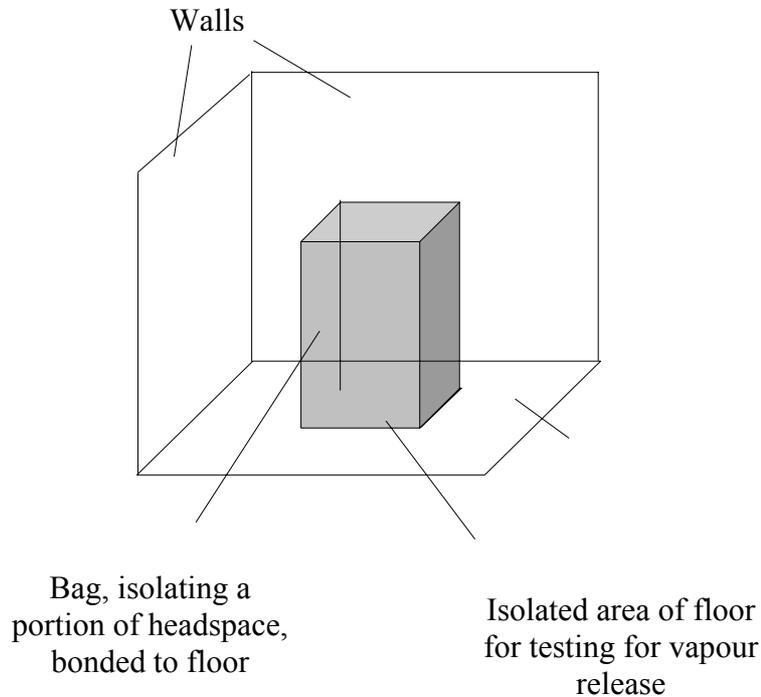


FIGURE 29 METHOD FOR SAMPLING HEADSPACE ABOVE AN ISOLATED AREA OF SOURCE MATERIAL

Various treatments could then be applied to the suspected source of contamination such as covering the floor with impermeable plastic, washing/scrubbing, treatment with H_2O_2 / Jet 5 (which may degrade CIPC on direct contact), painting, adding a fresh skim of concrete (in the case of the floor). The preferred approach would be to seal the chemical in, rather than attempt to remove it, if possible, since methods relying on direct contact with the CIPC may not penetrate to depth within the fabrics.

Towards the end of the project, the use of an ozone generator as a method for degrading airborne CIPC was suggested, but there was insufficient time to do the required trials. This is, however, considered a promising option. If done at the very low levels safe for human exposure, an in-store ozone generator could run throughout the season providing a constant supply of radicals to break down CIPC as it is released from the fabrics. Removal of CIPC may also stimulate the release from contaminated fabrics to replenish the air concentration, which may serve to deplete the reservoir of CIPC in the store. Ozone treatment in stores may also have other benefits including improved store hygiene and control of storage pathogens [e.g. Barnes (2005)] for control of conditions like silver scurf.

Overall, attempts to treat contaminated stores have not been successful, since it has been difficult to isolate which material in the store is responsible,

At present, the advice must still be that sensitive materials (e.g. seed potatoes, cereals etc) are not stored in buildings that have any history of CIPC treatment.

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