Final Report

Evaluation of CIPC application and behaviour and its influence on the variability of CIPC residues: small scale trials

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CONTENTS

1 SUMMARY 3
2 INTRODUCTION 4
3 MATERIAL AND METHODS 5
3.1 Mini-fog trials 5
3.2 Effect of condensation 6
3.3 Formulation 7
3.4 Fog quality 7
3.5 Semi-commercial trial 9
4 RESULTS 11
4.1 Mini-fog trials 11
4.2 Condensation 11
4.3 Formulation 19
4.4 Fog quality 30
4.5 Semi-commercial trials 32
5 DISCUSSION 36
6 CONCLUSIONS 39

1 SUMMARY

A fogging system was constructed to allow small-scale CIPC treatments to take place examining the role of condensation, formulation (proportion of solvent) and fog quality. Samples were analysed using conventional analytical chemistry and were also used for the development of methods for measurement of CIPC vapour release from tubers and a new CIPC particle visualisation method using UV fluorescence microscopy. Small-scale trials were inconclusive. For example, although condensation resulted in CIPC becoming harder to remove from tubers, this effect was not evident when the experiment was repeated. Differences in the CIPC vapour release from tubers were measured across experiments, however this method is not yet sufficiently robust to allow discrimination between small changes in the potential for vapour generation. Measurement of CIPC particle parameters (number, area, length and perimeter) using the new UV visualisation method did not correlate with other assessments.

Further work is required on CIPC analysis methodologies especially CIPC vapour concentration, the potential of tubers to generate CIPC vapour under varying storage conditions and how this affects efficacy of sprout control. The efficacy of CIPC is considered to be dependent on its ability to volatilise. Previous research has demonstrated that in the absence of particulate CIPC, or when particles are some distance from eye regions, effective sprout suppression is reliant upon movement of CIPC vapour to the sprout.

In a semi-commercial scale trial, CIPC was applied to separate boxes of potatoes during temperature pull-down (at either 10°C, 7°C or 3.5°C) to a holding temperature of 3.5°C. Applications at the warmer storage temperatures were associated with higher CIPC vapour concentrations. In addition, at the holding temperature of 3.5°C, CIPC vapour release tended to be greater in samples treated at the warmer temperatures. ‘Accumulation’ of CIPC on untreated tubers, located amongst treated tubers post-application, corresponded with CIPC vapour concentration and sprout control efficacy.

Results suggest changes in CIPC management in low-temperature stores could improve sprout control efficacy and reduce inputs. This work is currently being repeated.

2 INTRODUCTION

Previous research in bulk potato stores (Project R265) indicated that a significant amount of CIPC was redistributed in the storage period following application. It was considered that a better understanding of CIPC particle behaviour and how this could be influenced by application and/or storage conditions may enable this process of redistribution to be influenced constructively towards creating more even and predictable CIPC residues. Particular emphasis was given to the impact of storage temperature, the association of CIPC with a solvent, the influence of condensation and using airflow to examine different portions of fog as it settled over time. The attachment and release of CIPC to/from tubers was examined to determine if the capacity for redistribution was affected by the above noted conditions.

In the first and second years of the project a mini-fog system and associated chamber (equivalent to a store) were assembled/constructed and tested (Fig.1). The standard operating conditions developed for the fogger were: air temperature of 300°C with a flow rate of 0.2205m^3min^{-1}. These conditions were used throughout all trials conducted and reported here.

Under standard operating conditions the system was validated using application with a 50% methanol CIPC formulation. These trials indicated that application efficiency[1] was between 10-14% (representative of conventional commercial applications). CIPC particles had approximate lengths of between 2 and 20microns (deposited on waxed glass slides and assessed by light microscopy-Leica ATC 2000) and that CIPC concentration in the box air could be assessed satisfactorily over time as the fog settled out.

A more advanced technique for CIPC particle assessment was developed which utilised the robust UV stability of the carbon ring structure of chlorpropham. This provided sufficient signal strength to assess the deposited particles using UV fluorescence microscopy, while avoiding the use of solvents, adhesives or high and low temperatures, associated with other types of microscopy that would compromise the sample integrity. CIPC particle parameters were assessed by UV fluorescence microscopy (Zeiss Axioscope, O2 Zeiss density filter, Plan-Neo fluar 10x/0.30 Carl

[1] Application efficiency is the concentration of CIPC on tubers, as a proportion of that applied.

Zeiss E-PL10 x/20 eyepiece, RSImage software for camera, Photometrics CoolSNAP camera and Esivision (analysis) 3.2 software). Images were assessed using the aforementioned software for total particle count, then for individual particles: length of longest axis, perimeter and area (as viewed from above) on a micron scale.

As this was a new method under development, replication was high for all samples. Most often three tubers would be selected to represent a sample. From each tuber two sections were prepared. From each section three individual locations were imaged and assessed. All results were combined to generate a mean and associated statistics per sample.

It was determined in the second year that solid, solvent-free CIPC formulations could not be reproducibly applied through the mini-fog system, due to intermittent blocking of the fine bore nebulizer application system (used to introduce the CIPC formulation into the hot air stream) and delivery lines. It was concluded therefore that the best way to proceed was to look at a gradient of solvent concentration in CIPC formulations to examine if there were any changes in properties as a result of this association. Hence all treatments contained a solvent to varying extents.

3 MATERIAL AND METHODS

3.1 Mini-fog trials

The role of tuber condensation, formulation (solvent strength) and recirculation were investigated. In these studies small numbers of tubers were used and these were generally washed prior to experiments. Three methods of tuber CIPC analysis were used. CIPC deposit results were obtained by gently brushing tubers, without the use of any solvents, prior to the analytical extraction procedure. CIPC residue results were obtained by washing tubers under running tap-water and air drying prior to the analytical extraction procedure. Solvent washed results were obtained by ‘rinsing’ tubers with 20ml methanol. An additional extraction procedure was used in the formulation work when this was repeated.

Fig. 1. Mini-fog system with controllable hot-air source and chamber for location of samples.

3.2 Effect of condensation

Although CIPC is only sparingly soluble in water it was considered that condensation may change the properties of CIPC. Areas of condensation in store are usually associated with greater sprout growth. The aim of these trials was to investigate if there was any effect of the presence of condensation on tubers at the time of application or subsequent to application.

CIPC (2g, 50% w/v in methanol) was applied (300°C, 0.22m^3min^{-1}) to small batches of tubers (washed and graded to 45-50mm Ø) laid out on a steel mesh grid in the mini-fog chamber. Applications were made to tubers when these were dry and wet. Where treatment was made to dry tubers, 3 cycles of condensation-drying were carried out by transferring tubers between cold (4°C) and warm, humid (10°C & 95% RH) stores on successive days. Samples for wet treatments were held at 4°C and transferred to 10°C & 95% RH, to induce condensation, prior to application taking place. Application to wet tubers was delayed until temperature of these was 10°C, but tubers maintained a wet appearance. Condensation was induced on tubers treated 'wet' in the same way by transferring between cold and warm, humid stores on successive days.

Sampling of tubers was carried out after applications (24 hours) and after post-application condensation events. The effect of condensation on the 'strength' with which CIPC was retained on tubers was assessed. In addition, the ability of tubers to

generate CIPC vapour was assessed. Vapour release from single tubers (using three replicates) was assessed over two 1 week periods (7 and 14 days) in the first experiment and after an additional 12 weeks in the second experiment. The experiment was conducted in February 2011 and repeated in March 2011.

3.3 Formulation

The aim of the work was to investigate the effect of association of CIPC with a solvent, in the formulation, on CIPC behaviour. Assessment was made of fog settling time, deposition level on tubers, ease of removal of CIPC deposits from tubers, CIPC particle parameters and the capacity for vapour release from tubers. The trial was conducted at storage temperatures representative of processing and pre-pack industries (10°C and 3/3.5°C, respectively).

Approximately 10kg of washed tubers were placed in a tray in a single layer in the mini-fog chamber. Approximately 1.2 g CIPC was applied (300°C, 0.22m^3min^{-1}) as formulations with different concentrations of CIPC in methanol. Formulations of 10%, 30%, 50% and 90% (w/v) in methanol were made up using technical grade CIPC. Similar application rates (mass of CIPC) were obtained by adjustment of application time. The amount of CIPC applied in each case was recorded and was accounted for in the expression of the results.

The first run of this trial was conducted in June 2010 and it was repeated in April 2011. In the repeat trial an additional CIPC 'extraction procedure' was included consisting of a water wash (as per residue method) *and* a solvent wash with an air drying step between washes. In the repeat trial the cold store temperature used was 3.5°C instead of 3°C to enable the results to be related to other experimental work

3.4 Fog quality

The aim of the work was to examine CIPC fog quality and its interaction with potatoes, as the fog settled (ie as duration from time of fog production increased). It is anticipated that fog would have contained a higher proportion of relatively coarse particles at the initial extraction period. For this work, the lid of the chamber was modified to allow tubers in a pipe to be attached to the chamber and fog withdrawn, by the use of a fan, through the column of tubers.

Four layers of tubers were placed into 150mm Ø pipes on a metal grid. Tubers were graded at 45-50mm, washed and had approximately 6-7 tubers per layer. A freshly loaded pipe was used for each sampling occasion. 1.5g of CIPC was applied using the mini-fog at 300°C and 0.22m^3min^{-1} using a 50% CIPC in methanol formulation and a store temperature 10°C.

A fan was attached to the top of each pipe and during treatment was used to draw fog/air through the potatoes at a flow rate of c.2.5l/sec. The early treatment occasion was started at 5 minutes post-application and the late treatment occasion was started at 30 minutes post-application. The fog collection period was 30 seconds for the early treatment and 68 seconds for the late treatment. Different durations were used to draw an approximately equivalent mass of CIPC through each pipe based on previous data collected under the same conditions[2]

Air samples were taken before and after the column of potatoes to allow 'extraction efficiency' to be calculated, with samples collected in duplicate by solvent (methanol) trapping (Fig.2).

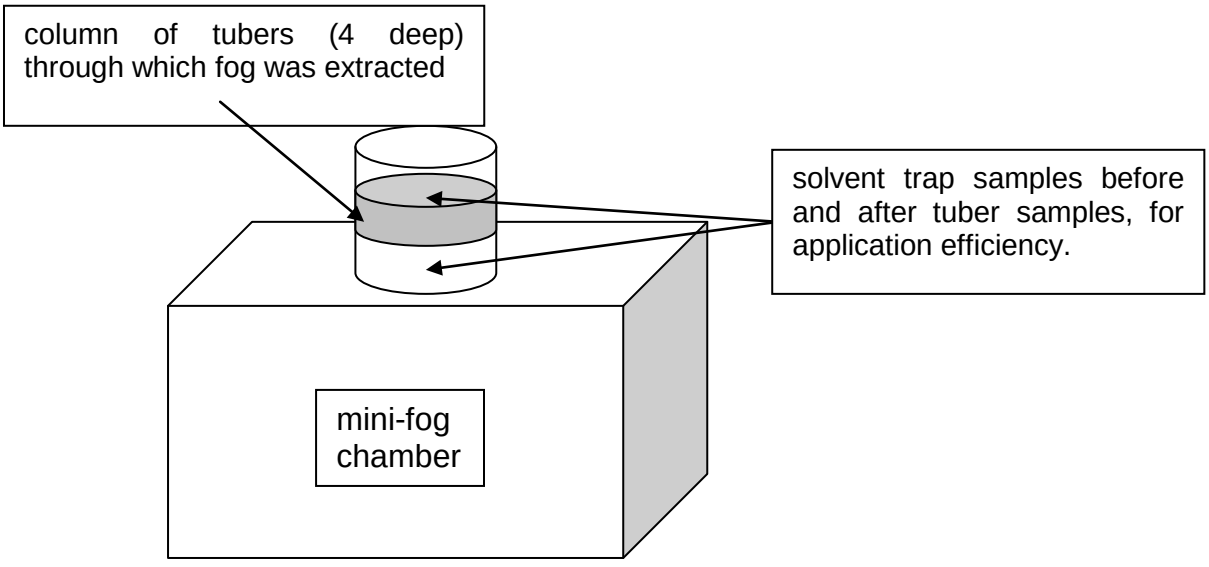


Fig. 2. Mini-fog chamber with adaptation for fog quality trial.

[2] 50% CIPC in methanol formulation fogged at 10°C, applying 1.5g CIPC giving an air concentration of c.500µg/l at 5 mins post-application and c.220µg/l at 30 mins post-application. Assuming replication of these conditions the two treatments should extract approximately 38mg of CIPC each [38160µg and 38058µg respectively for 5 minute and 30 minute treatment occasions].

3.5 Semi-commercial trial

The researchers were concerned that experimental work in commercial scale low-temperature, pre-pack stores had a risk of exceeding the maximum residue level for CIPC. Initial CIPC application was considered, by the store manager, not to have been fully effective and a further application was requested. This was considered to be as a result of limited re-distribution of CIPC following applications as a result of a low saturation vapour concentration at pre-pack storage temperatures. It was agreed with the sponsor, to continue work on a commercial scale only in warmer, processing type stores and additional work was carried out in stores at SBCSR to assist in understanding the apparent poor sprout control efficacy by CIPC in low temperature, pre-pack stores.

Four c.100kg capacity wooden boxes were made up as shown in Fig. 3, using the cultivar Maris Piper, including a netted sample for efficacy assessment and a randomised grid of tubers of cv Marfona for CIPC analyses, two tuber layers below the surface. All boxes were initially held in a CIPC untreated store. After loading, store temperature was reduced at a rate of 0.5°C per day and CIPC applied to a single box when crop temperature was 10°C, 7°C and 3.5°C. The fourth box was treated, at 3.5°C, when ‘eyes opened’.

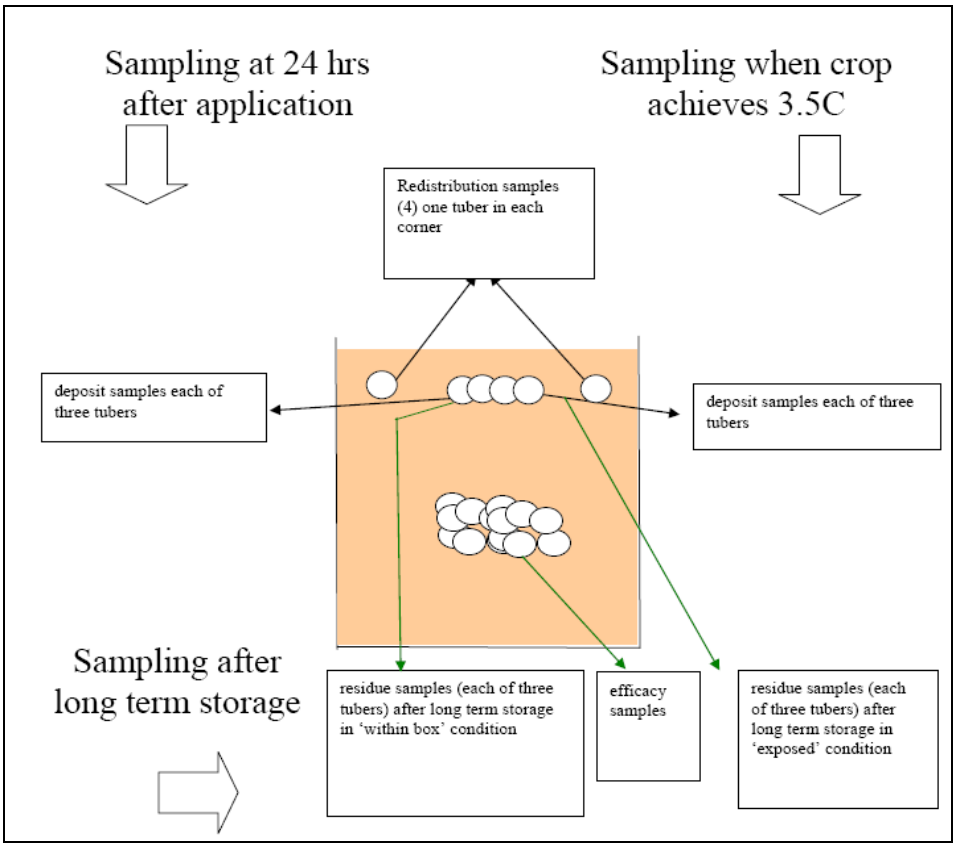


Fig. 3. Diagram of sample boxes, showing position of samples and timing.

CIPC applications were carried out in a separate 12-tonne capacity store, with chemical (*MSS ProLong*, United Phosphorus Limited) applied at a rate of 28ml (14 g) tonne^{-1} for 6 tonnes on each occasion, using a Swingfog SN-50. The store remained sealed for 24 hours after application. Following applications, initial CIPC deposit sample tubers were taken, and replaced with untreated tubers. Untreated tubers were sampled at critical phases (different application temperatures) and again replaced with untreated tubers, to allow the redistribution of CIPC (by the vapour phase) to be quantified.

After CIPC application, treated boxes were transferred to a separate (empty) store allowing assessments to be carried out in isolation from boxes treated previously. This store was also reduced to the holding temperature (3.5°) at 0.5°C per day. All treated boxes were transferred to a common holding store when the final temperature set point was achieved. Humidity was controlled (at 95% relative humidity) in the final, communal holding store.

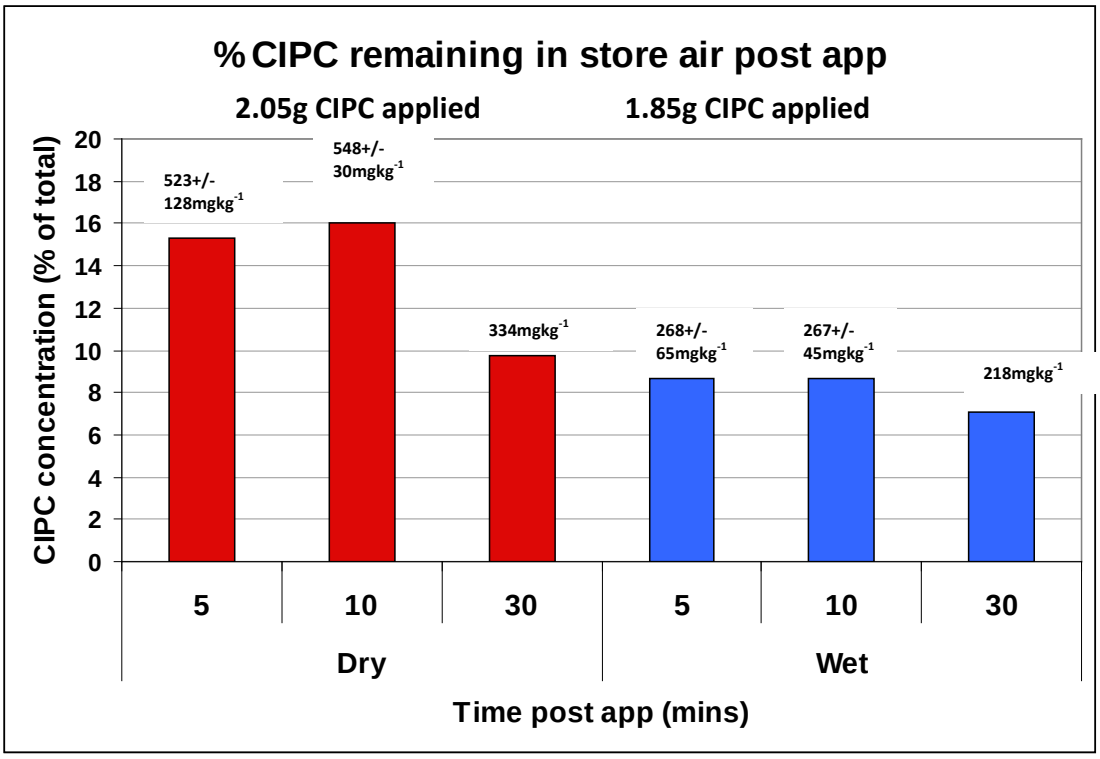
Each box was fitted with a ‘sample port’ terminating amongst tubers in the centre of the box. This was used to assess CIPC vapour concentration in air from within boxes after adsorption on *Tenax* tubes.

4 RESULTS

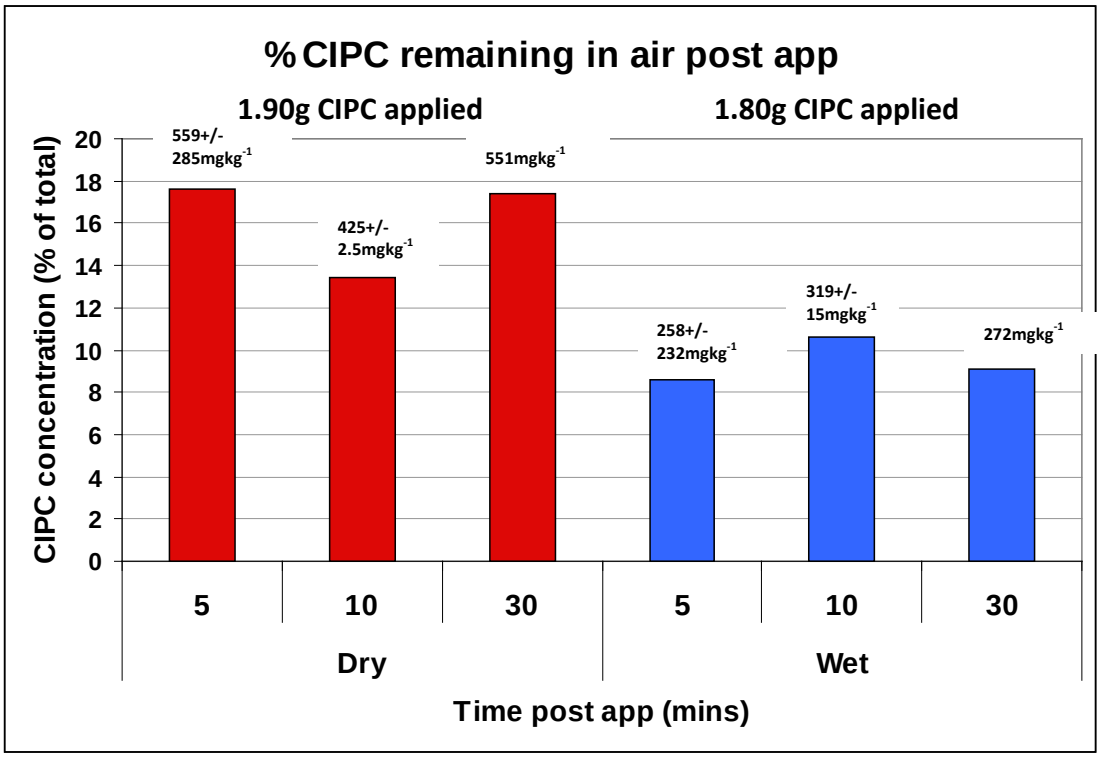
4.1 Mini-fog trials

4.2 Condensation

The concentration of airborne CIPC remaining after applications is shown in Fig. 4. In both trials there was a lower initial CIPC concentration in air when tubers were wet. Applications resulted in similar initial CIPC fog concentrations (5 minutes) however, in the second trial, the expected decline in CIPC concentration, with time, was not evident in both wet and dry treatments.



February 2011



March 2011

Fig. 4. Fog settling time in condensation trials, showing the absolute concentration remaining and the volume of CIPC applied.

Results of tuber analyses from applications to tubers when dry are shown in Fig 5. In the first experiment (Feb. 2011) application to dry tubers at 10°C, representing conventional practice, resulted in a mean CIPC deposit concentration of 4.3 mg/kg. Washing the tubers to remove loosely bound CIPC reduced the concentration of CIPC remaining attached to tubers to 2.9 mg/kg (the residue level). Solvent washing of tubers (leaving behind CIPC more tightly bound to the tuber than that which can be removed just by water) resulted in a further reduction, with just 1.6 mg/kg remaining attached to tubers. Condensation cycles, after application to dry tubers, significantly increased the 'solvent washed' concentration suggesting condensation, after application to dry tubers, increased the strength of attachment of CIPC to the tuber.

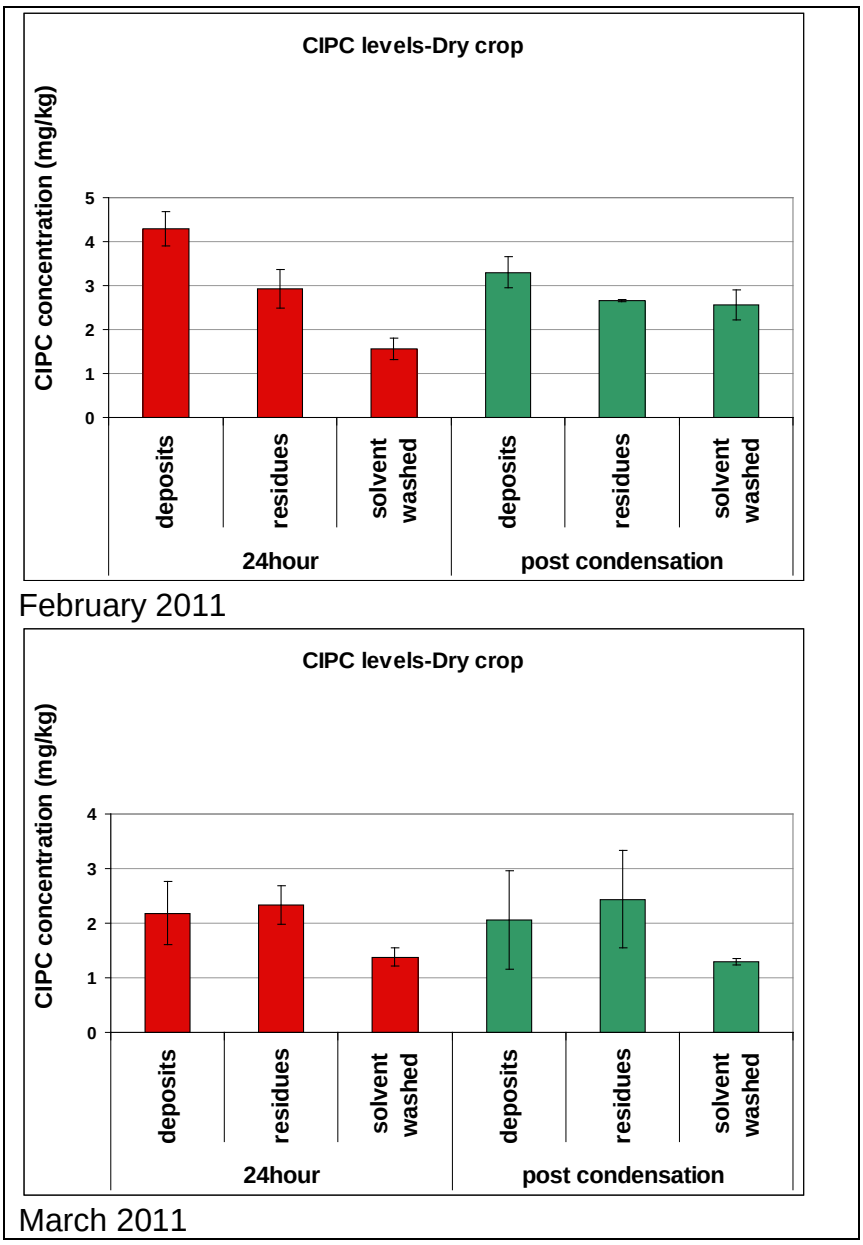


Fig. 5. Deposit, residue and solvent-washed tuber CIPC concentrations after application of CIPC to tubers without condensation.

When the experiment was repeated (March 2011) results however showed a different pattern. For crops treated when dry there was no difference in CIPC concentration of tubers when these were assessed for deposit or residue on crop sampled at 24 hours (before any condensation events) however solvent washing did reduce the concentration of CIPC remaining attached to tubers. For each of the 'extraction methods', when the experiment was repeated, there were no differences as a result of condensation, when application was made to dry tubers.

It is unclear why ‘deposit’ and ‘residue’ levels were similar for dry treated crops when the experiment was repeated and this result may not be representative. The statistical error associated with tuber CIPC concentration measurements was typically greater in the second experiment and overall CIPC concentrations lower.

Results of analyses following application of CIPC to tubers with condensation, at the time of application, are shown in Fig. 6. Differences in CIPC concentration between samples assessed for deposit, residue and following solvent-washing were very slight and not significant. This indicates that the availability of the chemical, to the different extraction methods, was influenced by the presence of a condensation layer at the time of application, with CIPC being generally more strongly bound to tubers.

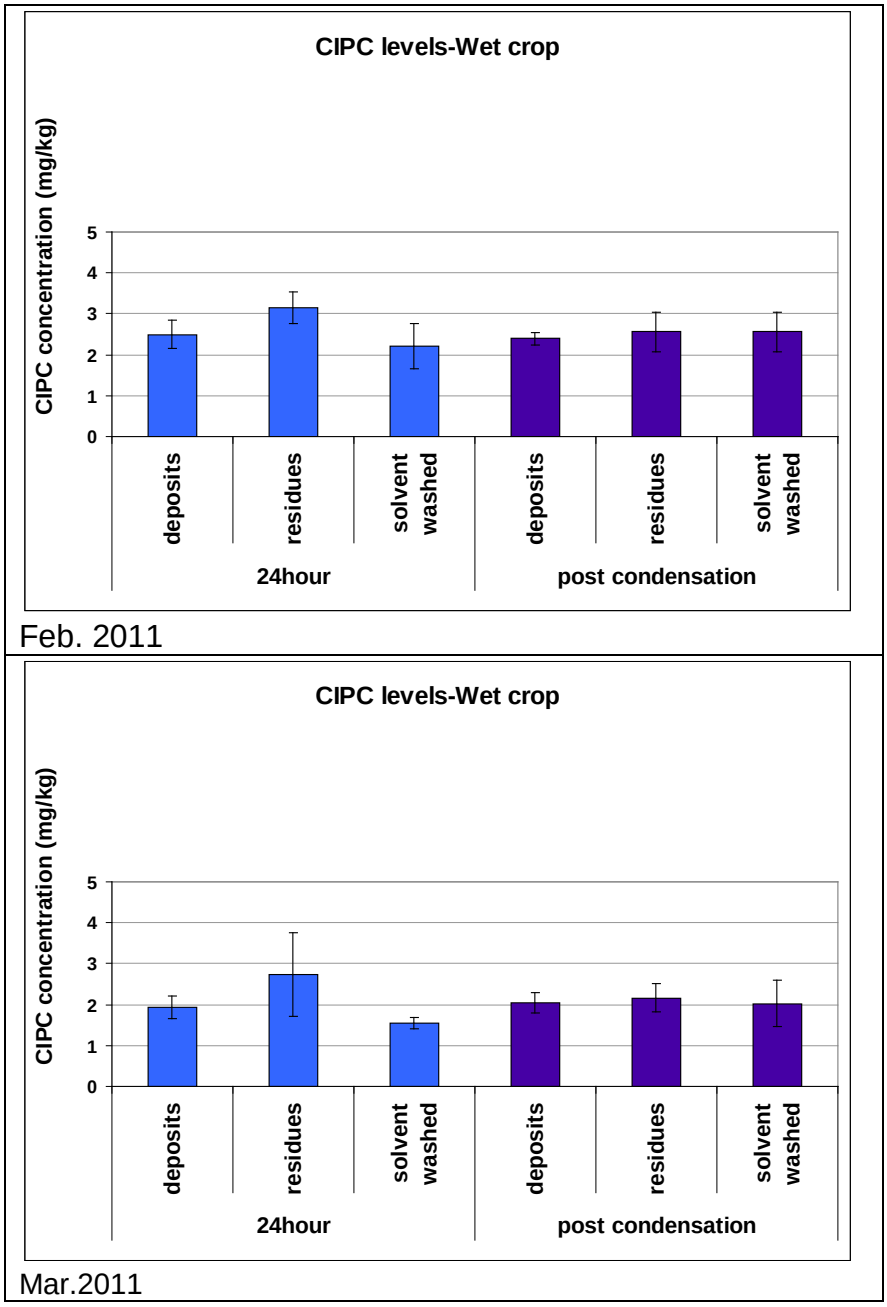


Fig. 6. Deposit, residue and solvent-washed tuber CIPC concentration after application of CIPC to tubers with condensation.

There was no significant reduction in CIPC by any water or solvent wash if tubers were wet at the time of application, compared with dry crop, which showed a reduction in CIPC concentration using solvent wash of between 34% and 63%. However, with water alone CIPC levels were only reduced in one of the trials.

CIPC particle area, particle length and particle perimeter were unchanged by condensation events in the first trial (February 2011, Fig. 7) when application was

made to tubers when dry. After further storage of the dry treated tubers however, (Dry 12 wks treatment) changes in the measures of CIPC particle dimensions were apparent. Similarly in tubers that were treated when wet, condensation events did not give rise to changes in the measures of particle dimensions until after the additional 12 week storage period. Additional storage in dry treated tubers resulted in increases in CIPC particle area, particle length and particle perimeter relative to 24 hour samples while in wet treated tubers, 'dimensions' reduced.

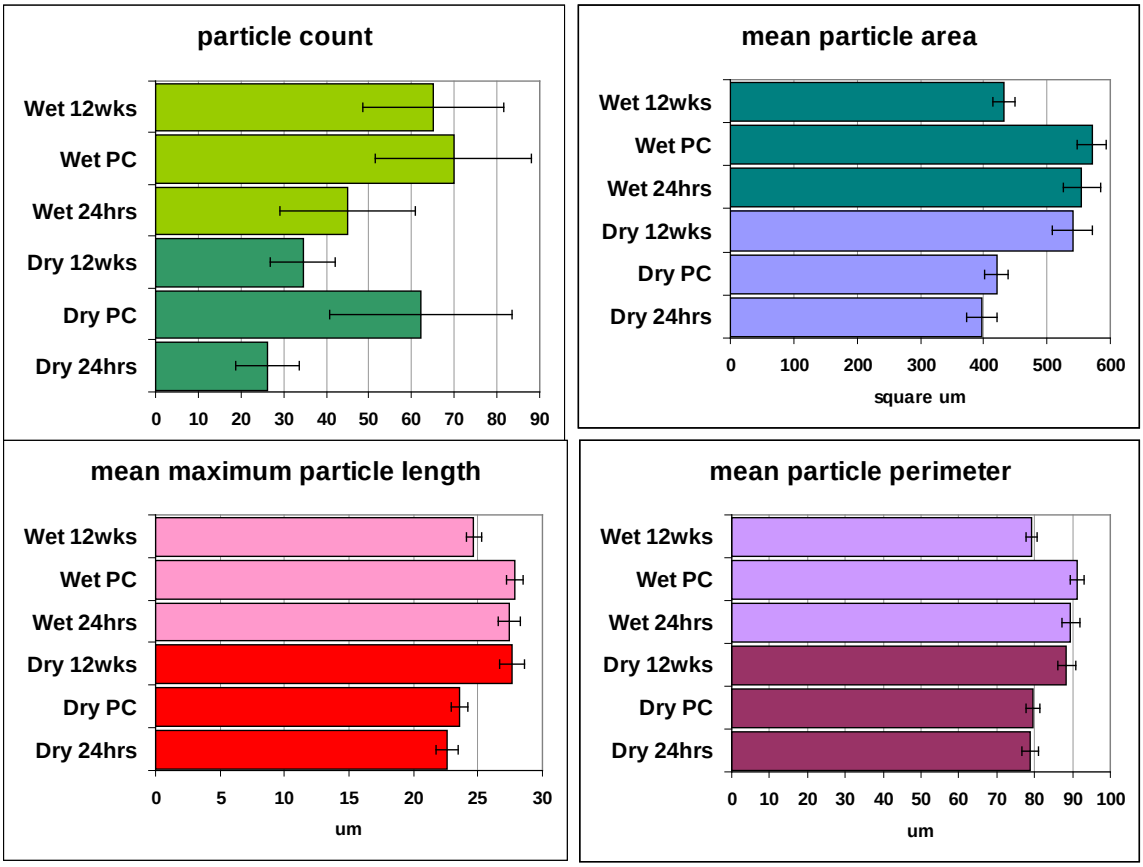


Fig. 7. CIPC particle parameters, effect of condensation trial Feb 2011

As was the case in the first trial, in this repeat condensation did not give rise to changes in CIPC particle dimensions when dry tubers were treated. However in this repeat, even after the extended storage treatment there was still no change. When wet tubers were treated, condensation resulted in an increase in dimensions (area, length and perimeter). Extended storage of the wet treated tubers, without condensation, tended to increase dimensions, in contrast to the previous trial, though differences were sometimes slight.

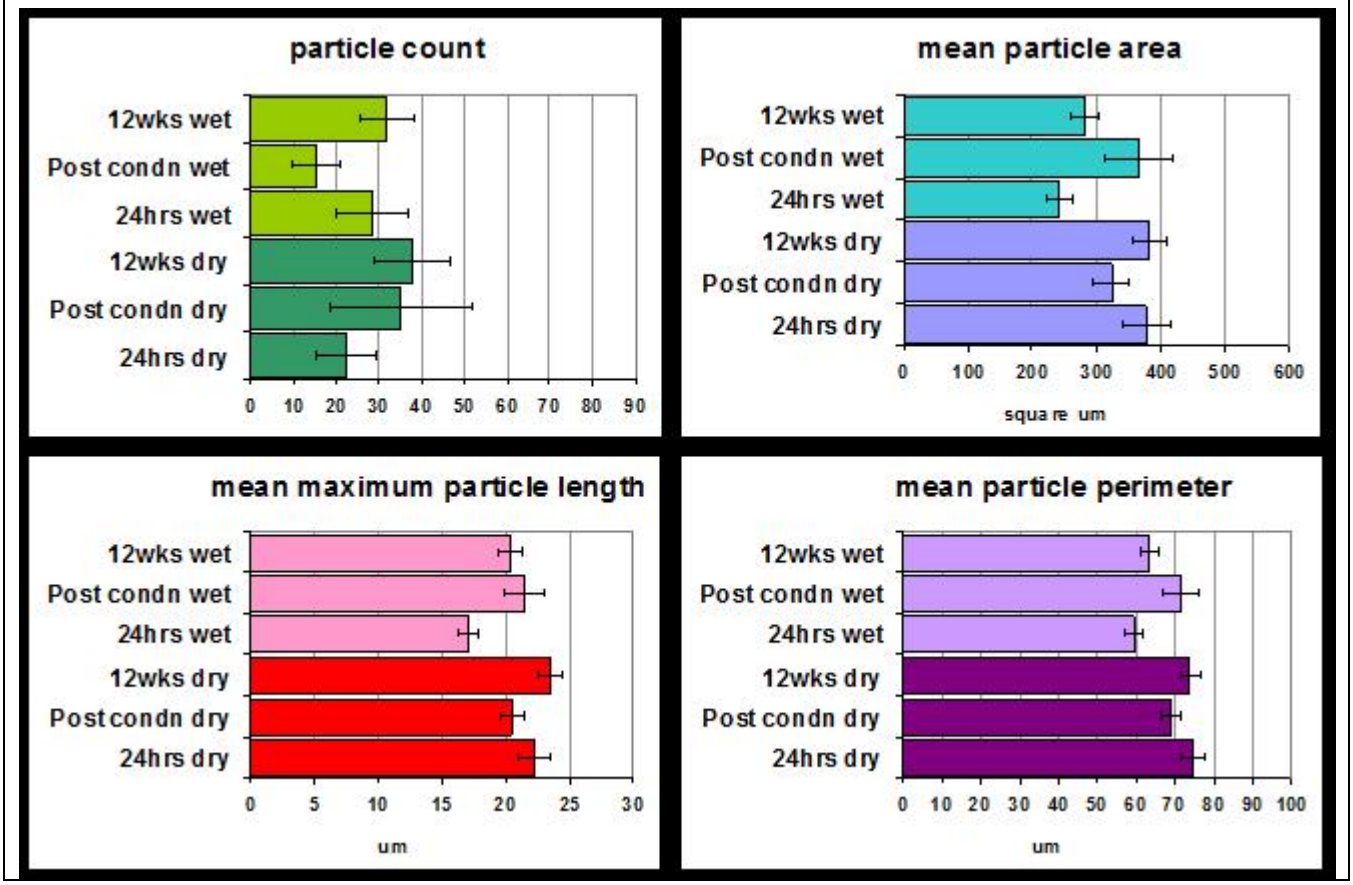


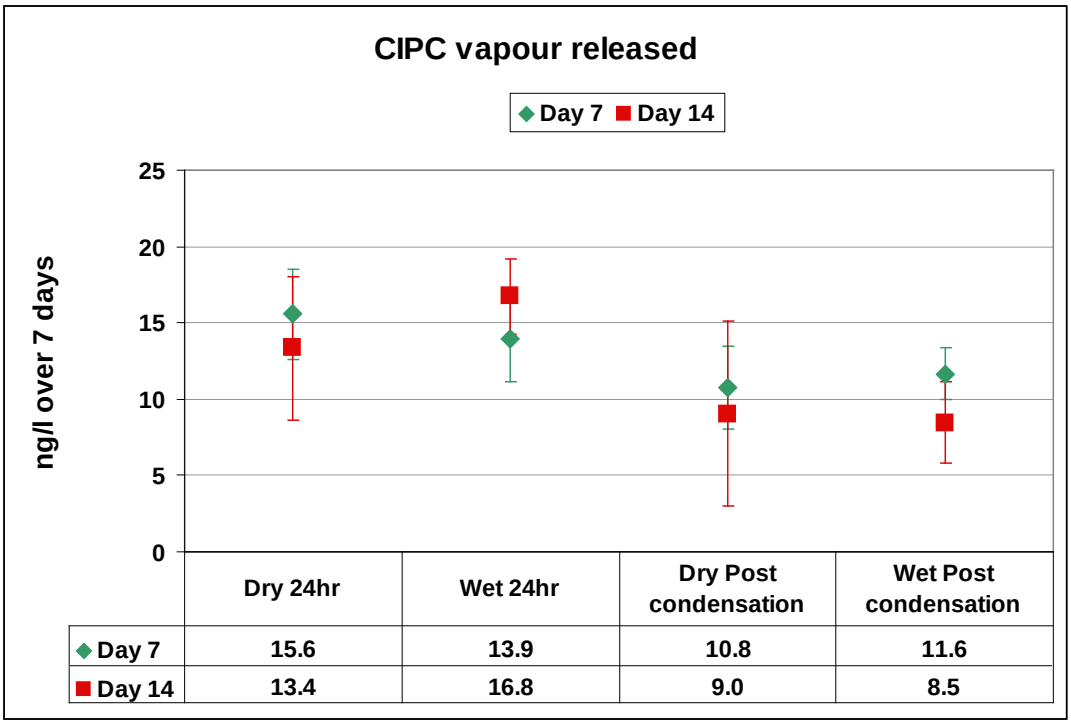
Fig. 8. CIPC particle parameters, effect of condensation trial Mar 2011.

Across repeats of the experiment the most reproducible result for all particle dimension measurements was found with the 24hrs Dry treatment, which gave very similar particle parameters of length, area, perimeter and count despite the mean deposit concentration being significantly lower in the later trial at 2.2mg/kg down from 4.3mg/kg in the first trial. With the exclusion of the 24hr Dry treatment generally particle count, mean area, length and perimeter values were lower in the repeat trial.

The effect of condensation, at the time of, and subsequent to CIPC applications, on CIPC vapour release is shown in Fig. 7. Vapour release was measured over two 7 day periods (Day 7 and Day 14) by drawing filtered air through sealed chambers containing single tubers (replicated three times) periodically through tenax tubes.

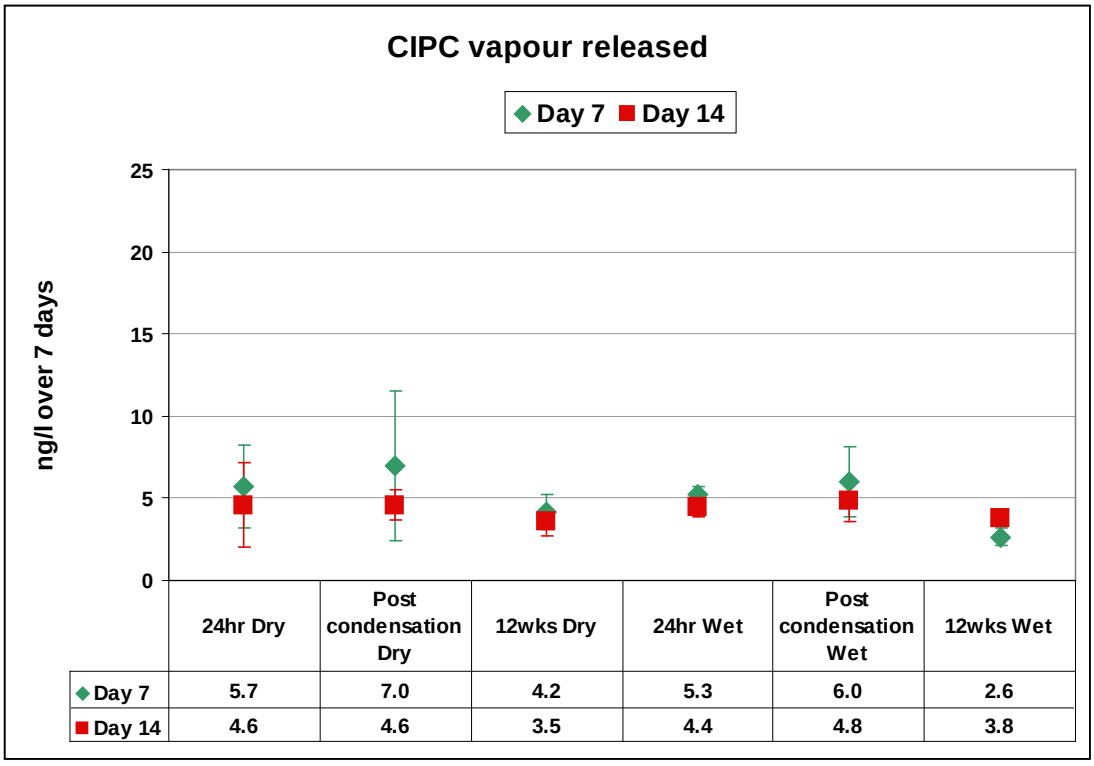
Variability in results for vapour release makes it difficult to draw conclusions. In general, vapour release was much greater following applications in the first experiment, and differences between treatments here were also greater, though not statistically significant. In the second experiment (March 2011) mean vapour release

over a seven day period was close to 5ng/l for all treatments, at around 30%-50% of the level in the first trial. Although tuber CIPC concentration (application efficiency) was slightly lower in the second experiment, this was not sufficient to reduce vapour release by >50%.



	Dry 24hr	Wet 24hr	Dry Post condensation	Wet Post condensation
Day 7	15.6	13.9	10.8	11.6
Day 14	13.4	16.8	9.0	8.5

February 2011



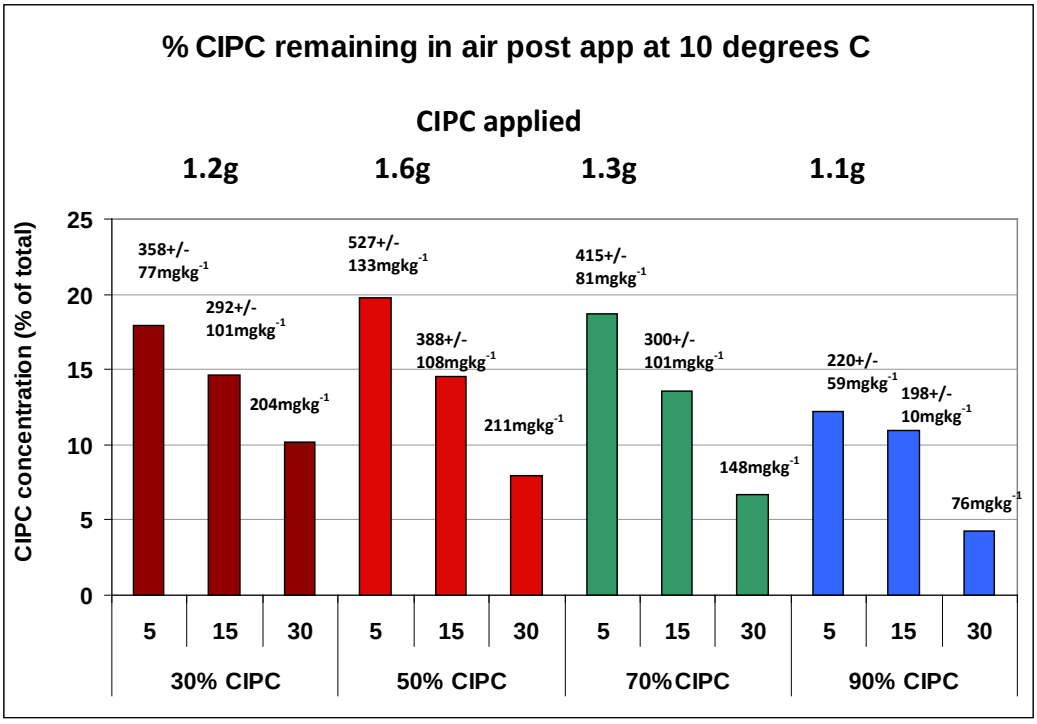
	24hr Dry	Post condensation Dry	12wks Dry	24hr Wet	Post condensation Wet	12wks Wet
Day 7	5.7	7.0	4.2	5.3	6.0	2.6
Day 14	4.6	4.6	3.5	4.4	4.8	3.8

March 2011

Fig.9. The effect of condensation on CIPC vapour release (February and March 2011 expts).

4.3 Formulation

Results for CIPC fog settling times are shown in Fig. 10 and 11 for 10°C and 3/3.5°C treatments respectively. There were no consistent trends from the different formulations. In the second experiment at 10°C the 70% CIPC formulation settled rapidly, with little remaining after 30 minutes. In the first experiment settling rate for 70% CIPC was similar to 30% and 50% solutions with 5-10% remaining after 30 minutes. There was a tendency for fog from the 90% CIPC solution to settle most quickly with generally less than 5% remaining after 30 minutes.



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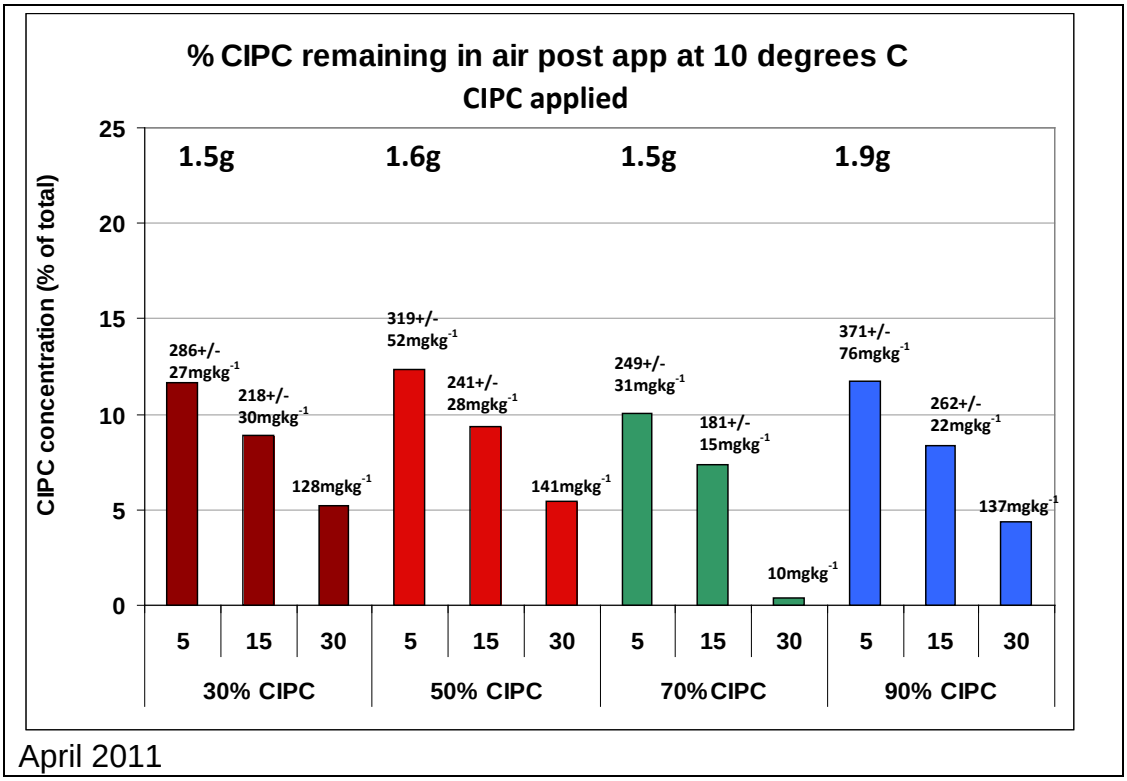
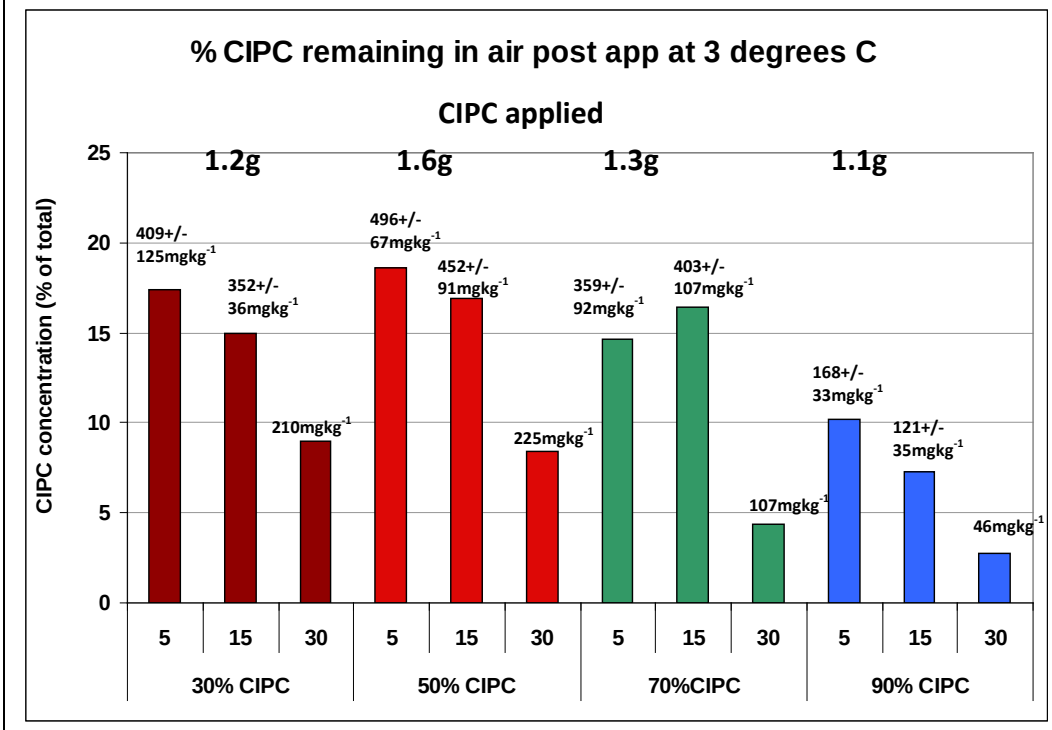


April 2011

Fig. 10. Fog settling time at 10°C, in solvent association trial, showing the absolute concentration remaining and the volume of CIPC applied.

The percentage settling results at 90% CIPC were similar in both trials at 5 and 30 mins post application. Across the concentration range, settling of fog typically occurred more rapidly in the second trial conducted in April 2011.



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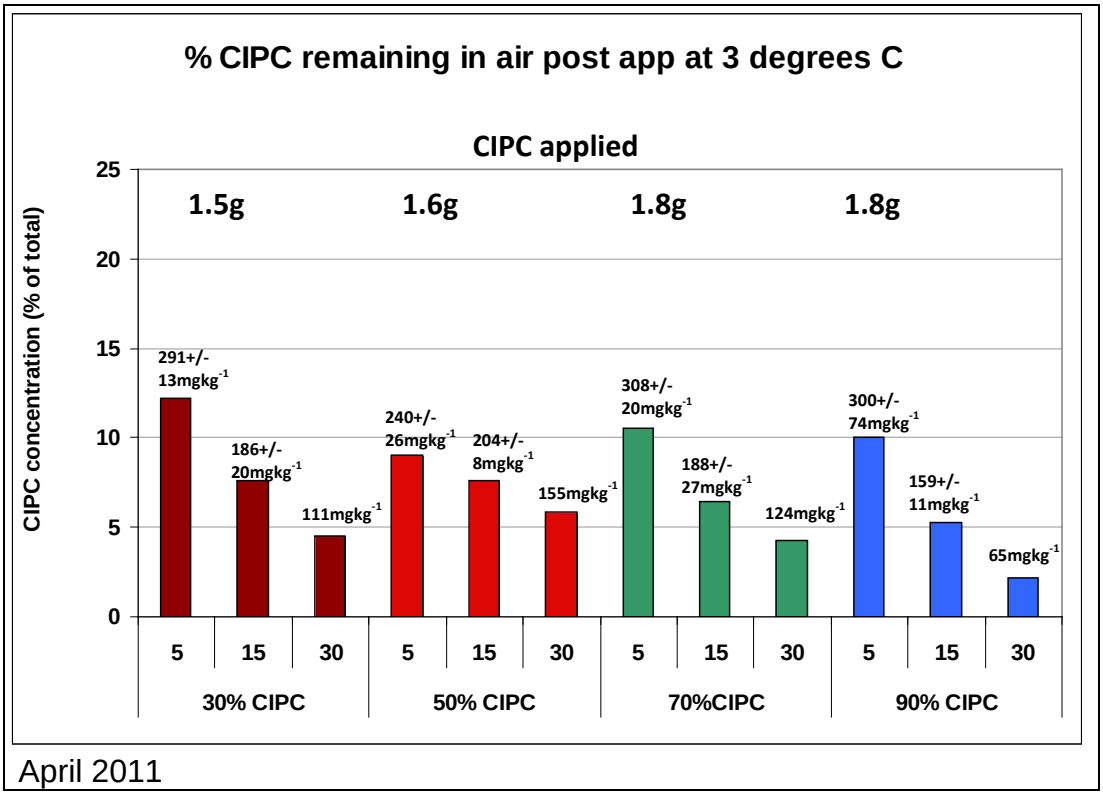
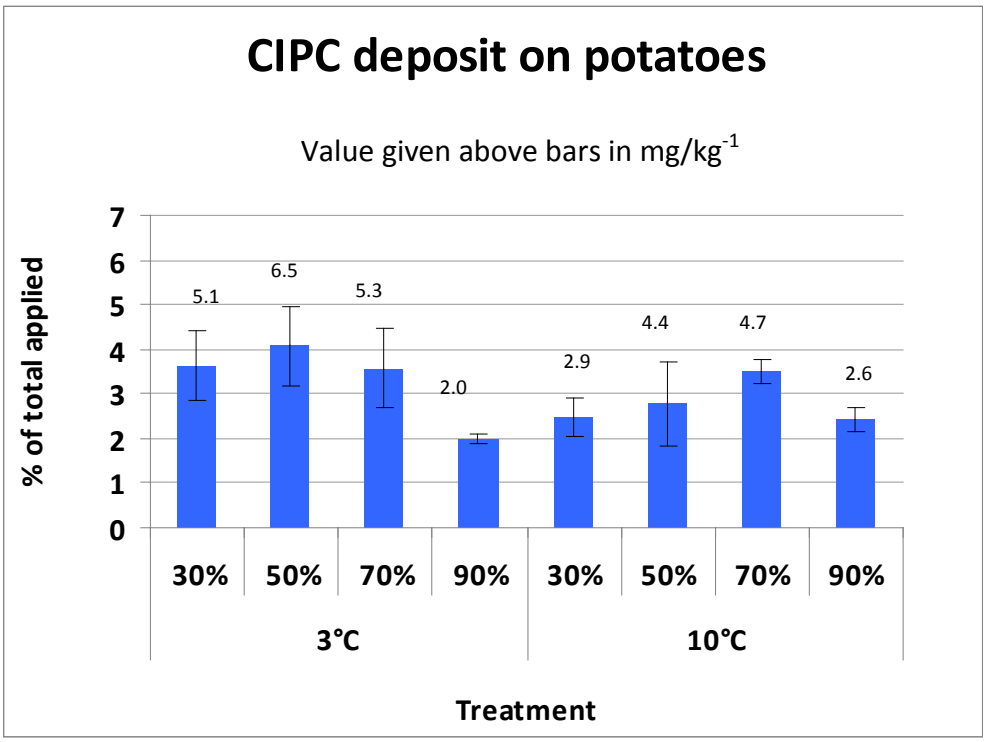


April 2011

Fig. 11. Fog settling time at 3°C, in solvent association trial, showing the absolute concentration remaining and the volume of CIPC applied.

Again it was seen that, at 90% CIPC formulation concentration, the percentage of fog settling was similar in both trials at 5 and 30 minutes post application, even at this lower ambient temperature. This is clear even though the fog settled more rapidly again in the second trial.

CIPC deposit levels on tubers are shown in Fig. 12. In the first experiment there were no differences in deposit concentration for 30%, 50% and 70% formulations when applied at 3/3.5°C or at 10°C and relatively low concentrations were recorded for the 90% formulation at both treatment temperatures. When the experiment was repeated a different pattern was evident with CIPC deposit levels generally lower (<2mg/kg compared with concentrations around 4mg/kg from the first experiment) especially at the lower treatment temperature. Efficiency of application was less in the repeat experiments perhaps as a consequence of the difficulty in reproducing applications of small amounts of CIPC in a system designed to mimic commercial scale applications. The effect was more pronounced at the colder ambient storage temperature.



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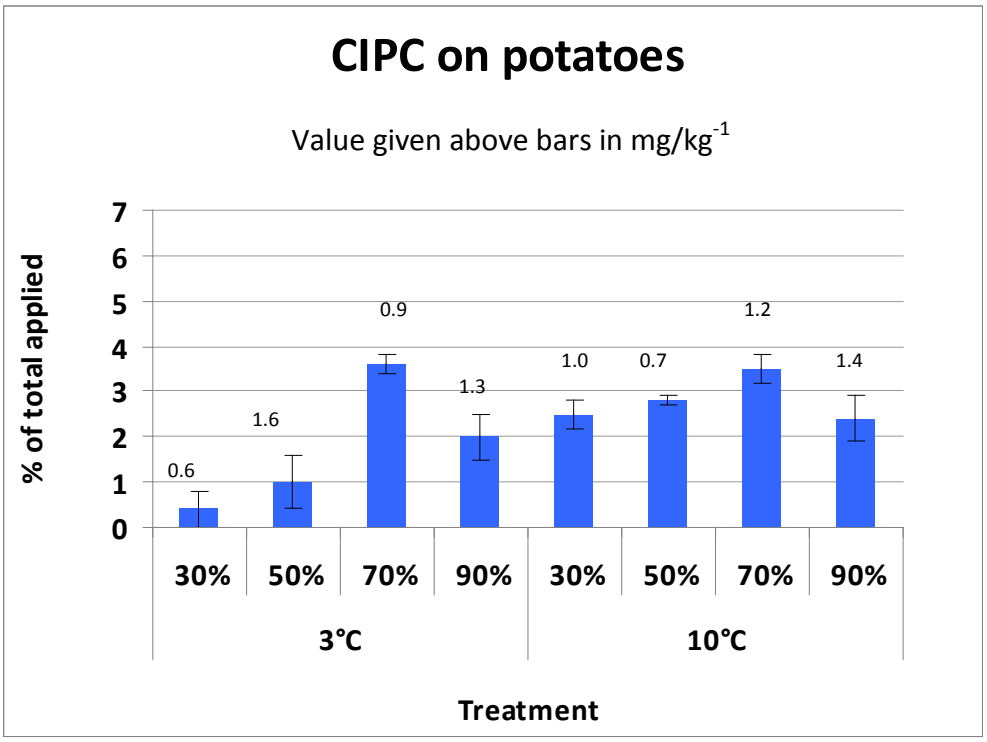


April 2011

Fig 10. CIPC deposit concentration on tubers in solvent association trials (absolute values).

Treatments carried out at 3/3.5°C in the first trial (Fig. 13) tended to have deposit concentrations greater than residue values (ie water washing effectively removed a

portion of the applied CIPC), which in turn were greater than 'solvent wash' values, however the differences between the 'extraction methods' tended to reduce as CIPC concentration in the formulation increased. Treatment at 10°C resulted in residue levels that were generally similar to deposit levels, with water removing little of the CIPC deposited. The 'solvent washing' procedure was particularly effective at CIPC removal at 3/3.5°C and 10°C application temperatures, using the 30% CIPC formulation.

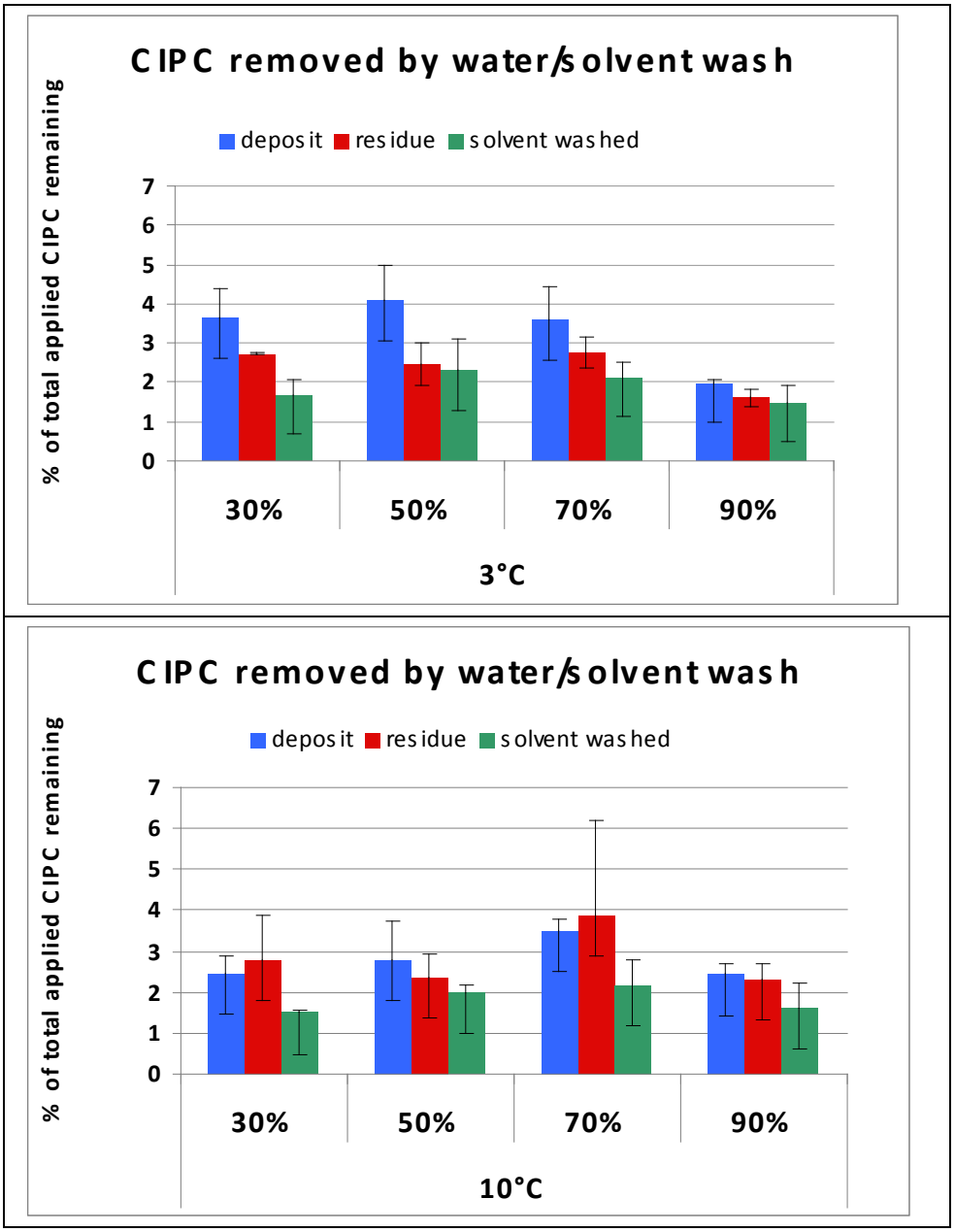


Fig. 13. CIPC removal from tubers with washing processes, 3°C and 10C treatment, June 2010.

In the repeat trial in April 2011 the deposit and residue levels found after treatment in a 10 degree storage temperature was very similar to the first trial, however at the colder storage temperature only the higher concentration CIPC formulations were close in value for deposit and residue concentration in both trials.

Both procedures that involved solvent washing were more effective at removing CIPC from crop treated at 3.5°C and 10°C. This effect was prominent across both storage temperatures.

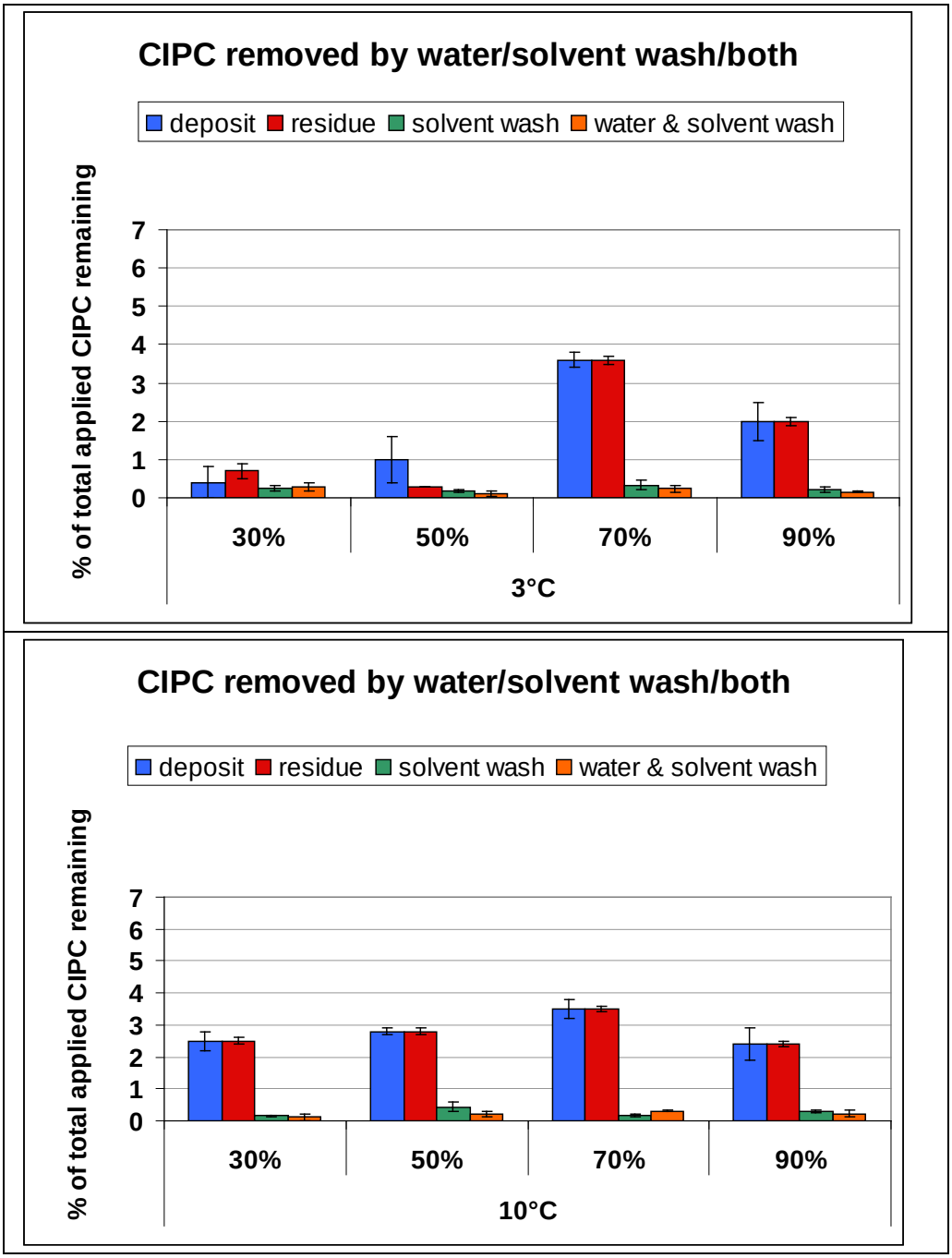
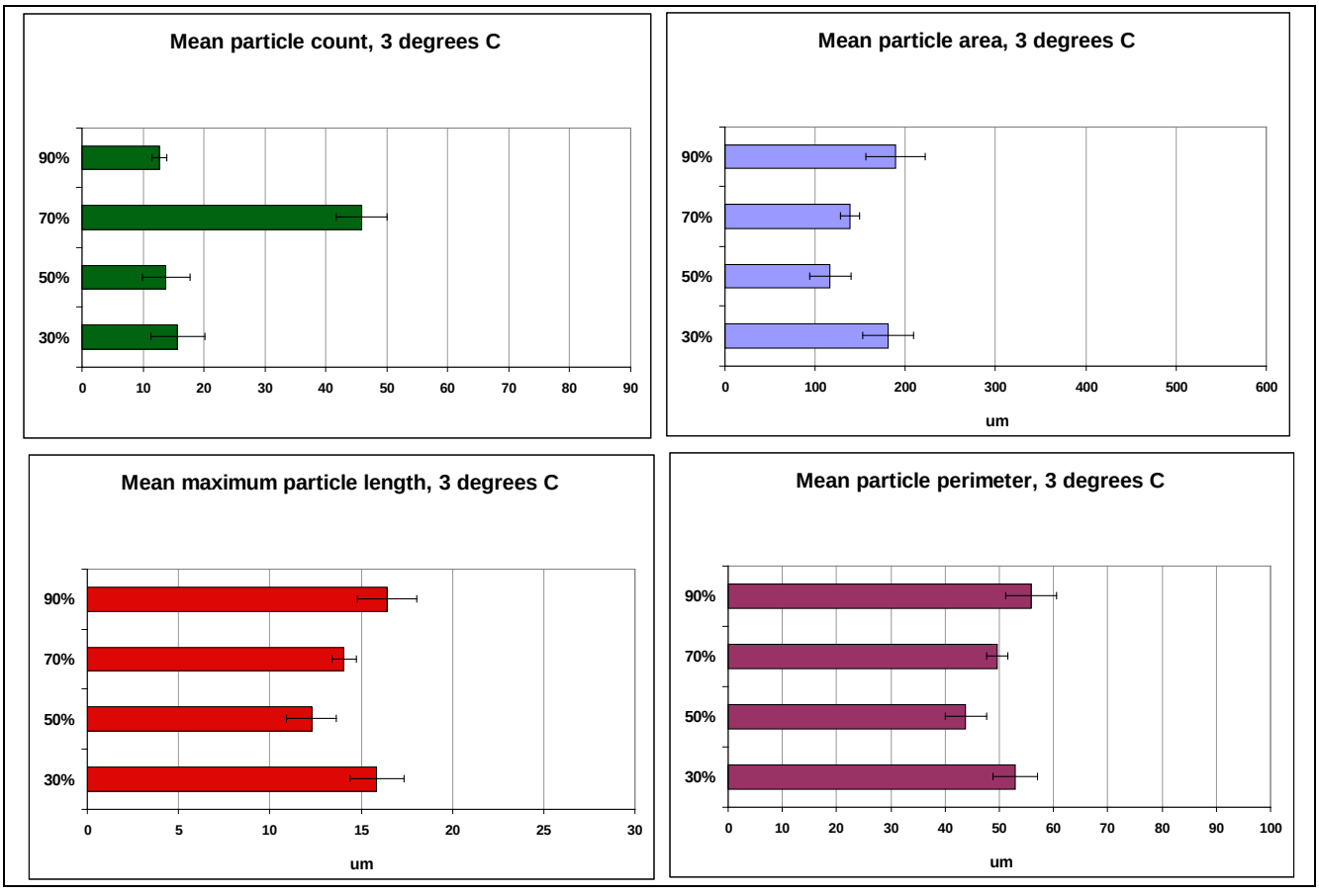


Fig. 14. CIPC removal from tubers with washing processes, 3°C & 10C treatments, April 2011.

In the first formulation trial increasing the concentration of CIPC in the formulation from 50% to 90% resulted in an increase in particle dimensions (area, length and perimeter) in tubers treated at 3°C (Fig. 15). The 30% formulation had particles with dimensions similar to the 90% formulation treatment. With applications to tubers at 10°C, CIPC particle dimensions were also similar from 30% and 90% formulations, but these were smaller (area, length and perimeter) than 50% and 70% formulations. Treatments at 3/3.5°C and 10°C did not result in major differences in physical characteristics of CIPC particles, with dimension measurements in the same range for both treatment temperatures. Particle counts were significantly higher from the 70% treatment at 3/3.5°C, and from 50% and 70% treatments at the 10°C treatment temperature. Higher particle counts for 50% and 70% treatments at 10°C were reflected by higher CIPC deposit levels, but this was not the case with the 30% solution at 3/3.5°C.



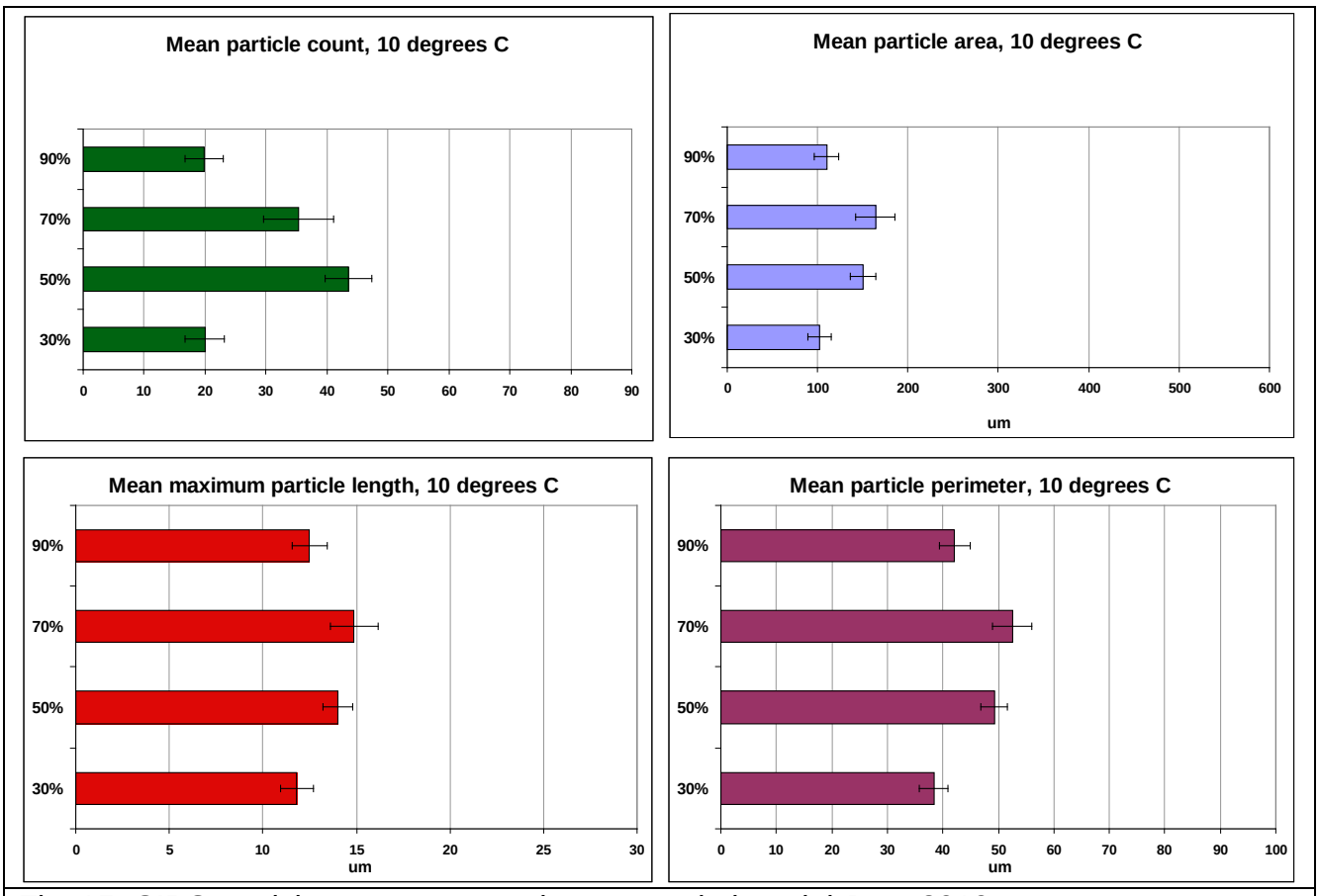


Fig. 15. CIPC particle parameters, solvent association trial June 2010.

When the trial was repeated (April 2011, Fig. 16) treatments at 3/3.5°C did not lead to significant differences in particle parameters (area, length, perimeter). Using a treatment temperature of 10°C, the 90% formulation resulted in particles with larger dimensions (area, length, perimeter). Relatively high particle counts occurred in the 30% formulation treatment at 10°C although this was not associated with a CIPC deposit level greater than other treatments.

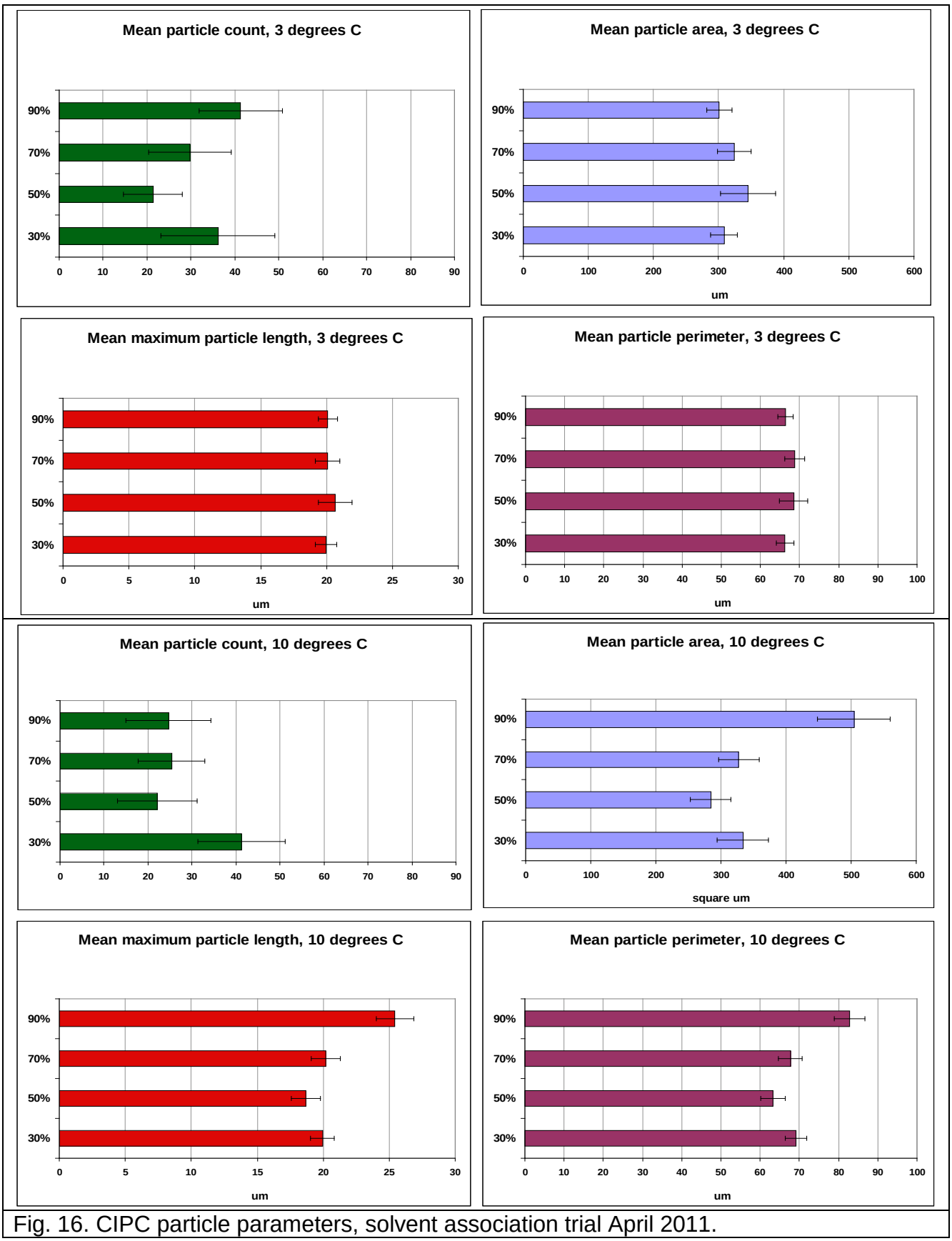


Fig. 16. CIPC particle parameters, solvent association trial April 2011.

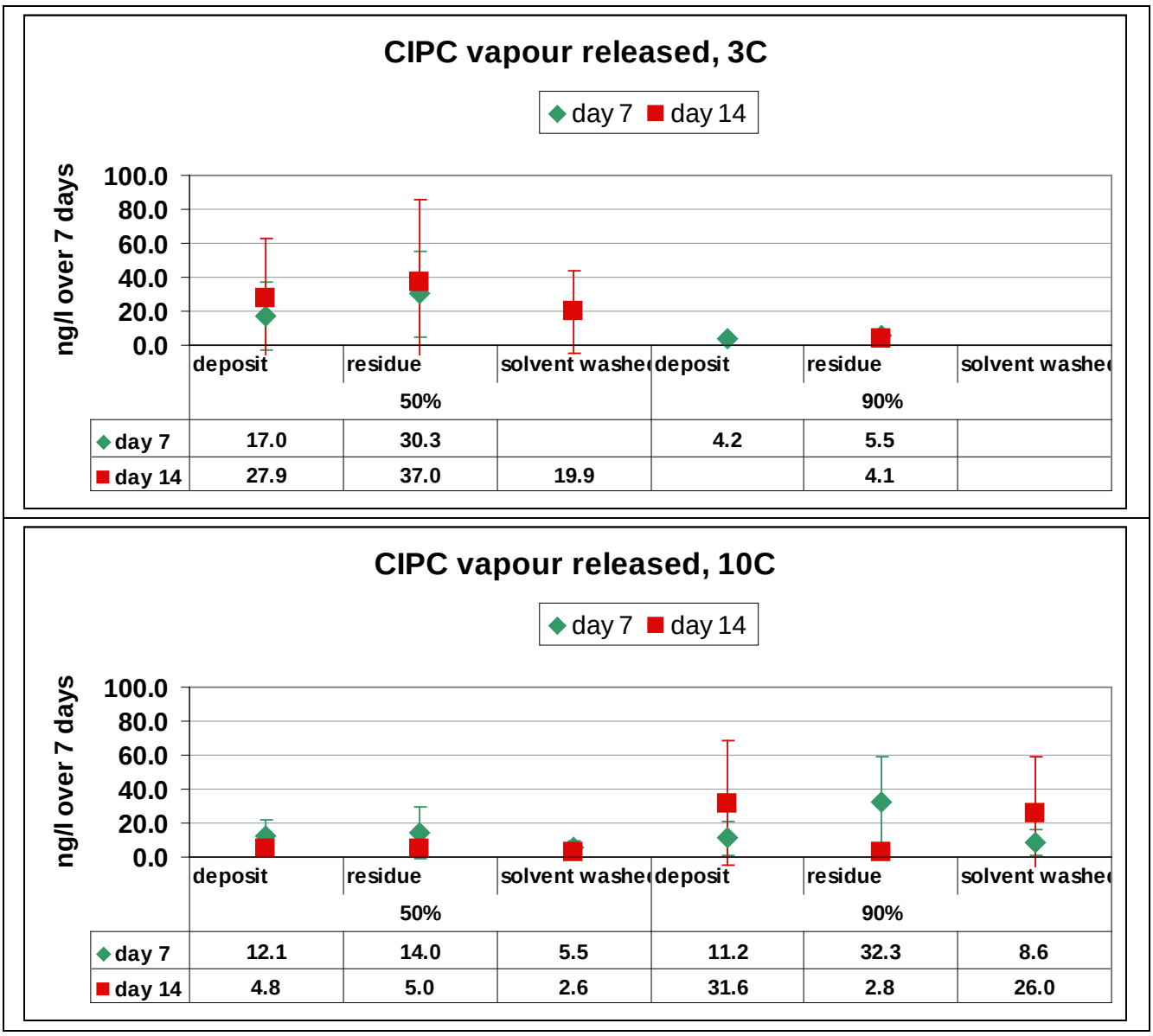


Fig. 17 CIPC vapour release, solvent association trial June 2010.

CIPC vapour release is shown in Fig. 17 for the June 2010 trial. Vapour release was generally higher from tubers treated with 50% CIPC at 3/3.5°C and from 90% CIPC at 10°C. Results were also associated with high levels of variability and so differences between treatments are not apparent. Lower levels of CIPC vapour were generated when the trial was repeated (Fig. 18, April 2011) with all treatments generating approximately 10 ng of CIPC vapour per litre of air.

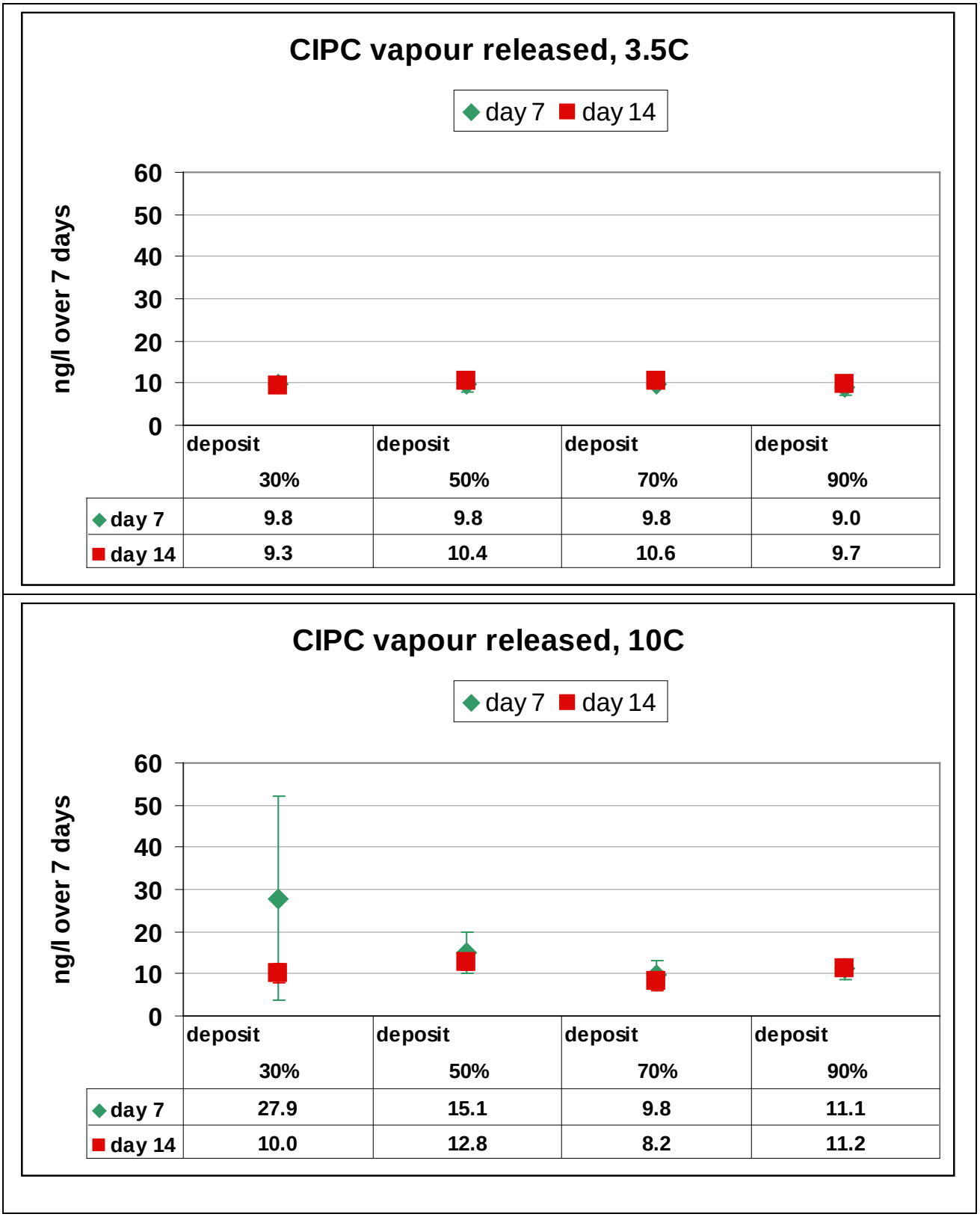


Fig. 18. CIPC vapour release, solvent association trial April 2011.

4.4 Fog quality

The changes in airborne CIPC fog concentration, as a result of air/fog passing through potatoes, is shown in Fig. 19. During the initial extraction period (starting five minutes after completion of fogging), there was a significant reduction (19%) in airborne CIPC concentration as a result of air/fog being drawn through the tubers. At the later period (starting after 30 minutes) there was no significant change in airborne CIPC concentration. It is anticipated that fog would have contained a higher proportion of relatively coarse particles at the initial extraction period.

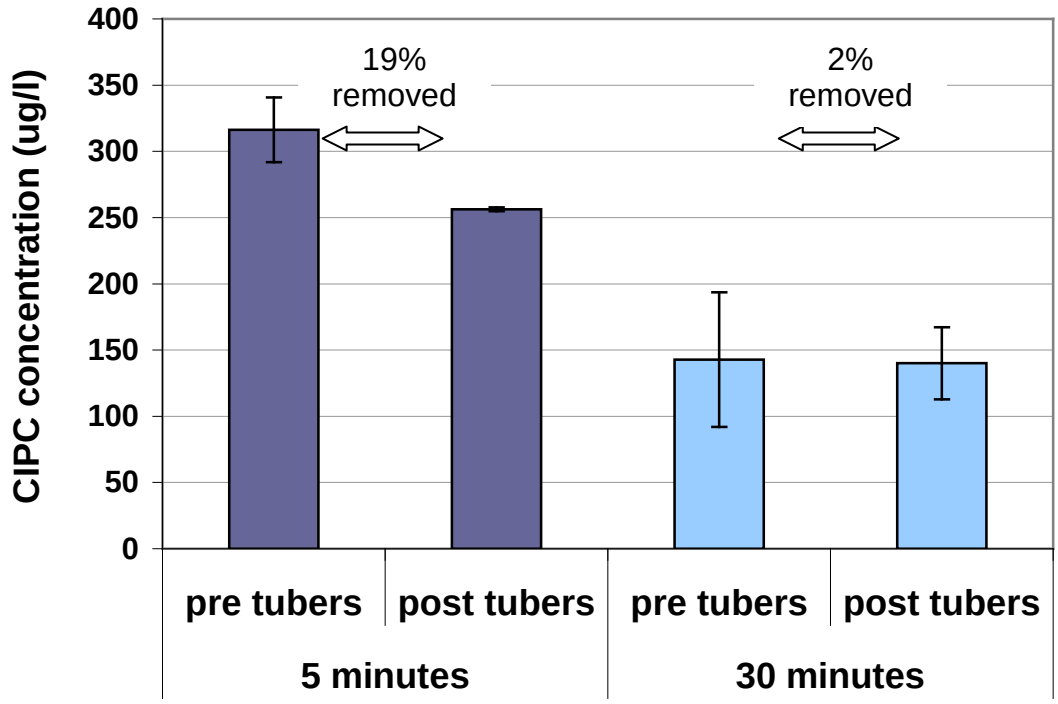


Fig. 19. CIPC concentration in air before and after passing through a column of tubers.

Deposit and residue levels were higher on crop from the 5 minute treatment. Only tuber samples obtained from the initial 5 min treatment (30 second duration extraction period) had a quantifiable concentration of CIPC, with a deposit of 0.04 mg/kg Table 1). The tubers 'filter' out more CIPC earlier in the application. In this case 17% more was removed by the tubers at 5 minutes post application than at 30 minutes post application.

Residue samples from this treatment and deposit and residue results from the 30 minute treatment were below the limit of quantification or below the limit of detection.

Table 1. Tuber CIPC deposit and residue concentrations.

treatment	CIPC (mg/kg)	
	deposit	residues
5 mins	0.04	blq[1] (0.008)
30 mins	blq (0.02)	bld[2]

[1]below limit of quantification
[2]below limit of detection

CIPC particle parameters from 5 and 30 minute treatments are shown in Fig. 20. The later, 30 minute treatment tended to have larger CIPC particles, but differences were slight.

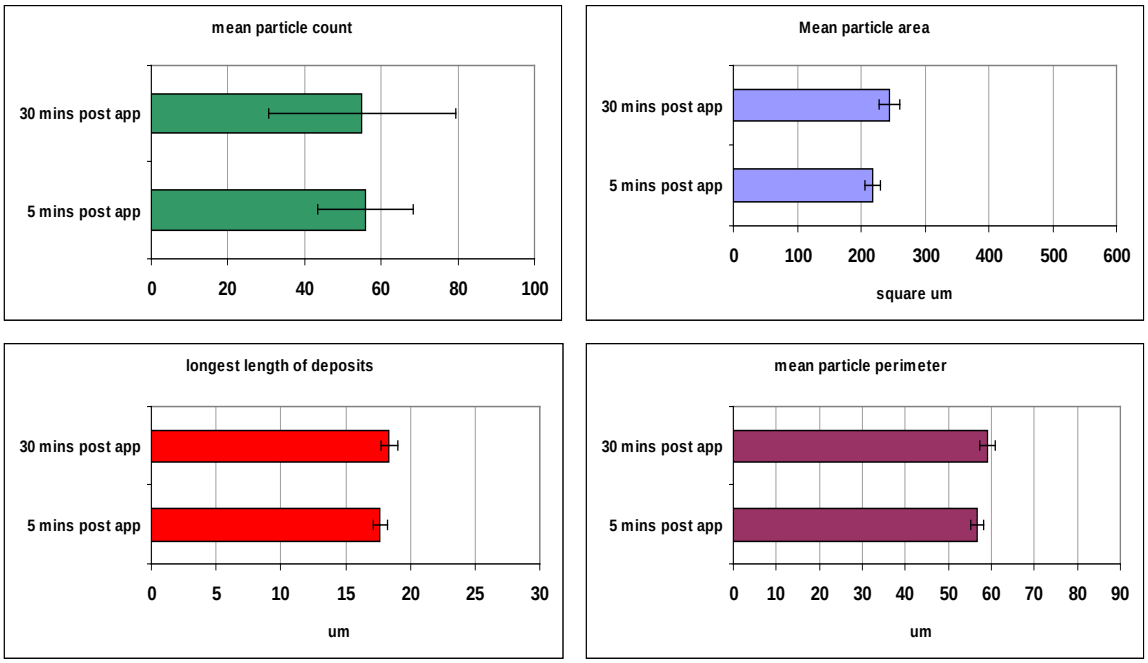


Fig.20. CIPC particle parameters in fog quality trial.

Results of CIPC vapour release from treated tubers are shown in Table 2. Release was measured from individual tubers, replicated three times, over two seven day periods. Although CIPC deposit levels were very low, quantifiable concentrations of CIPC vapour were released from tubers, albeit at a lower concentration than from other vapour release tests. Differences in vapour release concentration were not significant, although the highest concentration was from tubers with the highest CIPC deposit level.

Table 2. CIPC vapour release from tubers in fog quality trial.

treatment	day 7		day 14	
	ng/l	sd[1]	ng/l	sd
5 minutes	3.49	*1.345*	2.70	*0.858*
30 minutes	2.46	*0.848*	2.71	*0.767*

[1]standard deviation

4.5 Semi-commercial trials

Results of CIPC deposit analysis 24 hours after applications and when the 3.5°C target storage temperature was achieved are shown in Fig. 21. Applications carried out at 10°, 7°C and 3.5° e*arly* resulted in similar CIPC deposit levels in the range 2.8-3.1 mg/kg. CIPC deposit levels sampled when crops achieved 3.5°C were generally lower than respective samples at 24 hours but only significantly so from the 3.5°C *early* treatment. The final application (3.5°C *late*) resulted in significantly lower deposit levels, 1.6 and 1.4 mg/kg respectively for 24 hours and *at 3.5°C* samples.

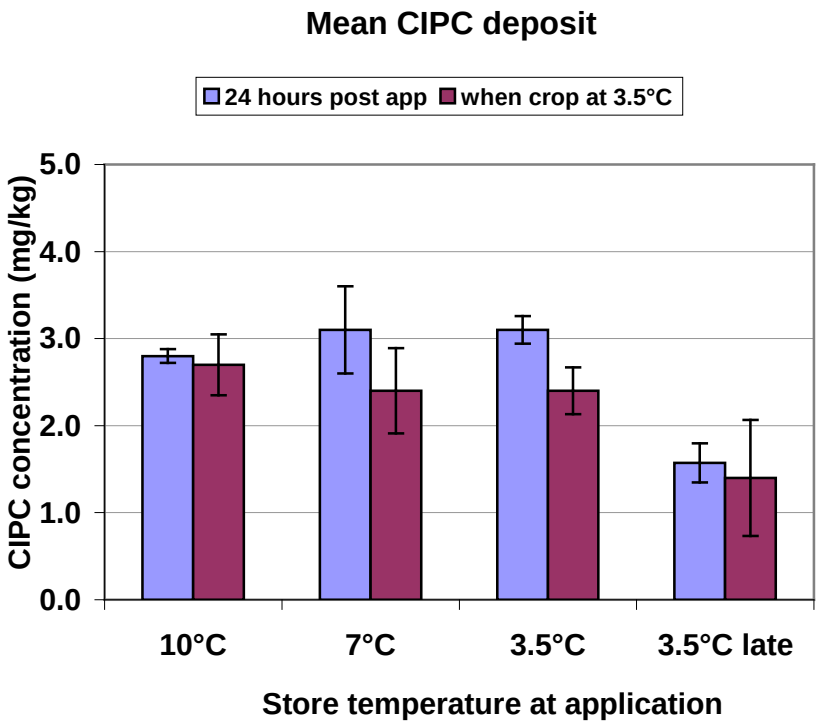


Fig. 21. Mean CIPC deposit levels, with 95% confidence interval, 24 hours after application and when target temperature was achieved.

CIPC residue levels at the end of storage are shown in Table 3. Tubers were obtained from within sample boxes (*in situ*) and from an exposed location (removed from box when target storage temperature achieved, and held in a net in a position in the store with relatively high airflow rates). Placement of samples in an exposed location

resulted in a lower CIPC residue concentration, relative to *in situ* samples, with reductions generally in excess of 50%. Residue levels remained significantly higher (*in situ* and exposed locations) in samples treated at a storage temperature of 10°C.

Table 3. CIPC residue levels at store unloading.

store temperature at application	CIPC residue (mg/kg)			
	in situ	SD	exposed	SD
10°C	1.9	0.52	0.7	0.06
7°C	1.0	0.26	0.3	0.07
3.5°C early	0.9	0.10	0.4	0.12
3.5°C late	1.2	0.40	0.5	0.07

CIPC vapour concentrations during pull-down and holding and holding alone stages of the trial are shown in Figs. 22 and 23, respectively. Vapour concentrations were obtained by sampling air from the middle of boxes, using a small, rigid tube located in boxes at the time of loading. Fig 22 shows the effect of store temperature on CIPC vapour , with higher storage temperatures associated with a higher concentration.

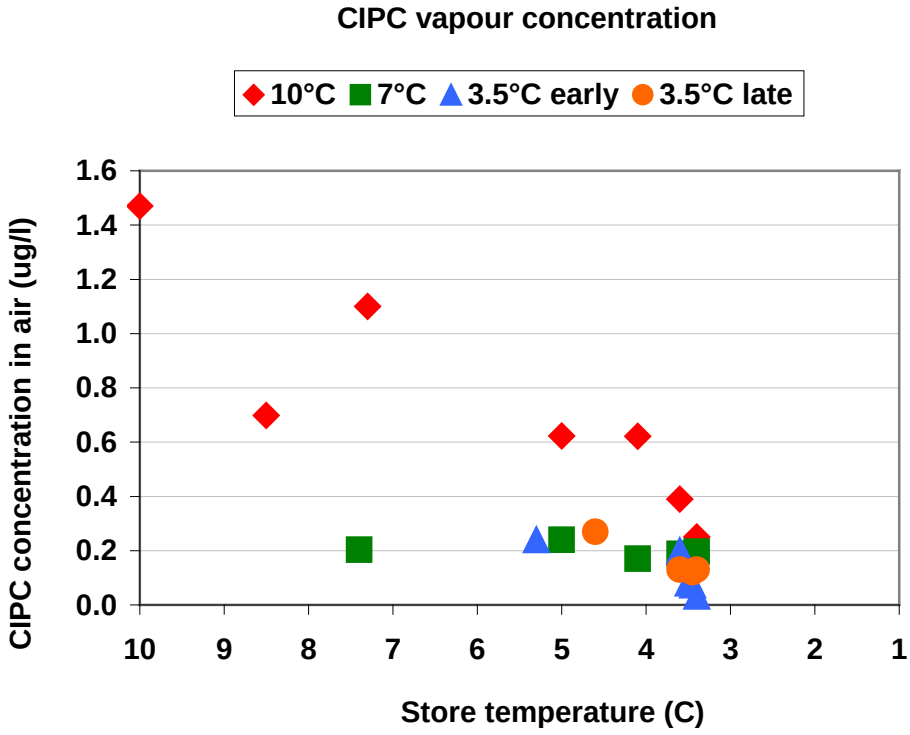


Fig. 22. CIPC vapour concentration during pull-down and storage phases.

Figure 23 shows the effect of store temperature at the time of CIPC application on CIPC vapour concentration at the target storage temperature (3.5°C). During storage at 3.5°C, data show a greater CIPC vapour concentration when applications were carried out at warmer storage temperatures. Mean concentrations were 0.26ug/l (SD 0.125), 0.18ug/l (SD 0.022) and 0.096 ug/l (SD 0.026) for 10°C, 7°C and 3.5°C early applications respectively. Therefore the vapour released from crop treated at 10degrees C was signficantly more than the vapour released from crop treated at 3.5degrees C (early). Late application at 3.5°C resulted in a higher CIPC vapour concentration (0.13ug/l, SD 0.006), compared with 3.5°C early, but this difference was not significant.

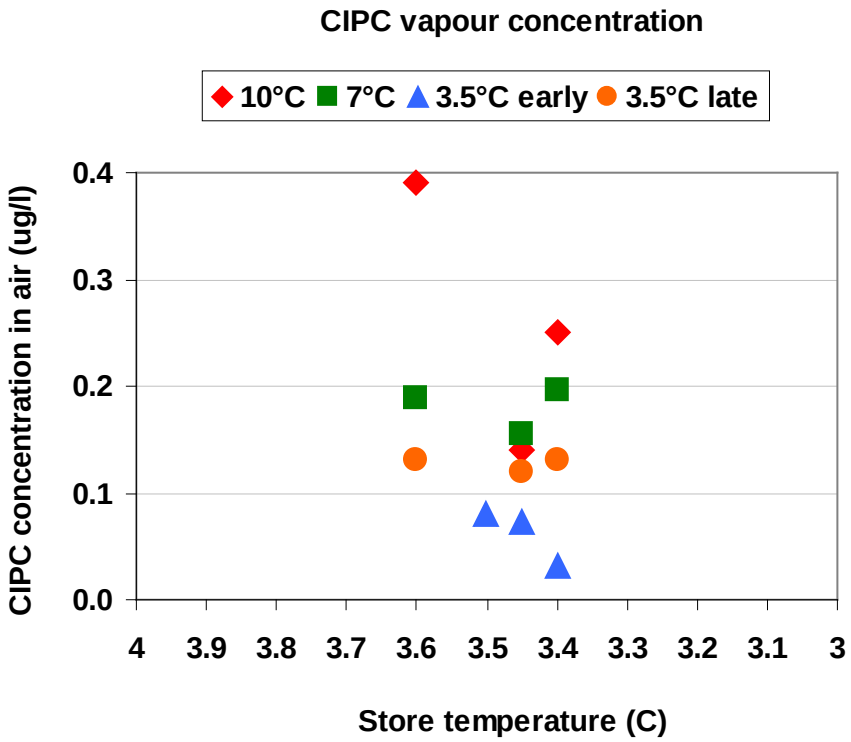


Fig. 23 CIPC vapour concentration during storage phase.

The ‘accumulation’ of CIPC on untreated tubers, placed in boxes following application and replaced at critical phases is shown in table 4. During the initial pull-down period (7 days), from 10°C to 7°C, the CIPC concentration of untreated tubers located in boxes 24 hours after application increased to 1 mg/kg. During pull-down from 7°C to 3.5°C (7 days for 10°C treatment and 8 days for 7°C treatment) both treatments

resulted in 0.4mg/kg CIPC on untreated tubers. During the holding period, with storage at 3.5°C between 19 or 20 November and 6 May, 10°C, 7°C and 3.5°C early treatments resulted in 0.5-0.6 mg/kg accumulating on untreated tubers. Although still an effective concentration of CIPC, this occurred over a much longer time interval.

For early treatments (10°C, 7°C and 3.5°C early) redistribution of CIPC is assisted by application at a warmer temperature. The higher vapour concentrations at warmer temperatures add weight to this observation The placing of untreated tubers in boxes of treated tubers would lead to some cross-contamination, by physical contact. This is thought to be unrelated to duration of exposure however and therefore similar across all 'treatments'.

Table 4. Absorption of CIPC (mg/kg) on untreated tubers during pull-down and holding phases.

treatment	10°C-7°C	7°C-3.5°C	3.5°- 6 May	6 May-27 July	total	rate (ug/kg/day)
10°C	1.0	0.4	0.6	0.3	2.3	8.6
7°C	-	0.4	0.6	0.1	1.1	4.2
3.5°C early	-	-	0.5	0.2	0.6	2.5
3.5°C late	-	-	-	0.5	0.5	6.4

Results of efficacy assessments carried out at store unloading (26 July, 2010) are shown in Table 5. Sprout length, sites of sprouting and proportion of tubers with sprouts tended to be smallest from earlier application of CIPC, though differences were relatively slight. There was a general trend of increased percentage of tubers sprouting as application temperatures decreased for early treatments. The late treatment had the highest percentage of sprouts overall. Samples were examined for skin spot (infection by *Polyscytalum pustulans*) at store unloading. Symptoms of the disease were not found.

Table 5. Efficacy assessments at store unloading.

treatment temperature	length of longest sprout	sd	sites of sprouting	sd	tubers with sprouts (%)
10°C	0.8	0.72	1.6	1.80	60
7°C	1.2	1.04	2.2	2.31	72
3.5°C early	1.1	0.49	1.9	1.50	92
3.5°C late	1.4	0.96	3.8	2.57	88

5 DISCUSSION

A system was developed for application of CIPC on a small-scale. The system consisted of a nebuliser, equivalent to the chemical pump on a conventional fogger, a source of temperature controlled hot air, equivalent to the *blower* and combustion chamber, and a chamber, equivalent to a potato store, where samples were located.

Initial plans were to use the small-scale applicator to assess properties associated with CIPC when applied as the pure, melted (technical grade) formulation, in comparison with conventional, solvent-based formulations. However, problems with solidification of the pure, melted formulation in the fine-bore tubing of the nebuliser, required for treatment of very small volumes of potatoes, could not be overcome. Instead of this experimental work was conducted with CIPC formulations made up in a range of concentrations (30%-90% w/v) in methanol.

In addition, a new method was developed for visualising applied CIPC particles on tubers. The method was based on UV fluorescence and as such did not involve sample preparation stages likely to interfere with the subject.

Experimental work examined the role of condensation, formulation (solvent association) and fog quality on characteristics of CIPC, using conventional analytical chemistry techniques as well as the new UV visualisation method.

Experimental work with the mini-fog system was not completely successful. In the condensation trial, data was gathered indicating that condensation on potatoes, after CIPC application increased the strength with which CIPC was retained on

potatoes, with a significantly higher proportion of the initial CIPC deposit remaining after solvent washing. However, when the work was repeated, condensation did not influence strength of attachment and solvent washed tuber concentrations were similar before and after condensation. When CIPC was applied to tubers with condensation there was little differentiation between deposit, residue and solvent-washed concentrations, and further condensation events did not change this. On both occasions the experiment was conducted, applications to wet potatoes resulted in a relatively low initial airborne CIPC fog concentration. The cause of this is not known.

Although significant differences in tuber CIPC deposit, residue and solvent-washed concentrations were obtained in the condensation trials, these were not reflected by significant changes in CIPC particle parameters (area, length and perimeter) or the propensity of tubers to generate CIPC vapour. Changes in CIPC particle parameters were sometimes greater as a result of delaying assessment.

In the formulation trial, results for airborne CIPC fog and tuber CIPC deposit concentration suggest that the application system was not functioning correctly when the experiment was repeated. In the second experiment much lower concentrations of CIPC deposited on tubers and the response to the different washing procedures was unusual in that water was typically ineffective at CIPC deposit removal, while those that involved an organic solvent were particularly effective. Although a very significantly lower deposit level of CIPC occurred on tubers in the second experiment, this was not reflected by results for the numbers of particles in the UV visualisation method or the CIPC vapour generated by tubers.

In the semi-commercial trial, results were obtained that could be of considerable importance. This work was carried out at SBCSR when commercial scale trials were suspended because researchers perceived a risk of exceeding the MRL.

In this work, a standard dose of CIPC was applied to separate boxes of potatoes at a range of temperatures during the initial pull-down to the target holding temperature (3.5°C). Applications at 10°C, 7°C and 3.5°C (early) were carried out within a two week period and resulted in similar CIPC deposit levels on crops. A later application at 3.5°C (late) was not as successful with a significantly lower CIPC deposit level (c. 1.5 ppm compared with c. 3ppm for the earlier treatments).

In the treatments carried out early (10°C, 7°C and 3.5°C *early*) there was an effect of storage temperature evident on CIPC saturation vapour concentration, with higher vapour concentrations at the warmer storage temperatures. This effect has been established and was anticipated. The absorption/adsorption of CIPC on to untreated tubers, located in boxes after the application, was greatest at the highest temperature, and reduced as temperature was reduced. Over approximately similar durations, pull-down from 10°C to 7°C resulted in twice as much CIPC accumulating on untreated tubers (1ppm) compared with the interval from 7°C to 3.5°C (0.4ppm). With crops at the target holding temperature (3.5°C) only very limited re-distribution took place, with an average of 0.6ppm over a storage period in excess of 5 months. The re-distribution of CIPC is considered to have taken place by the vapour phase and differences are thought to be due to the higher saturation vapour concentration at warmer temperatures. Although a proportion of 'accumulated CIPC' will be from physical contact with treated tubers, this is not thought to be related to duration, and therefore is anticipated to be constant for all treatments. These results indicate that air temperature, and its effect on saturation vapour concentration, is important in redistribution of CIPC and, because sprout control is effected by CIPC in the vapour phase, is also important in the success of sprout control. The reduced CIPC saturation vapour concentration at low storage temperatures may account for the apparent reduced efficacy of CIPC in low-temperature stores and the continued use of relatively high dose rates in storage scenarios where 'sprouting pressure' is anticipated to be relatively slight.

Additionally, volatilisation of CIPC during application, at a given temperature, appears to have been influenced by the temperature of the store to which it was applied. With crops in the temperature range 3.4°C-3.6°C more CIPC vapour was generated in boxes treated at the warmer storage temperatures. Although analysis of CIPC vapour concentration is not straightforward, data would suggest that air/crop temperature at which CIPC is applied can have an impact of physical properties of CIPC and its propensity to volatilise.

Airflow rate was important in re-distribution capacity of CIPC. Residue concentration at the end of storage (July) was assessed on tubers left *in situ* within sample boxes and on tubers removed from boxes and located in an exposed location

in store, where airflow rates were much greater. CIPC residue values were generally at least 50% lower in samples from the exposed location.

6 CONCLUSIONS

Results of the semi-commercial scale trial indicate that improvements in CIPC treatment of low-temperature stores can be achieved. The pre-pack industry is dominated by storage in non-positively ventilated boxes at very low storage temperatures (c. 2-4°C). Applications are frequently carried out relatively late, once the target storage temperature has been achieved. Applications of CIPC in such stores gives rise to relatively variable CIPC deposit/residue distributions, compared with positively ventilated box stores and, results indicate, the low saturation vapour concentration then limits re-distribution, thereby maintaining the initial (poor) distribution and sprout control efficacy. Results indicate re-distribution and efficacy of CIPC could be improved by carrying out CIPC applications earlier, during temperature pull-down, when stores are warmer. Results also indicate the importance of ventilation on CIPC residue decline, with samples exposed to comparatively greater air movement having residue values *c.*50% lower than corresponding samples held within (non-positively ventilated) boxes, where air speed is extremely low.

Further development of analytical techniques for CIPC are required. A new method using UV-fluorescence microscopy was developed. Although significant changes in parameters of CIPC particles were evident, it is difficult to correlate these with existing assessments. In addition, a reliable method for CIPC vapour analysis would be very useful – results for this are often particularly variable. Sprout control is thought to be effected by volatilisation of CIPC particles and an improved understanding of this is therefore fundamental to improving the use of CIPC.