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Isopropyl N-(3-chlorophenyl) Carbamate (CIPC) Residues in Potatoes Stored in Commercial Cold Stores in India

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Abstract Since no attempt has been made so far in India to determine isopropyl N-(3-chlorophenyl) carbamate (CIPC) residues in potatoes, it became necessary to determine its residues in potatoes which are being used for table and processing purposes. Using high-performance liquid chromatography, CIPC residues were determined in peels, peeled tubers and unpeeled tubers periodically during storage at 10–12 °C in commercial cold stores. The highest concentration of CIPC found in potato peels was 20.17 mg/kg fresh wt, whereas in unpeeled and peeled tubers the residue levels were very low ranging from 0.29 to 1.13 and 0.05 to 0.24 mg/kg, respectively. However, all residue levels observed were within the maximum residue level prescribed by the US Environmental Protection Agency. The experiments done to determine the dispersal and concentration of CIPC applied as an aerosol fog with respect to location and time showed that the distribution of CIPC within the cold store was uneven leading to large variations in residue levels in samples drawn from different parts of the store.

Keywords Aerosol application · Chlorpropham · High-performance liquid chromatography · *Solanum tuberosum* L. · Storage

Introduction

The sprout suppression effect of chlorpropham or isopropyl N-(3-chlorophenyl) carbamate (CIPC) in potatoes was first reported by Marth and Shultz (1952). It has been extensively used on potatoes across the world for sprout suppression during storage (Van Vliet and Sparenberg 1970; Boyd et al. 1982) and continues to be the

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most dominant chemical used for sprout suppression in potatoes (Anonymous 2002). Various formulations of this chemical have been tried on potatoes to achieve sprout suppression viz. powder/dust application (Wessel and Wustman 1990), dip treatment (Marth and Shultz 1952), and application of aerosol (Boyd et al. 1982; Kleinkopf et al. 1997). Out of these, the most successful method of CIPC application has been in the form of aerosol or fog (Anonymous 2002). Although CIPC has been used for a long time and a good deal of work has been done on its effectiveness, mode of application and determination of its residues in potatoes, this chemical was registered for use in India only in 1998. It has been used in several commercial cold stores since then. The chemical is available in liquid form (containing 50% active ingredient) and is applied as hot fog.

CIPC treated potatoes are being used in India for table and processing purposes. Because of health concerns it has become essential to determine CIPC residues in treated potatoes. The present study was aimed at determining CIPC residues in potatoes treated with CIPC hot fog in commercial cold stores in India, to ascertain whether the CIPC residues in treated potatoes are within the acceptable limit. CIPC is also applied in the form of dust in India when the quantity of potatoes stored is small.

Since CIPC application in the form of fog in commercial potato stores is a relatively recent practice in India, and it is applied through an inlet fixed on the ground floor and not through the ventilation system as is the practice in commercial cold stores in developed countries, it is not known whether the distribution of CIPC aerosol within the store is satisfactory. Therefore, an attempt was also made to determine CIPC residues in tubers stored at different sites within the store. The uniformity of distribution of CIPC aerosol and the persistence of CIPC on the tuber was also determined by comparing CIPC residue levels in tubers treated with aerosol with that of the tubers treated with CIPC dust.

This paper describes CIPC residues in treated tubers, the uniformity of distribution of CIPC aerosol and its persistence on the tuber. Furthermore, for the first time in India, an attempt has been made to determine CIPC residues in treated potato samples collected from commercial cold stores at different duration's of storage and it is hoped that the information presented here would be of interest to potato research workers in other countries.

Materials and Methods

CIPC Application

CIPC treatment was done in five commercial cold stores (viz. Indore ice and cold store, Narang cold store and Chatrakaran cold store at Indore and Ujjain ice and cold store and Katiyar cold store at Ujjain district) in Madhya Pradesh State of India during 2001. Well-cured potato tubers (cultivars Kufri Jyoti and Kufri Lauvkar) were stored at 10–12 °C temperature range and 85–95% relative humidity (RH) in chambers specially modified for CIPC treatment. The loading was done during the 3rd week of February to the 1st week of March. CIPC application was done twice; the first application was done at the time of sprout initiation (3rd week of March) and the second application was done after about 45 days of first treatment. A

commercial preparation of CIPC called "Oorja" manufactured by United Phosphorus Limited, Mumbai (India) was used. This is a liquid formulation containing 50% active ingredient. The application was made in sealed stores in the form of a thermal aerosol (hot fog) through an inlet fixed at about 1 m above the ground level. A fogger (Dyna fog, USA) was used for CIPC application and the dose applied was 40 ml per tonne of potatoes. After treatment the store was closed for 48 h to allow CIPC aerosol to settle down on the potatoes and then it was ventilated for 1 h to flush out the accumulated CO_2.

Sampling of Potatoes

Tuber samples were collected from locations near and away from the fogging point. For each location, five tubers each were taken from two hessian cloth bags and CIPC residue was determined in peels (peeling was done with a hand peeler to get 2 mm thick peels) and peeled tubers in composite samples. For the determination of CIPC residue in unpeeled tubers, another set of composite samples were used. Thus there were four samples per location and the samples were collected from five different cold stores. Each cold store was treated as a replication for statistical analysis. Similarly, to study the effect of pile height, tuber samples were collected from bags placed at a height of 1 m from the ground level (in the ground floor) and from bags placed at 6 m from the ground level (in the first floor). For the determination of CIPC residues on different dates during the storage period, five tubers each were taken from four hessian cloth bags randomly, pooled and two composite samples were made for each cold store on all the dates of observation from March to end of June.

For comparing CIPC residue levels in tubers treated with fog with that of the tubers treated with CIPC dust, 100 tubers of cultivar Kufri Jyoti were treated with CIPC dust (1% active ingredient (a.i.) in saw dust applied at the rate of 30 mg a.i./kg of tubers). The tubers were taken in a plastic container, applied with dust and rotated thoroughly for uniform distribution of dust. The container was sealed for 48 h. These tubers were stored in walk-in-chambers at 10 and 12 °C along with the tubers treated with CIPC aerosol at Central Potato Research Institute, Shimla in the year 2002. Both the applications, i.e., dust and aerosol were done on April 16. The second application of dust was given at the time of second fogging of potatoes in the walk-in-chambers on May 30. For this purpose, the previously dusted tubers were removed from the chambers and second dust application was done as described above. After treatment the tubers were again stored in the walk-in-chambers. Two sets of five tubers were collected randomly to make two composite samples for CIPC residue analysis. All the results were given statistical treatment according to Gomez and Gomez (1984).

CIPC Residue Analysis

The extraction of CIPC from tuber samples was done by the method earlier standardized in the laboratory (Singh and Kaul 1999). CIPC residue was determined in unpeeled whole tubers, peels (consisting of the skin and approximately 2 mm of the flesh) and peeled tubers (entire tuber without the peels) in composite samples. The samples were chopped and mixed thoroughly. A representative sample of 10 g

was taken into a 50 ml culture tube and n-Hexane (analytical reagent grade) was added for proper immersion of the samples. The extraction was done using n-Hexane, and 10 g each of anhydrous sodium sulfate and Kieselguhr were added in the mixture. The grinding was done with the help of pestle and mortar, and final clean up was done by passing the extract through celite. The extract was filtered and reduced to near dryness in 30 ml glass vials below 30 °C to avoid CIPC loss due to volatilization. These vials were sealed before further analysis by high-performance liquid chromatography (HPLC).

All solvents used for analysis of CIPC residues through HPLC were of HPLC grade (E-Merck India Ltd.). Water used in the mobile phase was Milli-Q grade (Millipore Inc., USA). The CIPC standard used was obtained from Sigma chemical company.

A modified procedure developed by Wilson et al. (1981) for HPLC analysis was standardized and the residues were analysed using the conditions described as follows:

Injector	Rheodyne injector with starter switch
Pump	Lachrom L-7100 isocratic (Merck-Hitachi, Darmstadt, Germany)
Column	250×4 mm Purospher RP-18e column
Oven	Lachrom L-7350 (Merck-Hitachi)
Detector	Lachrom L-7420 UV-visible detector (Merck-Hitachi)
Mobile phase	Methanol: Acetonitrile: Water in 35:35:30 ratio
Flow rate	1 ml/min
Column temperature	25 °C
Injection volume	20 μl
Detector wavelength and absorbance	236 nm set at 0.04 AUFS
Retention time	7 min from injection

The concentrated extract was dissolved in 200 μl of HPLC grade n-hexane and 20 μl of this sample (equivalent to 1 g tuber sample) was injected into the system for quantification. The residues in tuber samples were quantified by comparing the peak area with that of standard curve, since peak area vs. CIPC concentration was linear within the range of concentrations used in the investigations.

Results and Discussion

CIPC Residues

The mean CIPC residues in potato peels from commercial cold stores ranged from 1.86 to 5.19 mg/kg fresh weight, in unpeeled whole tubers they ranged from 0.29 to 1.13 mg/kg and in peeled tubers the range was from 0.05 to 0.24 mg/kg fresh weight (Fig. 1). The highest concentration of residue observed at any date in peels was 20.17 mg/kg, whereas the residues in unpeeled whole tubers and peeled tubers were much below this level at all sampling dates. The periodical observations showed that

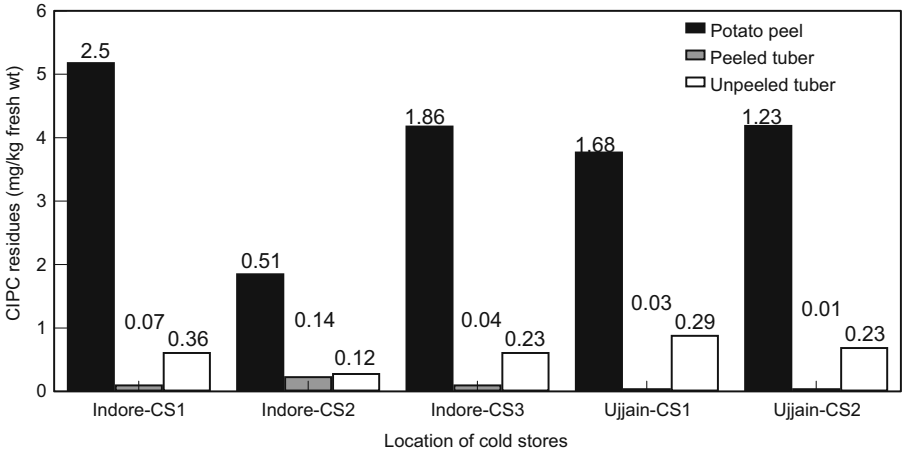

Fig. 1 CIPC residues (mg/kg fresh wt) in different parts of potatoes stored in five cold stores in Indore and Ujjain districts of Madhya Pradesh in India. CS stands for cold store and the data given is average of all the observations taken during the period of storage. (Values shown above each bar represent standard error)

there was not much variation in CIPC residues in peels or tubers over the storage duration. Although residues decreased after 1 month of first application, they increased again after second fogging of CIPC, and were almost constant thereafter (Fig. 2).

CIPC residues vary with the kind of formulation used, method of application and the storage duration. Wilson et al. (1981) measured CIPC residues to be as high as 45 mg/kg with CIPC aerosol treatment whereas Mondy et al. (1992) observed residues up to 400 mg/kg in peels and 10 mg/kg in the cortex when the tubers were dipped in 1% solution of CIPC. Camire et al. (1995) observed average residues in peels to be around 33 mg/kg when gaseous application of CIPC was made. Conte et al. (1995) observed very low residues (less than 1 mg/kg) in peeled tubers applied with CIPC aerosol, whereas, Lentza-Rizos and Balokas (2001) obtained unpeeled

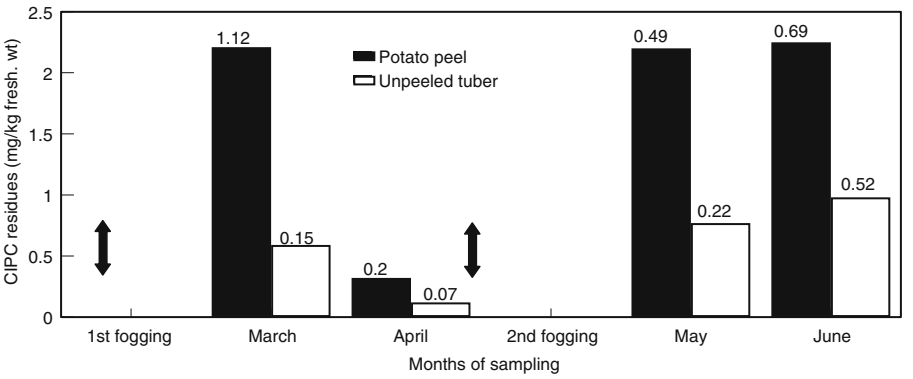

Fig. 2 CIPC residues (mg/kg fresh wt) in tubers observed at periodical intervals (data presented are the average of all the cold stores at respective dates and represent the mean of ten determinations). The values shown above each bar represent standard error

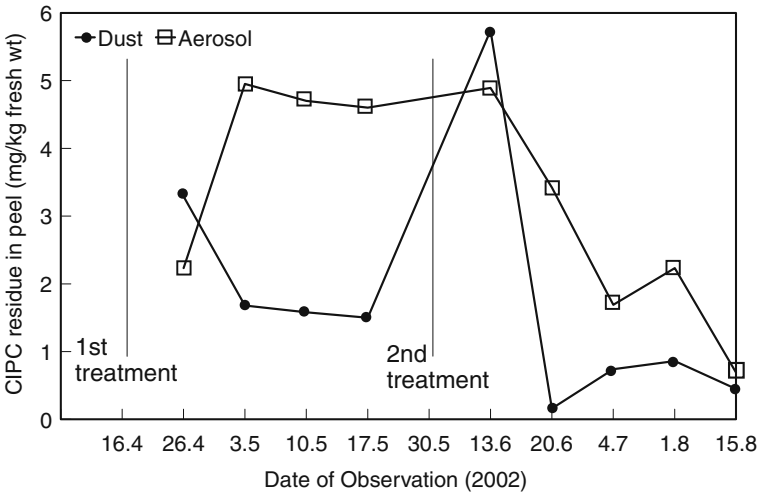

Fig. 3 CIPC residues in peels of potatoes (cv. Kufri Jyoti) treated with CIPC dust and aerosol and stored at 10 °C

tuber residues ranging from 0.7 to 7.6 mg/kg fresh weight with CIPC dusting. The dusting application by them showed decreasing trend of CIPC residues with the increasing storage duration. Singh and Kaul (1999) also observed a decrease in CIPC concentration over time with CIPC dust application. However, with aerosol application, Conte et al. (1995) did not find a significant decrease in CIPC residues with the storage duration. Our results indicate that residue levels decreased 1 month after first application but increased again after second application. This shows that two applications of CIPC are needed for suppression of sprout growth if potatoes are to be stored at 10–12 °C for a long duration of 5 months and more.

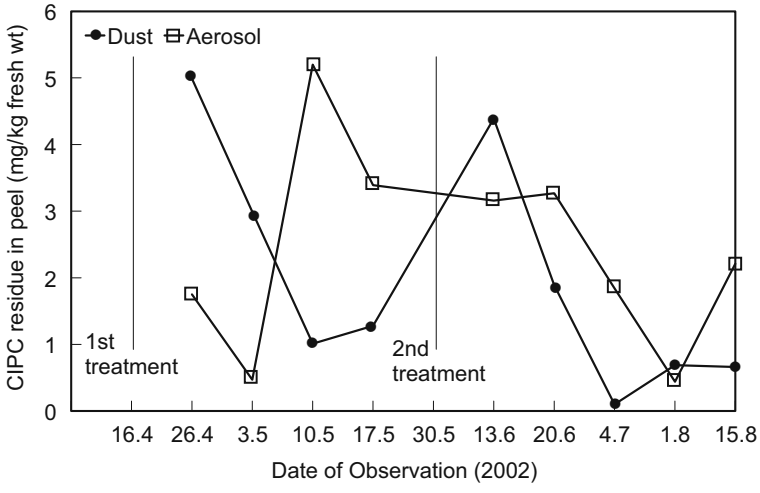

Fig. 4 CIPC residues in peels of potatoes (cv. Kufri Jyoti) treated with CIPC dust and aerosol and stored at 12 °C

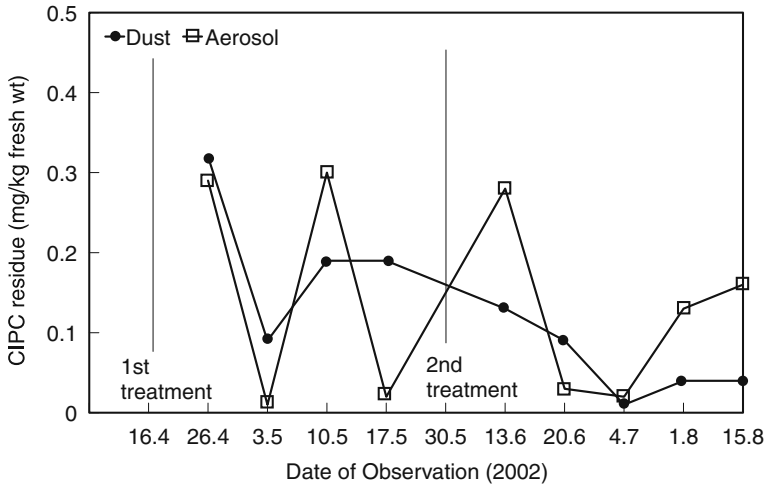

Fig. 5 CIPC residues in unpeeled tubers (cv. Kufri Jyoti) treated with CIPC dust and aerosol and stored at 10 °C

The persistence of CIPC residues on peels and in unpeeled tubers was studied by determining CIPC residues periodically after first and second treatment with CIPC dust and aerosol. At both the storage temperatures, i.e., 10 and 12 °C, the CIPC residues in peels of the tubers treated with CIPC dust showed a clear trend. It was high immediately after the first treatment and declined over time during the storage period with a sharp increase immediately after the second dusting (Figs. 3 and 4). When CIPC was applied in the form of aerosol, the CIPC residues in the peels were 20–82% higher than the dust application, indicating the increased efficiency of aerosol application. Although there was a general decline in the concentration of

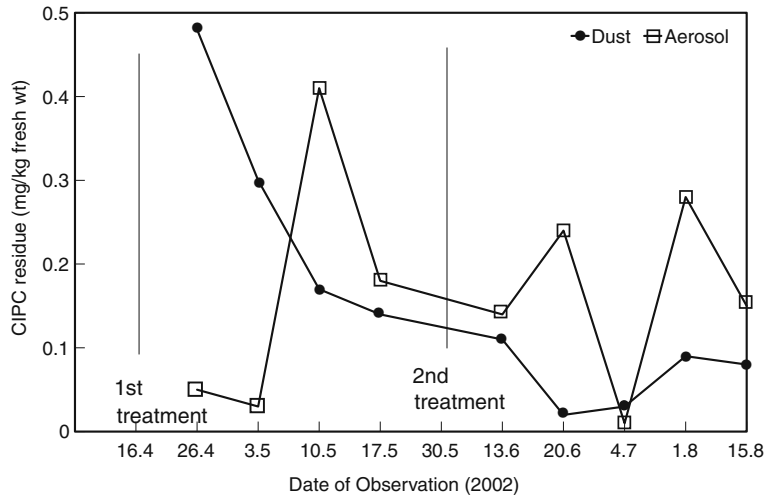

Fig. 6 CIPC residues in unpeeled tubers (cv. Kufri Jyoti) treated with CIPC dust and aerosol and stored at 12 °C

Table 1 CIPC concentration (mg/kg tuber) in tuber samples collected from hessian cloth bags placed near and away from the fogging point

Distance from the fogging point	Peel	Unpeeled tuber
Near (1–2 m)	2.34[a]	0.69
Away (8–18 m)	1.17	0.17
$LSD_{0.05}$	NS	0.43

[a] Average value of ten determinations

CIPC residues during the storage period, there were large variations in the values obtained. There was an increase in CIPC residue level immediately after second aerosol application although the increase was small compared with the second dust application.

In the unpeeled tubers, the CIPC residue level generally showed a decline with lesser variations with dust application and large variations with aerosol application (Figs. 5 and 6). The variations from sample to sample drawn at different times were much higher in unpeeled tubers compared to peels. The large variations in CIPC residues in peels and unpeeled tubers in samples drawn at different times during the storage period could be attributed to uneven distribution of CIPC aerosol within the store, leading to large variations from sample to sample. Uneven distribution of CIPC aerosol within the store has been observed by other researchers (Corsini et al. 1979; Kleinkopf et al. 1997) and Conte et al. (1995) have reported that CIPC residues can vary significantly as a function of sampling point in the storage cell.

There was a large difference between the residues measured in peels and unpeeled or peeled tubers. This kind of difference has been reported by most of the previous workers who observed CIPC residues to be almost ten times higher in peels than the unpeeled or peeled tubers (Corsini et al. 1979; Conte et al. 1995). Corsini et al. (1979) concluded that the minimum concentration of CIPC in the peel should be 20 mg/kg for complete inhibition of sprouting but we observed complete sprout inhibition even when the CIPC concentration in the peel was in the range of 1.86–5.19 mg/kg. The studies with radio-labeled CIPC have shown that highest quantity of CIPC is associated with peels and there is very little penetration of CIPC beyond the peel layer even after 6 months of storage (Coxon and Filmer 1985). The non-systemic nature of CIPC may be the cause for restricted penetration into the tuber which results in more residues on surface layer (peels) than the peeled tuber (cortex) or unpeeled whole tuber (peel and cortex together).

Table 2 CIPC concentration (mg/kg tuber) in tuber samples collected from hessian cloth bags placed at different heights in the chamber

Height	Peel	Unpeeled tuber
1 m from the floor level	0.96[a]	0.04
6 m from the floor level	0.63	0.03
$LSD_{0.05}$	NS	NS

[a] Average value of six determinations

CIPC distribution within the store

CIPC residue was higher in tubers stored near the fogging point while it was lower in tubers stored away from the fogging point (Table 1). The distance between these two locations across the chamber varied from 7–16 m depending upon the chamber size. The residue level was higher in tubers stored in the ground floor and lower in tubers stored in the first floor (Table 2). The differences in the residue levels in tubers stored in different floors could be attributed to greater amount of CIPC settling down on the potatoes in the ground floor as in the present method of CIPC application, the fog rises through the potatoes from the ground floor to the upper floors. Higher CIPC residue levels in potatoes near the bottom of the pile than those near the top of the pile have been reported (Kleinkopf et al. 1997). Corsini et al. (1979) also observed higher CIPC residue levels in potatoes collected from the bottom of potato piles from stores where CIPC application was made through the ventilation system with the CIPC fog rising from the bottom to the top through the pile.

The Environmental Protection Agency (EPA) had worked out a maximum residue level (MRL) for CIPC to be 30 mg/kg in potatoes (EPA 1996). The same value was proposed by FAO/WHO Codex Alimentarius Commission (2003). However, this is under reconsideration, since this limit precludes an estimate that the dietary intake would be below the acute reference dose. In none of the tuber samples, we observed the residues to be near to or above this MRL, even in peels where the residues were much higher than that in peeled or unpeeled tubers. This shows that the residues reported in the study were well below the MRL and the treated tubers were safe for human consumption. However, this MRL is being reviewed by the European Union, which is considering an MRL of 10 mg/kg from the year 2003 (Anonymous 2002). Once this MRL comes into effect, the commercial application of CIPC might have to be made more precise and in such a manner that the chemical is effective for sprout suppression without leaving much residues on potato tubers.

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