

# Final Report

## Understanding the Persistence, Transformation and Fate of CIPC (Chlorpropham) in Commercial Potato Stores to Help Guard Against Cross-Contamination.

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## 1. SUMMARY

### 1.1. Aim

The proposed research focuses on the distribution of CIPC (Isopropyl-N-(3-chlorophenyl) carbamate; chlorpropham) contamination in potato stores, the factors involved in cross contamination of other commodities and the decontamination issues surrounding stores, to enhance an understanding of the behaviour and transformation of CIPC residues within these environments. This will allow recommendations to be made for the re-use and/or decontamination of stores previously used for CIPC treated potatoes.

### 1.2. Methodology

Quantitative and qualitative analytical methods for trace level CIPC and 3-CA (3-chloroaniline) analysis in complex matrices, including building materials (concrete) and fresh commodities (grain) were developed. Various experimental designs to determine the route of cross contamination of grains were trialled in a laboratory environment prior to being used in real stores. Trials were then conducted in both research (Sutton Bridge Crop Storage Research; SBCSR) and commercial potato stores with a known history of CIPC use to study the route of cross contamination attributed to: (I) dislodged dust particles; (II) direct contact with the concrete flooring and (III) the headspace of the store.

### 1.3. Key findings

1.3.1 Qualitative (GCMS) and quantitative (HPLC) methods were successfully developed for the confirmation of CIPC and its metabolite 3-CA in complex matrices, concrete and grain. In addition, a HPLC UV/VIS method was assessed for the quantification of other chloroaniline isomers, enabling future photochemical degradation and decontamination studies.

1.3.2 Persistence and distribution of CIPC and 3-CA contamination in potato stores was quantified for the first time, improving our understanding of the behaviour of these chemicals. The developed methods successfully demonstrated the persistence of CIPC and 3-CA in the concrete flooring of commercial potato stores with histories of 16 and 25 years since the final application of CIPC. Depth distribution studies confirmed that concrete was pervious to CIPC and the degree of penetration may have been dependent on the physical nature of the concrete. As evident in both research and commercial stores, accumulation of CIPC residues in the flooring of the stores was increased with higher quantities of applied CIPC. Also, the concentrations were more likely to be higher in areas closest to the point of CIPC entry into the store and the degree of contamination in stores was influenced by the type of circulatory system used, causing heterogeneity of CIPC distribution.

1.3.3 Degree and route of CIPC and 3-CA cross contamination of grains in commercial potato stores was shown, allowing informed recommendations to be made on the future use of potato stores previously treated with CIPC. The research revealed that cross contamination of grains was feasible, irrespective of the CIPC levels in the concrete flooring and provided evidence that the headspace in the general store, the headspace above the concrete flooring and dislodged CIPC-contaminated dust particles in a store environment are all important routes of cross contamination.

1.3.4 3-decen-2-one was shown by computational and chemical methods to be ineffective as a decontaminant for CIPC contaminated concrete. Complexes formed between 3-decen-2-one and CIPC, in the presence of concrete, were confirmed but shown to be reversible, suggesting this chemical would be ineffective as a decontaminant. However, the inability of the complexes to alter the properties of CIPC present on the concrete and to prevent production of 3-CA suggests that 3-decen-2-one may be an alternative solvent for application of CIPC in stores.

#### **1.4. Practical recommendations**

It was concluded that storage of grains, and other commodities with a Maximum Residue Level (MRL) set at the limit of quantification for CIPC, are at significant risk of cross contamination in buildings where CIPC has previously been applied. Due to the longevity of the chemical residues and the widespread contaminant distribution within the store environment, no 'decontamination strategy fits all' recommendation could be made at this stage. Stores will need to be assessed individually, allowing tailor-made recommendations based on proposed end-use to be made.

This study showed the majority of CIPC residues were found within the top one centimetre of concrete, providing an indication on the depth of concrete that would require removal or treatment to allow stores to be re-used, which is invaluable information for the development of decontamination strategies. This study has also demonstrated that risk assessments based on the concentration of CIPC in concrete from a single location in a store is prone to inaccuracies because CIPC levels in the concrete flooring are heterogeneous.

## 2. INTRODUCTION

Food quality is of high importance to consumers and this is maintained by the use of pesticides (Mondy et al., 1992). Residues of pesticides can be a serious trade barrier and may constitute a risk to human health if they enter the food supply chain (Łozowicka, et al., 2012). Unintentional contamination of food products with pesticides can occur via storage surfaces (Garcia-Febrero et al., 2014) as illustrated by the case in the United Kingdom where unintentional cross contamination of cereal products with chlorpropham (Isopropyl-N-(3-chlorophenyl) carbamate; CIPC) resulted in thousands of packages of the product being withdrawn from shops (Curtis, 2006). The use of CIPC-contaminated grains in the manufacturing of the products was thought to be the source of the contamination, with the possible route of cross contamination being attributed to storage of grains in buildings contaminated with CIPC.

Chlorpropham is a sprout suppressant and a herbicide (Frazier and Olsen, 2014) and the most effective sprout suppressant used in the potato industry in the UK. The Chemical Regulation Division of the Health and Safety Executive (HSE) ensures compliance with MRL of 10 mg CIPC kg<sup>-1</sup> for potatoes, set by the European Commission (EC Regulation 1107, 2009). In the UK, the Potato Industry CIPC Stewardship Group ensures best practice use of CIPC as a sprout suppressant ([www.cipccompliant.co.uk](http://www.cipccompliant.co.uk)). CIPC is also used as a herbicide in the production of other food and ornamental crops and MRLs are set at their limit of quantification. For salad crops such as lettuce, the MRL becomes 0.05 mg kg<sup>-1</sup>; onions (0.05 mg kg<sup>-1</sup>); teas and coffees (0.05 mg kg<sup>-1</sup>); herbs and edible flowers (0.02 mg kg<sup>-1</sup>) (HSE, 2017). The emergence of CIPC residues in cereal products in the UK is currently of concern as the chemical is non-permissible on cereal crops. The MRL for CIPC on cereals is set at the limit of quantification which is 0.01 mg kg<sup>-1</sup>. In order to avoid cross contamination and in particular exceedance of the MRL set, it is recommended that the fabric of the stores be tested for CIPC and if there is uncertainty with respect to this, the store should not be used for non-potato crops.

Commercial pressures within the agriculture sector have contributed to the cross contamination of non-potato crops by CIPC. Many smallholder farmers in the UK are currently moving away from the potato sector and have utilised the vacated stores for storage of non-potato crops and/or farm equipment. The cross contamination of crops is problematic, even for farmers remaining in the potato sector, due to the fact that seed crops of any type and other commodities such as cereals coming into contact with CIPC contaminated stores, even for a short period of time, may have impairment of germination and/or become contaminated. The fate and distribution of CIPC and its possible degradation product, 3-chloroaniline (3-CA), in the fabric of potato stores, is not well understood and requires investigation. In addition, the possible routes of cross contamination of grain products with CIPC remain undetermined, hindering mitigation strategies.

The proposed research focuses on the distribution of CIPC contamination in potato stores, the factors involved in cross contamination of other commodities and the decontamination issues surrounding stores, to enhance an understanding of the behaviour and transformation of CIPC residues within these environments. This will allow recommendations to be made for the re-use and/or decontamination of stores previously used for CIPC treated potatoes.

The aims of the project were:

1. To develop quantitative and qualitative analytical methods for trace level CIPC and 3-CA measurement in a range of complex matrices, including building materials such as concrete and fresh commodities such as grain.
2. To determine the magnitude and distribution of CIPC contamination in potato stores.
3. To investigate the route and degree of CIPC and 3-CA cross-contamination in non-potato crops stored in buildings with a history of CIPC use.
4. To understand the behaviour of CIPC under store conditions, allowing appropriate decontamination strategies to be developed.

### 3. MATERIALS AND METHODS

#### 3.1. Development and validation of HPLC and GCMS methods for the analysis of chlorpropham (CIPC) in concrete

A successful and precise analytical method was developed and validated for quantifying CIPC in aggregate and reconstituted concrete. The sample processing methodology was effective in producing a powdered concrete matrix for recovery experiments. The instruments' responses for CIPC were successfully assessed for errors in analysis; producing high precision, sensitivity and linearity. The method was fully validated for reconstituted and aggregate concrete at three concentration levels (0.4, 4.0 and 40.0  $\mu\text{g g}^{-1}$ ). The CIPC recoveries for reconstituted concrete were in the range 90.7-97.0%, with relative standard deviations between 2.14-3.01%. The accuracy and precision of the method for aggregate concrete was lower, relative to the reconstituted concrete, but still acceptable, with higher recoveries and %RSD values (92.0-134  $\pm$  4.88-5.80). This may be due to a matrix effect. The method was sensitive for analysis of CIPC in reconstituted (Limit of detection (LOD) is 0.029  $\mu\text{g g}^{-1}$  and Limit of quantification (LOQ) is 0.096  $\mu\text{g g}^{-1}$ ) and aggregate (LOD 0.069  $\mu\text{g g}^{-1}$  and LOQ 0.230  $\mu\text{g g}^{-1}$ ) concrete. The method is reliable and efficient and will be suitable for analysing CIPC in the concrete of potato stores.

##### 3.1.1. Preparation of concrete samples prior to analysis

Aggregate and reconstituted concrete blocks (obtained from Aggregate Industries and Bradstone UK respectively) were chopped into approximately 25 g portions using a hammer and chisel. The 25 g portions were then crushed using a Retsch® Crusher (Haan, Germany). The crushed samples were collected in a 125  $\mu\text{m}$  Endecotts sieve (London, England) and shaken at 175 r.p.m for 30 minutes on a Retsch® Shaker (Haan, Germany). Sieved samples of size 125  $\mu\text{m}$  were stored in 20 mL screw cap glass vials (PerkinElmer, USA) at room temperature.

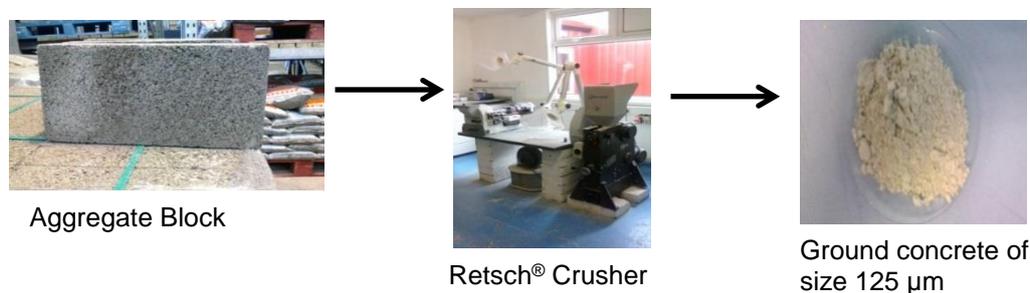


Figure 3.1 Processing of concrete for extraction.

##### 3.1.2. Spiking of concrete samples for recovery experiments

Five gram portions of aggregate and reconstituted concrete were weighed into glass screw-top jars. The contents of the jars were spiked with 20  $\mu\text{L}$  and 200  $\mu\text{L}$  of CIPC in acetonitrile solution of concentrations 100  $\mu\text{g mL}^{-1}$  and 1000  $\mu\text{g mL}^{-1}$  to give concentrations of 0.4, 4.0 and 40  $\mu\text{g g}^{-1}$  CIPC to concrete content. A 30 minute period was allowed for the CIPC to interact with the concrete matrix and for evaporation of the solvent. Five replicates were prepared for each spiking level.

### **3.1.3. Soaking and shaking method for extracting CIPC**

A soaking and shaking extraction method was used to extract CIPC from the spiked concrete samples. After the 30 minute incubation period, acetonitrile (20 mL) was dispensed into each jar and the screw cap replaced. The samples were placed on a shaker (IKA) for 30 minutes at 175 r.p.m and then left at room temperature overnight. The following morning, the samples were shaken for 15 minutes at 175 r.p.m. A glass Pasteur pipette was used to transfer the supernatant of the soaked extract from each jar into 20 mL glass vials. A 2 ml disposable syringe was used to measure approximately 1 mL of the respective supernatants. A 0.2 µm PTFE membrane (VWR International, USA) was fitted onto each syringe and the supernatants were filtered into a 2 mL HPLC vial and stored at 4 °C for analysis. Finally, 20 µL of the supernatant was analysed by high-performance liquid chromatography with UV detection and gas chromatography coupled with mass spectroscopy.

#### **3.1.3.1. HPLC Method**

The HPLC system consisted of a manual Rheodyne® injector model 7725 with a solvent pump (LC-20 AD Prominence Liquid Chromatograph SHIMADZU), a DGU-20 A3 Prominence Degasser (SHIMADZU) and a SPD-20 A Prominence UV/VIS Detector (SHIMADZU). The column was housed in an oven (Cluzeau Info Labo 560-Cil). Data acquisition and processing were performed with LC Solution software.

Chromatographic separation was performed on a Genesis C18 analytical column (250 mm × 10 mm i.d., 4 µm). The mobile phase was acetonitrile and water in a ratio 60:40 (v/v) which was delivered at a flow rate of 1.5 mL min<sup>-1</sup>. The UV chromatographs were recorded at 210 nm wavelength. This was the optimised method for CIPC analysis.

#### **3.1.3.2. GCMS method**

A GCMS method was assessed for quantifying CIPC and a comparison was made with the previously validated HPLC UV/VIS method. The intra- and inter-day assessments of the GCMS instrument, using standard solutions, showed lower precision as compared with the HPLC UV/VIS method. In addition, the low recovery and precision obtained for spiked concrete samples, using GCMS, suggested that the method was unsuitable for quantifying CIPC. However, the GCMS method was suitable for qualitative analysis of CIPC and will be ideal for confirmation of CIPC in concrete samples from real potato stores.

#### **3.1.3.3. GCMS system and chromatographic conditions.**

A Shimadzu GC MS-QP 2010 instrument was used for analysis of CIPC. Separations were carried out using a ZB-5MS column (30 m x 0.25 mm i.d. 0.25 µm film thickness) with a stationary phase comprising 5% Phenyl-Arylene and 95% Dimethylpolysiloxane (Phenomenex®, UK). Injections were done in splitless mode where 1 µL was injected at a temperature of 220 °C and a purge flow of 3 mL min<sup>-1</sup>. The temperature of the detector was set at 260 °C and the total run time for analysis was 19.20 minutes. There was an initial step at a temperature of 80 °C and hold time of 0.5 minutes, followed by a four step temperature increase: i) + 30 °C min<sup>-1</sup> to 125 °C for one minute, ii) + 25 °C min<sup>-1</sup> to 180 °C for 3 minutes, iii) + 25 °C min<sup>-1</sup> to 280 °C for 4 minutes, iv) + 20 °C min<sup>-1</sup> to 300 °C for 2 minutes. Helium was used as the carrier gas where a constant pressure of 10.3 psi with a linear velocity of 38.1 cm min<sup>-1</sup> was maintained. An electron ion source temperature of 260 °C and interface temperature of 250 °C were employed for MS, where ion masses were scanned from 40 to 350 m/z at 3333 scans per second. LC Solution software release 3.40 was used for data acquisition and processing. The identification of CIPC in concrete samples was achieved by comparing the mass spectral patterns with those of standard CIPC solutions and by using the NIST/EPA/NIH mass spectral library (NIST 05) and NIST mass spectral search program version 2.0d. The mass spectral pattern for CIPC is as follows:

CIPC (213/215 m/z: parent ion; 153/154 m/z: m-chlorophenyl isocyanate; 171/173 m/z: free acid formed from isopropyl residue; 127/129 m/z: chloroaniline).

### **3.2. Development and validation of HPLC and GCMS methods for the analysis of chlorpropham (CIPC) and 3-Chloroaniline (3-CA) in concrete.**

A HPLC UV/VIS method based on the acetonitrile soaking extraction was developed for the extraction and determination of 3-CA and CIPC in concrete. The efficiency of the method was assessed through a recovery study at 3-CA and CIPC concentration levels of 0.4, 4.0 and 40.0  $\mu\text{g g}^{-1}$ . The CIPC recoveries were 94-106% with %RSD values between 1.0-4.1. The 3-CA recoveries were lower, ranging between 85-98% with acceptable precision (%RSD values of 1.0-9.5). The method was sensitive for analysis of both chemicals based on the LOD (3-CA 0.012  $\mu\text{g g}^{-1}$  and CIPC 0.10  $\mu\text{g g}^{-1}$ ) and LOQ values (3-CA 0.041  $\mu\text{g g}^{-1}$  and CIPC 0.333  $\mu\text{g g}^{-1}$ ). The method was deemed suitable for quantifying both compounds.

Crushed concrete samples from real stores (3 g) were extracted in 10 mL of acetonitrile. The samples were extracted as detailed previously and analysed by HPLC UV/VIS and GC-MS.

#### **3.2.1. HPLC Method**

The HPLC system consisted of a manual Rheodyne® injector model 7725 with a solvent pump (LC-20 AD Prominence Liquid Chromatograph SHIMADZU), a DGU-20 A3 Prominence Degasser (SHIMADZU) and a SPD-20 A Prominence UV/VIS Detector (SHIMADZU). The column was housed in an oven (Cluzeau Info Labo 560-Cil). Data acquisition and processing were performed with LC Solution software.

Chromatographic separation was performed on a Genesis C18 analytical column (250 mm x 10 mm i.d., 4  $\mu\text{m}$ ) at a column temperature of 25°C. The mobile phase was acetonitrile and water in a ratio 80:20 (v/v) which was delivered at a flow rate of 1.0 mL  $\text{min}^{-1}$ . The UV chromatographs were recorded at 208 and 240 nm wavelength. This was the optimised method for simultaneous analysis of 3-CA and CIPC analysis.

#### **3.2.2. GCMS system and chromatographic condition.**

A Shimadzu GC MS-QP 2010 instrument was used for analysis of CIPC and 3-CA. Separations were carried out using a ZB-5MS column (30 m x 0.25 mm i.d. 0.25  $\mu\text{m}$  film thickness) with a stationary phase comprising 5% Phenyl-Arylene and 95% Dimethylpolysiloxane (Phenomenex®, UK). The temperatures of the injector and detector were set at 225 °C and 180 °C, respectively. The injection volume was 1 or 8  $\mu\text{L}$  at a purge flow of 3 mL  $\text{min}^{-1}$  in split mode. Total run time for the analysis was 17.33 minutes, with an initial temperature of 120°C and hold time of 2 minutes, followed by a linear increase at a rate of 15°C  $\text{min}^{-1}$  to 200°C and a hold time of 10 minutes. The carrier gas was helium which was maintained at a constant pressure of 10.3 psi with a linear velocity of 38.1 cm  $\text{sec}^{-1}$  at 80.0°C (oven temperature). Parameters for the MS were as follows: electron impact (EI) source temperature of 180°C, interface temperature of 300°C. Ion masses were scanned from 30 to 400 m/z at 5000 scans per second. Data acquisition and processing were performed with LabSolution software, GCMS Solution version 2.50 SU1. The identification of CIPC and 3-CA in concrete samples was achieved by comparing the mass spectral patterns with those of standard CIPC and 3-CA solutions and by using the NIST/EPA/NIH mass spectral library (NIST 05) and NIST mass spectral search program version 2.0d.

Spiked samples gave mass spectral patterns for CIPC and 3-CA which were consistent with the expected spectra. This confirmed the presence of both chemicals in spiked concrete. The mass spectral patterns for 3-CA and CIPC are as follows:

CIPC (213/215 m/z: parent ion; 153/154 m/z: m-chlorophenyl isocyanate; 171/173 m/z: free acid formed from isopropyl residue; 127/129 m/z: chloroaniline).

3-CA (127: m/z parent ion; 45 m/z and 65 m/z).

### **3.3. Development of an HPLC UV/VIS method for the separation of chloroaniline isomers.**

Thermal degradation of CIPC during application may produce 3-CA and 2-CA (Smith et al., 2013). The formation of 4-chloroaniline (4-CA), an isomer of 3-CA and 2-CA, is not produced from degradation of CIPC but is part of the molecule of several herbicides (monolinuron, monuron and buturon) and may be formed from these chemicals in the environment (Freitag et al., 1984). It was therefore important to establish an analytical method that was able to distinguish between 2-CA, 3-CA and 4-CA.

#### **3.3.1. Preparation of stock standard solutions**

HPLC-grade 3-chloroaniline (3-CA, 99% purity), 2-chloroaniline (2-CA, 98%) and 4-chloroaniline (4-CA, 99%) were purchased from Fisher Scientific and used to prepare 1000  $\mu\text{g mL}^{-1}$  stock solutions. Working standard solutions of the respective chemicals in the range 0.01  $\mu\text{g mL}^{-1}$  – 10.0  $\mu\text{g mL}^{-1}$  were prepared by diluting the 1000  $\mu\text{g mL}^{-1}$  stock solution with acetonitrile as required. A mixed 2-CA, 3-CA and 4-CA standard containing 100  $\mu\text{g mL}^{-1}$  solution and working mixed standard solutions in the range 0.01  $\mu\text{g mL}^{-1}$  – 10.0  $\mu\text{g mL}^{-1}$  were prepared by diluting the 100  $\mu\text{g mL}^{-1}$  solution with acetonitrile as required.

#### **3.3.2. Separation of isomers using HPLC UV/VIS**

1.0  $\mu\text{g mL}^{-1}$  2-CA, 3-CA and 4-CA isomer standard solutions were analysed as detailed below. The HPLC system consisted of a manual Rheodyne® injector model 7725 with a solvent pump (LC-20 AD Prominence Liquid Chromatograph SHIMADZU), a DGU-20 A3 Prominence Degasser (SHIMADZU) and a SPD-20 A Prominence UV/VIS Detector (SHIMADZU). The column was housed in an oven (Cluzeau Info Labo 560-Cil). Data acquisition and processing were performed with LC Solution software. Chromatographic separation was performed on a Genesis C18 analytical column (250 mm  $\times$  10 mm i.d., 4  $\mu\text{m}$ ) at 25°C. The mobile phase was buffered 0.1% formic acid in 35% acetonitrile and 65% water at a flow rate of 0.6  $\text{mL min}^{-1}$  and UV chromatograms were recorded at dual wavelengths 208 and 240 nm.

### **3.4. Development and validation of HPLC and GCMS methods for the analysis of chlorpropham in crop commodities.**

A HPLC UV/VIS method coupled with acetonitrile extraction previously developed for analysis of CIPC in concrete was adopted and validated for non-organic wheat. The method was validated at nominal levels of 0.04 and 4.0  $\mu\text{g g}^{-1}$ , producing recoveries of 65 and 95%, respectively, with %RSD values of 5.6 and 3.4%, respectively. The method will be ideal for quantifying CIPC in cross contaminated samples close to the LOD of CIPC, and despite the lower recovery, good precision was obtained at a nominal value of 0.04  $\mu\text{g g}^{-1}$ . The method was sensitive for organic and non-organic wheat with LOD (organic: 0.004  $\mu\text{g g}^{-1}$ , non-organic: 0.016  $\mu\text{g g}^{-1}$ ) and LOQ (organic: 0.016  $\mu\text{g g}^{-1}$ , non-organic: 0.054  $\mu\text{g g}^{-1}$ ) values, respectively, confirming its robustness.

#### **3.4.1. Samples used in method development.**

Prior to the method development, several samples were collected and assessed for matrix effects. A preliminary assessment was conducted to determine the type of commodity and brand of products to be used in the method development. Three types of grains (wheat, oat and barley) were selected for the preliminary assessment and grain samples were obtained from three sources:

(A) Two brands of pearl barley (Great Scot and Sainsbury) were purchased from Sainsbury supermarket in East Kilbride, UK. The Great Scot Pearl Barley (500 grams) and Sainsbury Pearl

Barley (500 grams) were both products of more than one country but were packed in the UK and France, respectively.

(B) Samples of oats, wheat and barley (500 grams each) were obtained from a farm in Scotland.

(C) Two samples of oats (which were from the same batch) and one wheat sample were kindly provided by AHDB Sutton Bridge Crop Storage Research, Lincolnshire, UK.

Subsequent to the preliminary assessment, non-organic wheat samples collected from a farm in Scotland were used in the method development. Organic wheat samples (special spelt wheat) were purchased from Holland and Barrett, Germany, and used as a control.

### **3.4.2. Sample preparation prior to analysis.**

A preliminary assessment was conducted to determine: (I) the effect of grinding on the matrix effects in HPLC UV/VIS analysis of the grain extract and (II) the ease of extracting CIPC from ground and unground grain. Duplicate oat samples (5 grams) were separately milled using a Fritsch Tüvcert mill (Germany). The milled samples were separately sieved using a 125  $\mu\text{m}$  Endecotts sieve (London, England). The husk portions ( $>125 \mu\text{m}$ ) of the respective samples were re-milled. The first powder collected and the re-milled husk portions for the respective samples were recombined and thoroughly homogenised by manual mixing. The milled samples were stored in plastic containers at room temperature.

### **3.4.3. Spiking of samples for recovery experiments.**

Two sets of spiking experiments were conducted: (I) A preliminary assessment to determine the effect of the matrix on the analysis of different commodities, to enable the selection of a suitable commodity for field trials. (II) Assessment of the precision of the extraction process for the selected commodity for field trials.

#### **(A) Preliminary assessment.**

Duplicate portions (5 grams) of ground oats, unground oats and wheat were spiked with 200  $\mu\text{L}$  of CIPC solution of concentration 100  $\mu\text{g mL}^{-1}$ , to give a CIPC concentration of 4.0  $\mu\text{g g}^{-1}$ . A 30 minute period was allowed for the CIPC to interact with the matrix of the samples and for evaporation of solvent. Samples were extracted and analysed as described previously. A subsample of oat (100 grams), collected from the same batch of previously analysed oats, and a wheat sample (100 grams), were subsequently analysed using duplicate five gram portions of each at a spiking level of 4.0  $\mu\text{g g}^{-1}$ . Non-spiked samples were also extracted and analysed.

#### **(B) Assessment of extraction precision.**

Subsequent to the preliminary assessment in (A), wheat was selected as the commodity for field trials. Recovery experiments were conducted initially at a very low level of suspected cross contamination (0.04  $\mu\text{g g}^{-1}$ ) using five replicates. Non-organic wheat samples (5 grams) were spiked with a CIPC stock solution of 10  $\mu\text{g mL}^{-1}$  to give a concentration of 0.04  $\mu\text{g g}^{-1}$ . Triplicate recovery experiments were then conducted at a nominal level of 4.0  $\mu\text{g g}^{-1}$  using non organic wheat (5 grams), spiked with a CIPC stock solution of 100  $\mu\text{g mL}^{-1}$ . Again, a 30-minute period was allowed for the CIPC to interact with the surface of the grains and for solvent evaporation. The spiked samples were extracted and analysed as described previously. Non-spiked wheat and an acetonitrile blank were also taken through the extraction process and analysed.

The Scottish wheat sample was selected for method development and was used in the LOD and LOQ determination to represent general non-organic wheat. The organic wheat obtained from Holland & Barrett was used as a control sample and for field trials because it was CIPC-free and had no matrix effects.

#### **3.4.4. HPLC UV/VIS system and chromatographic conditions.**

The HPLC system consisted of a manual Rheodyne® injector model 7725 with a solvent pump (LC-20 AD Prominence Liquid Chromatograph SHIMADZU), a DGU-20 A3 Prominence Degasser (SHIMADZU) and a SPD-20 A Prominence UV/VIS Detector (SHIMADZU). The column was housed in an oven (Cluzeau Info Labo 560-Cil). Data acquisition and processing were performed with LC Solution software.

Chromatographic separation was performed on a Genesis C18 analytical column (250 mm × 10 mm i.d., 4 µm). The mobile phase was acetonitrile and water in a ratio 60:40 (v/v), which was delivered at a flow rate of 1.5 mL min<sup>-1</sup>. The UV chromatographs were recorded at 210 nm wavelength for CIPC analysis

#### **3.4.5. GCMS system and chromatographic condition.**

A Shimadzu GC MS-QP 2010 instrument was used for analysis and separations were carried out using a ZB-5MS column (30 m x 0.25 mm i.d. 0.25 µm film thickness) with a stationary phase comprising 5% PhenylArylene and 95% Dimethylpolysiloxane (Phenomenex®, UK). Injections were done in splitless mode where 1 µL was injected at a temperature of 220 °C and a purge flow of 3 mL min<sup>-1</sup>. The temperature of the detector was set at 260 °C and the total run time for analysis was 19.20 minutes. There was an initial step at a temperature of 80 °C and hold time of 0.5 minutes, followed by a four step temperature increase: i) + 30 °C min<sup>-1</sup> to 125 °C for one minute, ii) + 25 °C min<sup>-1</sup> to 180 °C for 3 minutes, iii) + 25 °C min<sup>-1</sup> to 280 °C for 4 minutes, iv) + 20 °C min<sup>-1</sup> to 300 °C for 2 minutes. Helium was used as the carrier gas where a constant pressure of 10.3 psi with a linear velocity of 38.1 cm min<sup>-1</sup> was maintained. An electron ion source temperature of 260 °C and interface temperature of 250 °C were employed for MS, where ion masses were scanned from 40 to 350 m/z at 3333 scans per second. LC Solution software release 3.40 was used for data acquisition and processing.

### **3.5. Preliminary assessment of an HPLC UV/VIS method for detecting 3-CA and CIPC in grains.**

The HPLC UV/VIS method developed and validated for the detection of 3-CA and CIPC in concrete was used in a preliminary assessment to determine if 3-CA and CIPC could be detected on grains. A spiking experiment at a nominal level of 4.0 µg g<sup>-1</sup>, using intact non organic wheat grains, was conducted. Five grams of non-organic wheat were spiked with 200 µL of a 100 µg mL<sup>-1</sup> 3-CA and CIPC standard solution. The spiked samples were left for 30 minutes followed by extraction and HPLC analysis as described previously. The recoveries of 3-CA and CIPC were >90%. The ease of extracting 3-CA from the surface of the grains suggested that there was insufficient binding of this chemical to the molecules on the surface. In addition, the GCMS methodology, described for detecting CIPC and 3-CA in concrete, will be used to confirm the presence of 3-CA in cross-contaminated trial samples if required.

## 4. RESULTS

### 4.1. Degree of Chlorpropham and 3-Chloroaniline contamination in Potato Stores.

#### 4.1.1. Store designs and histories.

Two identical research stores with similar dimensions of 4.5 m × 3.46 m × 5.13 m (height × width × depth), a potato holding capacity of 12 tonnes and a Plenum circulatory system were assessed (Figure 4.1). Research store 1 was frequently used for trials and therefore was fogged with CIPC several times (at least 8 kg CIPC) for 23 years, whereas research store 2 was a new store which only had one application of CIPC (0.108 kg CIPC). CIPC was not circulated into research store 1 prior to the installation of the plenum circulatory system. In both research stores, CIPC entered via a vent in a door at the back of the store. The plenum system in the research stores can be manipulated to circulate CIPC by: (I) positive ventilation through the crop, (II) open recirculation ventilation through the boxes, but not through the crop and (III) conditioned air discharge above the boxes. The only difference between research stores 1 and 2 was the location of the plenum which was on the right hand side for store 1 and the left hand side for store 2. Potatoes were stored in boxes in these stores. The stores are currently used for studies pertaining to potato storage. The deposition of chemicals in the stores was compared in terms of the circulatory system (plenum) because both stores were identical and had the same circulatory system, making ease of comparison feasible.

Two commercial stores designated A (with eighteen seasons of application; estimate of total CIPC applied: 2,040 kg) and B (with at least five seasons of application; estimate of total CIPC applied: 319 kg) were assessed in this study. The total amounts of CIPC applied to the commercial stores were estimated using their histories. Estimates of the total amount of CIPC applied were calculated using the maximum application rate of 63.75g CIPC t<sup>-1</sup> and the metric tonne capacity of the store. The total amount of CIPC applied to store A was 2,040 kg (63.75 g t<sup>-1</sup> × 16 years × 2000 t) and to store B was 319 kg (63.75 g t<sup>-1</sup> × 25 years × 200 t). The dimensions of commercial stores A and B were (length × width) 36.5 m × 18.2 m and 18.3 m × 13.7 m, respectively. Potatoes were stored to a depth of 4.5 m and 1.8 m in stores A and B, respectively. Both were bulk stores with potato holding capacities of 2000 and 200 tonnes, respectively. In commercial store A, CIPC was introduced using a Superfog machine (Superfog, 2018) into a main duct at the back of the store and under a fan. The main duct was continuous with all underground lateral ducts (7.2 m × 0.38 m × 0.3 m: length × width × depth) evenly distributing the CIPC (Figure 4.2). In commercial store B, the point of CIPC entry into the store was via galvanised ducts 2 and 4 (Figure 4.3). A Swingfog machine was used to apply CIPC directly into the ducts in this store. Commercial stores A (which was built in 1983) and B (which was built in 1972) are no longer used for storage of potatoes and the final applications of CIPC into these stores were in 2000 and 1990, respectively. The deposition of residues in the concrete flooring of the respective commercial stores was compared. The effect of deposition in terms of the machinery used to apply CIPC was not investigated.

#### 4.1.2. Preliminary evaluation of the crushing process to evaluate the weight loss of concrete.

The processing procedure in this study was evaluated to determine the weight loss of concrete after crushing. The intact cores and layers of each core from all stores were weighed prior to and after crushing. There was a 3-9% loss of concrete after the processing of samples for cores collected from commercial store A.

### 4.1.3. Preliminary evaluation of the method for extracting CIPC from industrial contaminated concrete.

For each batch of sample analyses, the recovery of CIPC from the spiked concrete matrix was evaluated to determine the efficiency of the extraction process to remove residual CIPC. In the preliminary analysis of the industrial samples, the number of extractions required for adequate removal of CIPC from the concrete matrix was unknown. Therefore, an initial experiment was conducted using samples from the back and right hand side of commercial store A. The layers from these samples were consecutively extracted twice and the percentage CIPC recovered from each layer was calculated. 90-100% of CIPC was recovered from the first extract of concrete, with CIPC concentrations of 0.196-23.3  $\mu\text{g g}^{-1}$  (Table 4.1). This suggested that one extraction using one gram of concrete was sufficient to remove CIPC residues from the powdered concrete. Subsequently, samples with higher CIPC concentrations (1.81-104.1  $\mu\text{g g}^{-1}$ ), from the front and left hand side of commercial store A, were sequentially extracted until no CIPC was detected. The CIPC concentrations in the first extracts were greater than 90%, thus confirming one extraction was again sufficient for removing residues from the concrete matrix (Table 4.1). One gram of crushed concrete was deemed sufficient for quantifying CIPC in the industrial samples.

Table 4.1 CIPC concentration ( $\mu\text{g g}^{-1}$ ) in sequential extracts and the number of times a sample was extracted in parentheses.

Concentration of CIPC in each layers in the cores ( $\mu\text{g g}^{-1}$ )			
	1 <sup>st</sup> cm	2 <sup>nd</sup> cm	3 <sup>rd</sup> cm
<b>Position of Core</b>			
Back of store	23.6 (1)	1.78 (1)	0.196 (1)
	2.10 (2)	0.193 (2)	0.00 (2)
Right hand side of store	15.4 (1)	0.383 (1)	
	1.41 (2)	0.00 (2)	NS
Left hand side of the store	28.8 (1)	0.658 (1)	
	1.92 (2)	0.00 (2)	NS
	0.288 (3)	0.00 (3)	
	0.00 (4)		
	0.00 (5)		
Front of store	106 (1)	4.05(1)	1.36 (1)
	6.95 (2)	0.419 (2)	0.455 (2)
	0.654 (3)	0.00 (3)	0.00 (3)
	0.00 (4)		
	0.00 (5)		

NS-Not sampled

A representative sample from commercial store A was selected to test the reproducibility of the extraction and HPLC UV/VIS method. A portion of crushed concrete from this sample was thoroughly homogenised and split into three subsamples. The subsamples were subsequently extracted and analysed by HPLC UV/VIS. The CIPC concentrations obtained were similar (mean = 9.7  $\mu\text{g g}^{-1} \pm 3.49$  %RSD), suggesting that the extraction and homogenization procedures were suitable for CIPC quantification.

#### 4.1.4. Depth distribution of CIPC in research and commercial potato stores.

The distribution of CIPC was studied in the two research and two commercial potato stores. The concrete flooring of all stores was cored in locations that were in close proximity to, or remote from, the point of CIPC entry into the store. The length of the cores depended on the ease of penetration of the drill into the floor. Intact cores were sectioned into layers and ground prior to HPLC UV VIS analysis. The depth distribution was determined from the CIPC concentrations ( $\mu\text{g g}^{-1}$ ) in the descending layers of each core. Three cores were collected from the two research stores at measured distances from the plenum, front of the store (entrance) and the point of CIPC entry into the store at the back (door) (Figure 4.1).

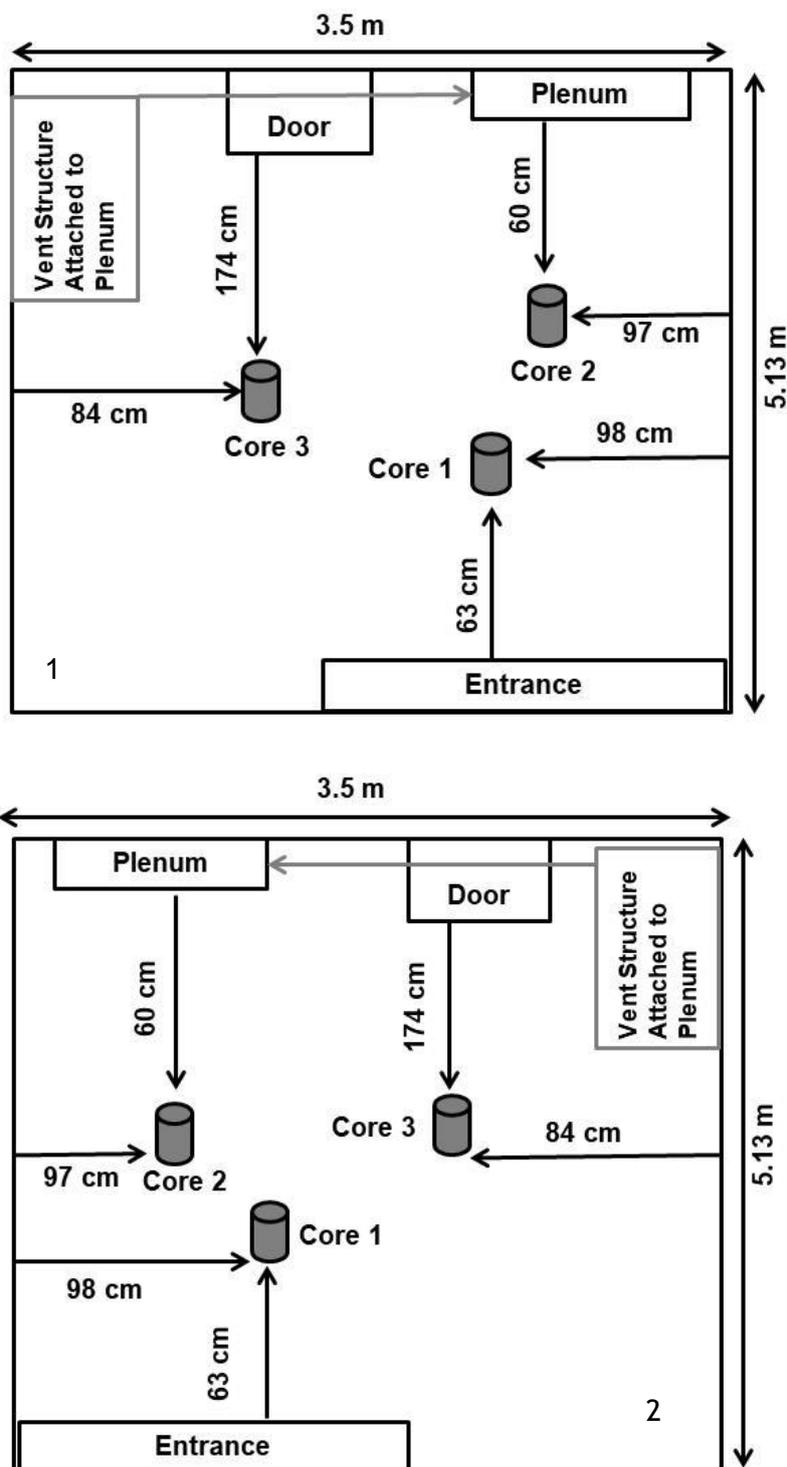


Figure 4.1 Floor plan for research stores 1 (1) and 2 (2). Grey cylinders represent the cores collected (adapted from Douglas et al. 2018b)

A total of four preliminary cores were collected at measured distances from evenly distributed lateral ducts in commercial store A. The point of CIPC entry into commercial store A was at the back. These cores were collected on the left-hand side, right-hand side, front and back of the store (Figure 4.2).

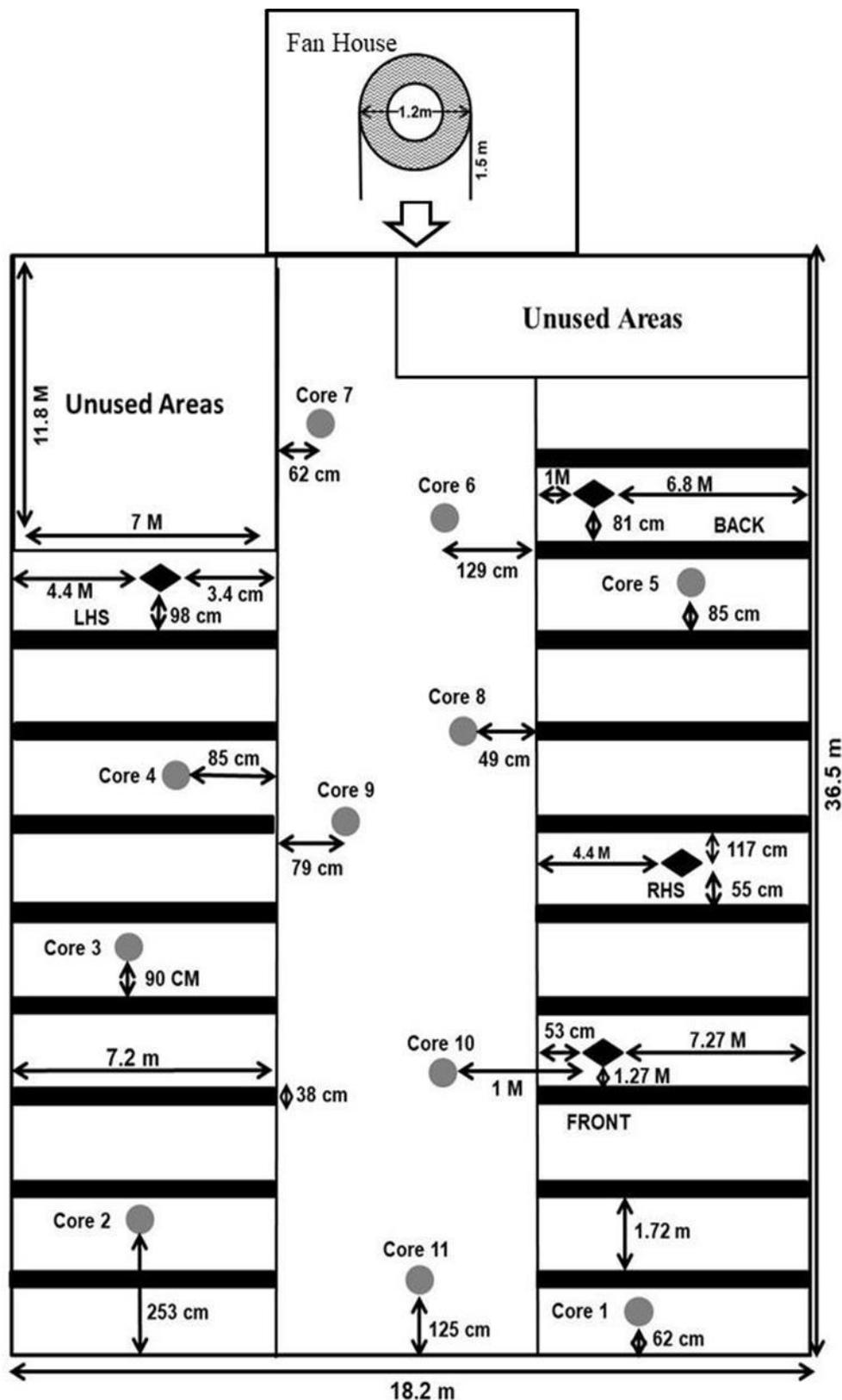


Figure 4.2 Floor plan for Commercial Store A, indicating positions of cores. Black rectangles represent the lateral duct outlets that were relevant to the sampling pattern. LHS and RHS represent the left hand side and right hand side of the store, respectively (reproduced from Douglas et al. 2018b).

In commercial store B, four cores were collected at measured distances from the galvanized ducts (point of CIPC entry) (Figure 4.3). Three of these cores were not intact and it was impractical to section them. Therefore, these cores were processed in their entirety as one sample extracted and used to determine the total distribution in the store. The remaining intact core was sectioned, processed and analysed for the depth distribution study.

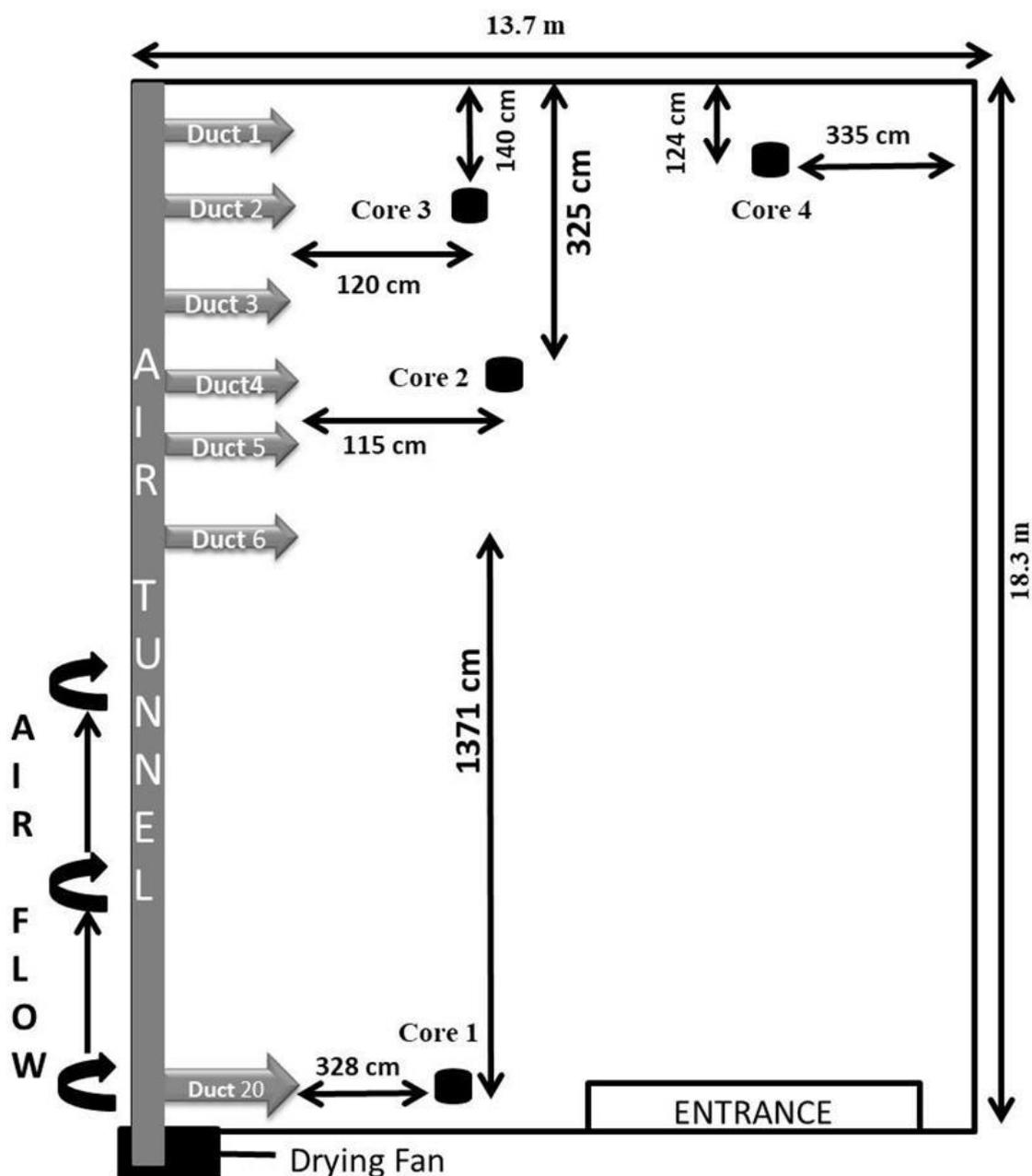


Figure 4.3 Floor plan of commercial store B showing position of cores (black discs) (reproduced from Douglas et al. 2018b).

#### 4.1.4.1. Depth distribution of CIPC in research stores

For each research store, three cores were collected at measured distances (Figure 4.1) in the vicinity of the plenum, the front of the store (entrance) and at the back of the store (door) near the point of CIPC entry. The majority of CIPC (90 to 100 %) was found in the first centimetre layer of each core. There was a decrease in CIPC concentration in the descending layers of each core, indicating penetration to a depth of between 3 and 4 cm (Figure 4.4).

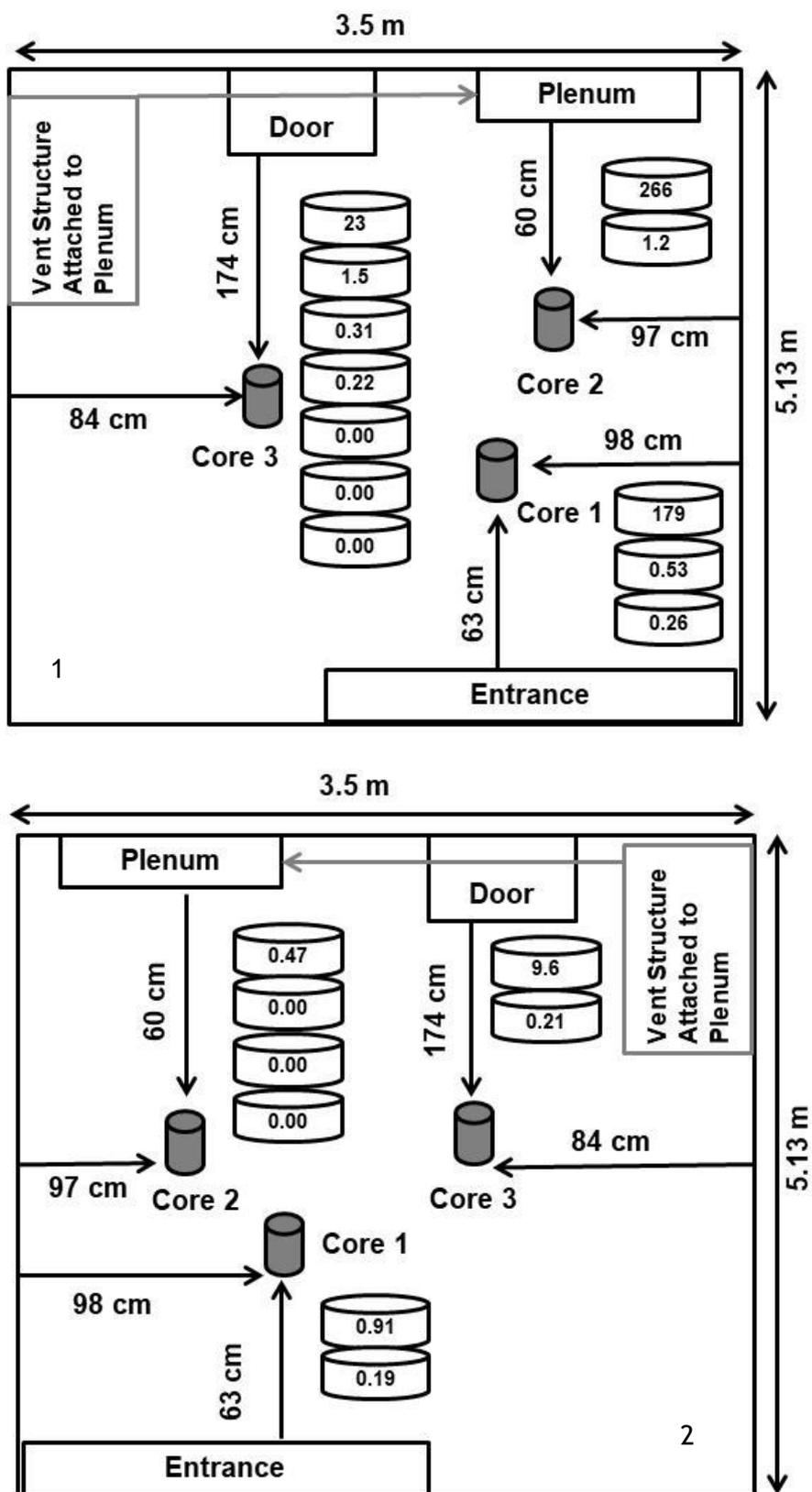


Figure 4.4 Diagrammatic representation of: 1) research store 1 (several applications) and 2) research store 2 (single application), indicating positions of cores (grey cylinders) and CIPC concentrations ( $\mu\text{g g}^{-1}$ ) in each one-centimetre layer (disc). Depth of CIPC distribution depicted by descending discs (reproduced from Douglas et al. 2018b).

#### 4.1.4.2. Depth distribution of CIPC in commercial stores.

The majority of the CIPC (90-100%) was found in the first centimetre of the cores collected from commercial store A, with a trend of decreasing concentration in the descending layers up to a depth of 3 cm (Table 4.2), as similarly observed in the research stores. The penetration of CIPC into the flooring of commercial store B (Table 4.2) relative to the other stores, was more pronounced as evidenced in: (I) 47% retained in the first centimetre layer of core 3 and (II) percentages of 35, 15 and 4 in the 2nd, 3rd and 4th depth increments, respectively. Core 3 was the only intact core obtained from commercial store B and this was used in the depth distribution study. The other cores crumbled due to the structural integrity of the concrete. It was noted that the concrete samples from the commercial stores were different in physical appearance to the research stores. Commercial store B samples seemed more porous and this would explain the penetration of CIPC in the descending layers.

Table 4.2 CIPC concentration ( $\mu\text{g g}^{-1}$ ,  $n=1$ ) and percentages of total in parentheses in each layer of each core from commercial stores A and B (Douglas et al., 2018b).

Concentration of CIPC in each layer in the cores ( $\mu\text{g g}^{-1}$ )				
	1 <sup>st</sup> cm	2 <sup>nd</sup> cm	3 <sup>rd</sup> cm	4 <sup>th</sup> cm
Position of cores in commercial store A				
Back	23 (91)	2.0 (8)	0.20 (0.8)	NS
Right hand side	17 (98)	0.38 (2)	NS	NS
Left hand side	29 (98)	0.66 (2)	NS	NS
Front	104 (94)	4.5 (4)	1.8 (2)	NS
Position of core in commercial store B				
Duct 2: core 3	472 (47)	352 (35)	150 (15)	36 (4)
NS-Not sampled				

#### 4.1.5. Lateral distribution of CIPC in research and commercial potato stores.

The cores used in the depth distribution study were used to determine the lateral distribution of CIPC in the potato stores. This was calculated as the total concentration in individual cores ( $\mu\text{g g}^{-1}$ ). The mass of CIPC in each layer of each core was calculated then the masses in each layer summed and converted to a total concentration ( $\mu\text{g g}^{-1}$ ) by dividing by the total weight of the uncrushed core. The heterogeneity of CIPC in the first centimetre layer of the flooring, in commercial store A was further explored in the lateral distribution study. The heterogeneity was determined using random and systematic sampling patterns to collect eighteen additional cores (Figures 4.5 and 4.6). A systematic sampling pattern was used to collect eight cores in proximity to the front core (Figure 4.6). Core number 10, which is positioned 1 metre from the front core, was used as a central point in the sampling pattern. The front core, along with cores A, B and C, were positioned 1 metre from the central core in a cross pattern and formed an outer circle around core 10. Four cores - D, E, F and G were collected in a diagonal pattern and at 0.5 m distances from the central core. This formed an inner circle pattern around the central core.

#### **4.1.5.1. Lateral distribution of CIPC in research stores.**

The CIPC distribution in the research stores was determined using the total CIPC concentrations in the three respective cores. The order of distribution, in terms of the concentration levels in the three identical cores, was different for both stores although the same ventilation system was used. The distributions of CIPC in research store 2, from highest to lowest concentrations, were in the order: Back (door)  $5.6 \mu\text{g g}^{-1}$ : Front (entrance)  $0.58 \mu\text{g g}^{-1}$ : Plenum  $0.11 \mu\text{g g}^{-1}$ . This was the expected distribution, based on the circulatory system employed. The potato boxes were located in front of the plenum and would have hindered the contact of CIPC with the concrete flooring. In addition, the circulatory system employed positive ventilation through the crop which would hinder CIPC contact with the concrete in the vicinity of the plenum. Hence, the lowest concentration was observed in the concrete in the vicinity of the plenum. The front of the store had no obstacles on the concrete and hence the mobile fog would be in direct contact with it. This explains the second highest distribution at the front. The point of CIPC entry into the store was via the back door and this may explain the highest CIPC concentration.

The distribution of CIPC in research store 1, from highest to lowest concentrations, were in the order: Plenum  $112 \mu\text{g g}^{-1}$ : Front (entrance)  $63 \mu\text{g g}^{-1}$ : Back (door)  $3.4 \mu\text{g g}^{-1}$  which was not expected, based on the circulatory system used. The high concentrations observed in the vicinity of the plenum and front may be caused by accumulation of CIPC prior to the installation of the plenum system. CIPC was not circulated in store 1 prior to the installation of the plenum. This suggests that the accumulation and distribution of CIPC in concrete is influenced by circulation. The magnitude of contamination in both stores was influenced by the quantities of CIPC applied. Store 1, with the highest quantity of applied CIPC, had the greater magnitude of contamination.

#### **4.1.5.2. Lateral distribution of CIPC in commercial stores.**

The distribution of CIPC in the commercial stores was determined as described for the research stores. The commercial stores were not identical; however, comparisons were made because both were bulk stores and the same dosage of CIPC ( $63.75 \text{ g t}^{-1}$ ) was applied to each. The magnitude of contamination in these stores was influenced by the quantities of CIPC applied. The magnitude of contamination in commercial store A which was fogged with an estimated 2,040 kg of CIPC (18 seasons of application: last application 2000) was less relative to store B, fogged with an estimated 319 kg of CIPC (5 seasons: last application 1991). Store A had concentrations varying between  $6\text{-}48 \mu\text{g g}^{-1}$  in the top three centimetres, in contrast to B with concentrations varying between  $0.58\text{-}304 \mu\text{g g}^{-1}$  in the top four centimetres. The distribution trends in stores A and B may be explained in terms of (I) the type of ducts used to introduce CIPC into the stores and (II) the ventilation system used to distribute the CIPC. In store A, CIPC was applied as a fog via lateral underground ducts that were evenly positioned throughout the store. Based on this duct arrangement, it was expected that the applied CIPC and eventual accumulated residues in the concrete floor would have been evenly distributed. However, the trend observed (Table 4.3) suggests that other factors were influencing the distribution. The highest concentrations of accumulated residues at the front ( $48 \mu\text{g g}^{-1}$ ) and lowest at the back ( $6.7 \mu\text{g g}^{-1}$ ) may be due to dispersed particles caused by fans located at the back which were functional after application. This further confirms the effect of circulation on the accumulation of CIPC in the concrete flooring. In store B, CIPC entered via above-ground galvanized ducts and was routinely applied via ducts 2 and 4 and occasionally via duct 6. CIPC was blown across the store from left to right. The trends observed suggest that the accumulation of residues in the flooring was affected by the point of CIPC entry (Table 4.3). Concrete cores 2 ( $304 \mu\text{g g}^{-1}$ ) and 3 ( $216 \mu\text{g g}^{-1}$ ), that were nearest to the entry ducts, had the highest concentrations relative to core 1 ( $0.58 \mu\text{g g}^{-1}$ ) which was remote from all entry ducts. Core 4 ( $10 \mu\text{g g}^{-1}$ ) which was aligned with duct 2 but remote from it (distance of 10.35 m), had significantly lower levels of CIPC relative to core 3 ( $216 \mu\text{g g}^{-1}$ ) which was nearest to duct 2 (1.2 m). CIPC was not circulated in store B to effect even distribution and as such, residues accumulated in areas of the concrete that were closest to the points of entry.

Table 4.3 Total CIPC concentration ( $\mu\text{g g}^{-1}$ ) in each core for commercial stores A and B (Douglas et al., 2018b).

Position of cores	CIPC concentration ( $\mu\text{g g}^{-1}$ )
Commercial store A	
Back	6.7
Right hand side	7.8
Left hand side	18
Front	48
Commercial store B	
Front: core 1	0.57
Duct 4: core 2	304
Duct 2: core 3	216
Duct 2: core 4	10

#### 4.1.6. Heterogeneity of CIPC distribution in a commercial store

The heterogeneity of CIPC distribution in stores was explored using samples from commercial store A. Commercial store A was easily cored and the intact cores were sectioned without crumbling. The top 1-cm layers of an additional 18 cores, collected using random and systematic sampling patterns, were analysed to determine the heterogeneity of CIPC distribution in the concrete flooring. These were selected for study because >90% of the CIPC was found to accumulate in this layer. The distribution was lowest at the back of the store ( $14\text{-}31 \mu\text{g g}^{-1}$ ) and highest at the front ( $104\text{-}1667 \mu\text{g g}^{-1}$ ), as shown in the random sampling pattern (Figure 4.5). CIPC was introduced at the back of the store into a lateral duct system and distributed throughout the store. The higher concentrations at the front are therefore conceivable with this system of application. The concentrations around a central core ( $498 \mu\text{g g}^{-1}$ ) were in the range of  $65\text{-}778 \mu\text{g g}^{-1}$ , as depicted by the systematic sampling pattern (Figure 4.6), highlighting further that accumulation of CIPC in the concrete flooring was heterogeneous. The fan system and/or the location of the fans seemed to have influenced the distribution and eventual accumulation of CIPC in the flooring.

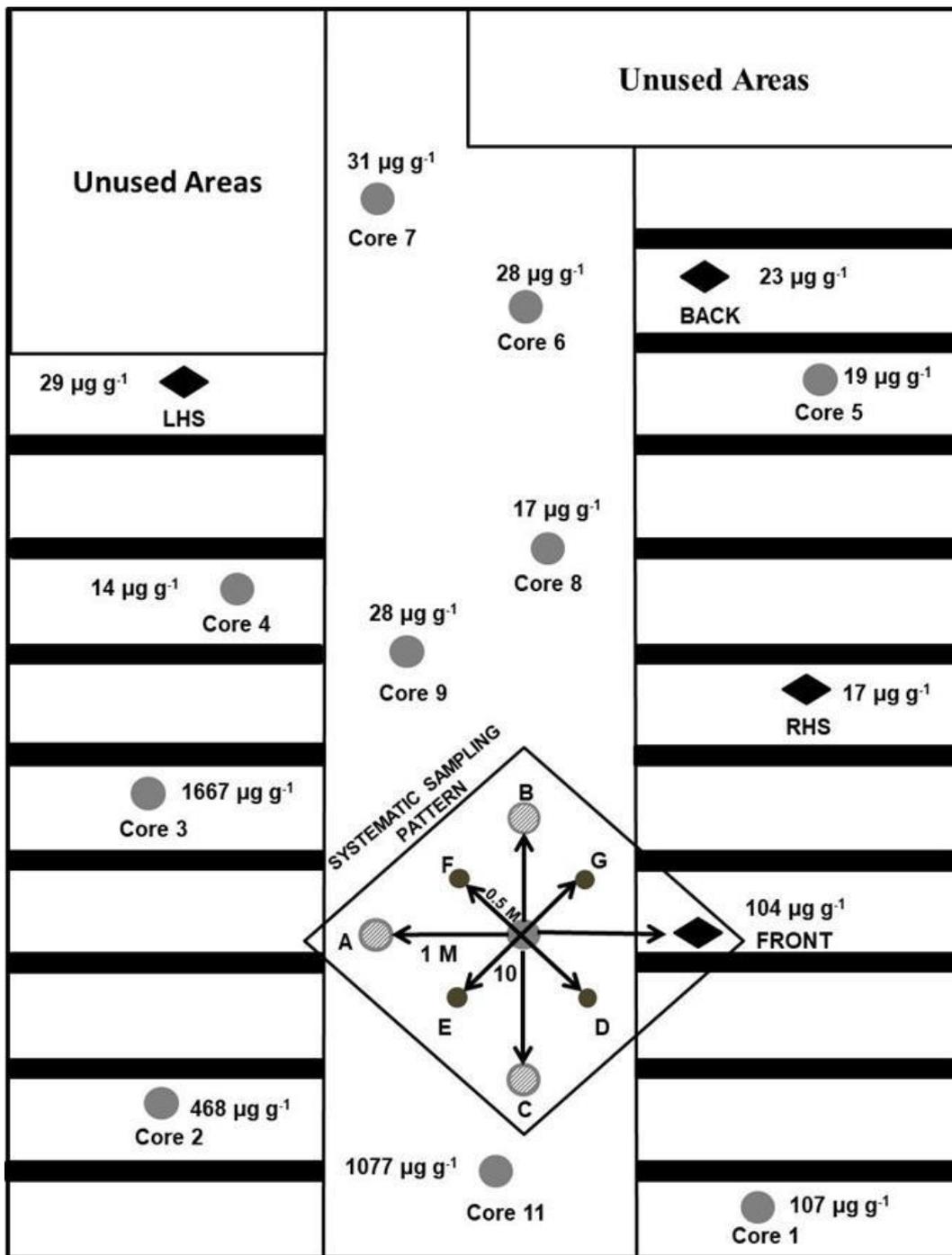


Figure 4.5 Floor plan for commercial store A, indicating positions of cores and respective CIPC concentrations in the first 1-cm layer of the cores. Black rectangles represent the lateral duct outlets that were relevant in the sampling pattern. LHS and RHS represent the left hand side and right hand side of the store respectively (reproduced from Douglas et al. 2018b).

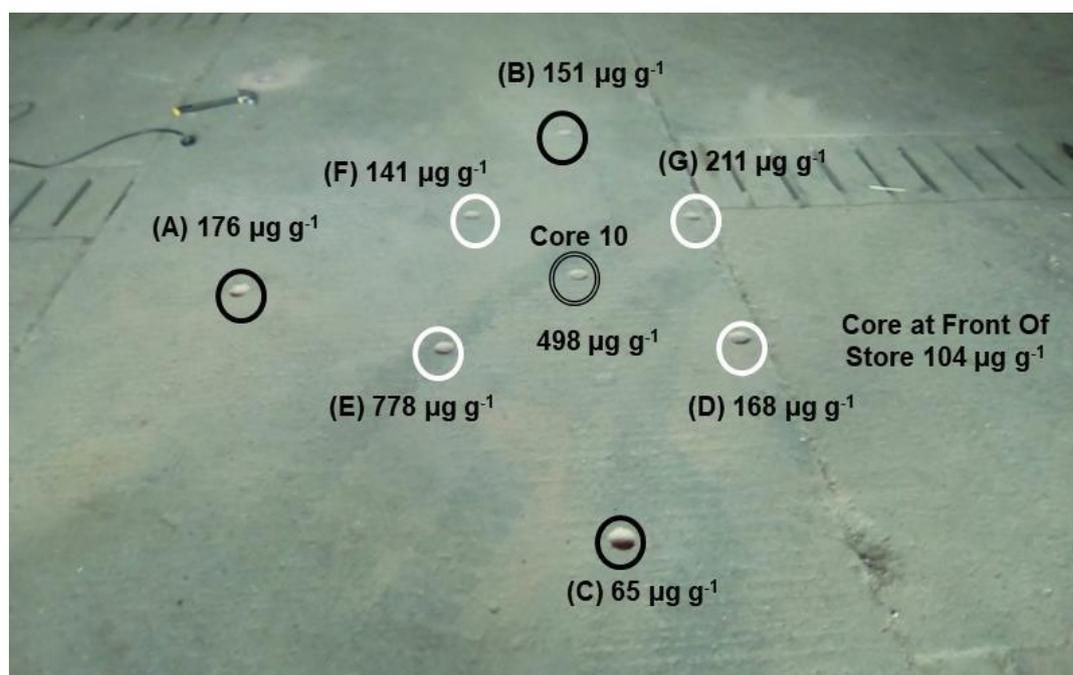


Figure 4.6 CIPC concentrations ( $\mu\text{g g}^{-1}$ ) for each core in the systematic sampling from commercial store A.

#### 4.1.7. Confirmation of CIPC in commercial potato stores using GCMS

The presence of CIPC in the commercial and research store samples was confirmed using GCMS. The sample patterns and similarity search were consistent with that of CIPC (213/215 m/z: parent ion; 153/154 m/z: m-chlorophenyl isocyanate; 171/173 m/z: free acid formed from isopropyl residue; 127/129 m/z: chloroaniline).

#### 4.1.8. Distribution of 3-Chloroaniline in potato stores

The quantities of 3-CA and CIPC in commercial store samples were determined using HPLC PDA detection. Selected samples from commercial stores A and B were analysed. The 3-CA and CIPC concentrations obtained in core 9 (store A) were  $4.74 \mu\text{g g}^{-1}$  and  $27.65 \mu\text{g g}^{-1}$ , respectively, whereas the concentrations in core 3 (store B) were  $5.83 \mu\text{g g}^{-1}$  and  $323 \mu\text{g g}^{-1}$ , respectively. The purity obtained was 99.9 % for both chemicals, thus confirming the presence of 3-CA and CIPC in the concrete samples. The 3-CA and CIPC quantities in core 7 (store A) were  $1.16 \mu\text{g g}^{-1}$  and  $31.2 \mu\text{g g}^{-1}$ , respectively, with purities of 94.9% and 99.7%, respectively. The 3-CA purity percentage was low compared to the other samples, suggesting uncertainty in terms of confirmation, and this may be due to the lower 3-CA concentration relative to the other samples. These samples were subsequently analysed by GCMS to confirm the presence of both chemicals.

The quantification of 3-CA and CIPC in commercial store samples was further investigated using HPLC UV/VIS. The 3-CA and CIPC concentrations in core 3 (store A) were  $38 \mu\text{g g}^{-1}$  and  $1666 \mu\text{g g}^{-1}$ , respectively, whereas in core 7 (store A) the values were  $1.12 \mu\text{g g}^{-1}$  and  $39.72 \mu\text{g g}^{-1}$ , respectively. HPLC and PDA analyses produced similar 3-CA and CIPC concentration values for core 7, confirming the robustness of the PDA method, irrespective of the low purity. The purity of the 3-CA peaks using UV/VIS detection was assessed with the 208/240 nm ratio. The ratios for an undiluted and diluted sample of core 3 were 2.7 and 3.0 respectively. The undiluted sample ratio seemed to coincide more closely with the ratios of the standards, suggesting that assessment of the 3-CA purity may be possible at higher concentrations using these two wavelengths. GCMS was used to further confirm the presence of both chemicals in samples assessed by the HPLC UV/VIS method.

A GCMS method was adopted from Barbin et al. (2013) to confirm the presence of 3-CA in industrial concrete from the commercial stores. The effect of this method on the degradation of CIPC in samples was examined prior to the analysis of commercial store samples. Standard solutions of 3-CA, CIPC and a mixture of CIPC and 3-CA were used to assess the method. The method was able to detect CIPC and no 3-CA peak was observed in standard solutions containing CIPC only. The retention times for 3-CA and CIPC were 4.02 and 8.15 minutes, respectively. Concrete samples (from commercial stores A and B) gave mass spectral patterns for CIPC and 3-CA which were consistent with the expected spectra. This confirmed the presence of both chemicals in commercial-store concrete. The mass spectral patterns for 3-CA and CIPC are as follows:

CIPC (213/215 m/z: parent ion; 153/154 m/z: m-chlorophenyl isocyanate; 171/173 m/z: free acid formed from isopropyl residue; 127/129 m/z: chloroaniline).

3-CA (127: m/z parent ion; 45 m/z and 65 m/z).

Due to the presence of 3-CA in concrete samples from commercial stores A and B, these samples may be contaminated with other chloroaniline isomers and were therefore analysed using the isomer method. Concrete samples from commercial stores A and B were only contaminated with 3-CA and confirmed the absence of 2-CA and 4-CA.

Overall, the persistence of 3-CA was evident in industrial concrete using PDA and UV/VIS detection and confirmed by GC-MS analysis. The 3-CA concentrations in the first centimetre layer of the concrete flooring in store A ranged from 4.74-38  $\mu\text{g g}^{-1}$ , highlighting the persistence at this depth.

## **4.2. An HPLC UV/VIS method validation for the analysis of chlorpropham in crop commodities**

### **4.2.1. Preliminary assessment to determine the effect of grinding on matrix effects and CIPC recoveries from oats**

Oat samples were used in a preliminary assessment to determine the suitability of a sample preparation procedure (milling) prior to HPLC UV/VIS analysis of CIPC in grains. The milling procedure was examined to determine: (I) the effect of a ground oat matrix on CIPC analysis using HPLC UV/VIS, (II) the efficiency of the extraction procedure to remove CIPC from the ground oat matrix and (III) the efficiency of the extraction procedure to remove CIPC from the surface of unground oats. The experiments were conducted at a CIPC concentration of 4.0  $\mu\text{g g}^{-1}$ . The presence of interfering peaks and the complexity of the matrix of the ground sample were more pronounced relative to the unground oat matrix, suggesting that grinding may be detrimental in the analysis of CIPC. Approximately 67% of CIPC absorbed by the ground matrix was recovered with the acetonitrile extraction (after subtracting the concentration of the artefact peak (0.957  $\mu\text{g g}^{-1}$ ) in the clean samples from that of the spiked sample) with good precision (0.23% RSD). The extraction procedure was able to remove CIPC from the surface of intact/unground oat samples with a recovery of 99.9% and good precision (0.63% RSD). This percentage was ascertained after subtraction of the artefact peak (0.060  $\mu\text{g g}^{-1}$ ) concentration from the concentration that was observed in the non-spiked un-ground oat. The high concentration observed for the artefact peak in the non-spiked ground sample may be caused by both surface and non-surface (matrix) contamination. This may explain the lower recovery obtained relative to the unground sample where surface contamination was the factor affecting the concentration of the artefact peak. The complexity of the matrix was enhanced by grinding and the recoveries were lower relative to the unground samples, therefore, the unground processing methodology was adopted for future studies.

#### **4.2.2. An examination of the matrix of different grains, collected from different geographical locations, on the analysis of CIPC using HPLC UV/VIS**

Oats, barley and wheat samples were obtained from farms in England and Scotland. Pre-packaged grains (barley and wheat), purchased from local supermarkets that were products of Germany and France, were also used in this study. Grains (oats, barley and wheat) obtained from Scotland had no artefact peak at the retention time of CIPC; however, samples of oats and wheat obtained from England had artefact peaks present at this retention time. Pre-packaged grains (barley: Scots Brand and wheat: Holland & Barrett) were free from artefact peaks at the retention time of CIPC, whereas Pearl Barley from Sainsbury's had a non-uniform peak, producing a concentration of  $0.032 \mu\text{g g}^{-1}$ . Overall, the Scottish barley and wheat samples showed the least matrix influence in the vicinity of the CIPC retention time and hence seemed the most promising for method development and field trials. The Scottish wheat sample was selected for method development and was used in the LOD and LOQ determination to represent general non-organic wheat. The organic wheat obtained from Holland & Barrett was used as a control sample and for field trials because it was CIPC free and had no matrix effects.

A HPLC UV/VIS method coupled with acetonitrile extraction previously developed for analysis of CIPC in concrete was adopted and validated for non-organic wheat. The method was validated at nominal levels of  $0.04$  and  $4.0 \mu\text{g g}^{-1}$ , producing recoveries of 65 and 95%, respectively, with %RSD values of 5.6 and 3.4%, respectively. The method will be ideal for quantifying CIPC in cross contaminated samples close to the LOD of CIPC, and despite the lower recovery, good precision was obtained at a nominal value of  $0.04 \mu\text{g g}^{-1}$ . The method was sensitive for organic and non-organic wheat with LOD (organic:  $0.004 \mu\text{g g}^{-1}$ , nonorganic:  $0.016 \mu\text{g g}^{-1}$ ) and LOQ (organic:  $0.016 \mu\text{g g}^{-1}$ , non-organic:  $0.054 \mu\text{g g}^{-1}$ ) values' respectively, confirming its robustness.

#### **4.2.3. Method for concentrating samples below the LOD prior to GCMS analysis**

The suspected cross contaminated oat and wheat samples, collected from England, had CIPC concentrations of  $0.019 \mu\text{g mL}^{-1}$  (equating to  $0.076 \mu\text{g g}^{-1}$ ), which was below the limit of detection of the GCMS instrument. The method for concentrating samples below the LOD was developed using a CIPC stock solution of  $0.01 \mu\text{g mL}^{-1}$ . Subsequently, CIPC-free Scottish wheat and suspected contaminated English oat and wheat samples were concentrated as follows: A total volume (300 mL) of grain extract and CIPC stock solution containing  $0.01 \mu\text{g mL}^{-1}$  were evaporated to dryness at  $20^\circ\text{C}$  (Heidolph WB 2000, Germany) using a Bibby Rotary Evaporator RE 100 (Germany) coupled to a Büchi Vac® V-500 pump (Germany). The evaporated samples were re-dissolved into 500  $\mu\text{L}$  of acetonitrile, giving a final concentration of approximately  $6 \mu\text{g mL}^{-1}$  for the concentrated CIPC stock solution. Qualitative analysis using GCMS was performed to confirm the presence of CIPC in suspected cross contaminated samples.

The concentrated CIPC standard ( $0.01 \mu\text{g mL}^{-1}$ ) spectrum obtained at 9.1 minutes was consistent with CIPC, suggesting that the method of concentrating the standard was efficient for improving the detection at levels close to the LOD of the instrument. Subsequently, suspected cross contaminated oat and wheat sample extracts, along with a non-organic clean wheat sample extract, were concentrated and analysed. The spectra obtained for the oat and wheat samples collected from England were consistent with CIPC suggesting the possibility of cross contamination during transportation. The farm in England where the wheat sample was obtained was visited and a sample of wheat was retrieved from the exact place where the first batch was collected. Care was taken in terms of packaging the sample for transportation. The sample was collected in a plastic bag using latex gloves, triple wrapped in aluminium foil and then stored in a solid plastic container. The sample was transported in a back pack and was not in any physical contact with contaminated surfaces including any within the vehicle. This sample was extracted and analysed by HPLC UV/VIS and was CIPC free, suggesting the possibility of cross contamination of the previous oat and wheat samples during transportation. This was invaluable information because precautionary measures were implemented for packaging, storing and transporting samples for field trials. In addition, this highlights the ease of cross contamination of commodities with CIPC coming in contact with contaminated surfaces. The

GCMS spectrum for the non-organic wheat sample from Scotland was inconsistent with CIPC, suggesting that it was CIPC free. However, another chemical was identified in this sample at the retention time of 9.1 and was confirmed to be benzenesulfonamide (molecular weight 199). This may be due to the selective herbicide chlorsulfuron which is used to control broadleaf weeds and some grasses in wheat (Royuela, Muñoz-Rueda and Gonzalez-Murua, 1990). The robustness of the GCMS method in distinguishing between CIPC-free grains and cross-contaminated grains at levels close to the limit of detection was confirmed.

### **4.3. Preliminary experimental designs for studying the degree and route of cross contamination of grains in a real store environment.**

Based on the preliminary assessment, glass beakers and sieve cloth of pore diameter 355  $\mu\text{m}$  were selected for materials to be used in the trials investigating the route of cross contamination in real stores. An experimental design (in terms of glassblowing modifications) was examined prior to the study. Glass beakers (600 mL) were modified to form a tight seal for retention of volatile residues of both chemicals, allowing the contamination caused by headspace in real stores to be studied. The beakers were initially modified by removal of the spouts followed by inversion of the edges and flattening to produce flanges. The flanges were subsequently refined by manual lapping with carborundum and annealing at 500  $^{\circ}\text{C}$ , aiding the sealing of adjoining containers to each other, producing a headspace of 10 cm. Sieve cloth (355  $\mu\text{m}$ ) (Plastok Associates Ltd, UK) was fixed between the containers to act as a support for the grains. This preliminary modification was carried out to have an idea of: (I) the glassblowing techniques that would be required to seal the edges of the beakers, (II) the type of glass that was to be used for future studies and (III) the ability of the taut sieve cloth to maintain the weight of the grains. The apparatus produced seemed promising for real store studies and further modifications (in terms of beaker size to allow a large surface area for chemical interaction) were subsequently made for the store trials.

### **4.4. Degree and Route of Chlorpropham and 3-Chloroaniline Cross Contamination of Grains in Commercial Potato Stores**

#### **4.4.1 Modification and designs of glassware used in field trials**

The commercial stores employed in this study are currently used for the storage of farm equipment. Therefore, due to spacing restrictions, two sets of glassware were designed to suit the available areas in the stores where the trials were executed. There was sufficient space in commercial store B to facilitate larger containers, enabling a larger surface area of grains to be exposed to the atmosphere of the store. Therefore, borosilicate glass beakers (3 L) with diameter 15 cm were selected for modifications. The beakers were modified as detailed above to produce flattened and smooth surfaces to enable sealing with adjoining containers and other surfaces such as concrete. The bases of selected beakers were removed to facilitate air interactions with the headspace of the store or above the surface of the concrete flooring. The spacing in store A was restricted, therefore, smaller glass containers were designed for trials in this store. Glass containers of diameter 5 cm and height 1 cm were designed from borosilicate glass.

#### **4.4.1. The degree and route of CIPC cross contamination of grains in commercial stores: cross contamination trial in commercial store A**

Commercial store A was fogged with CIPC for 18 seasons, with the last application in 2000. CIPC entered this store via a main duct and was subsequently distributed through evenly positioned lateral ducts. The CIPC distribution in this store was previously determined using random and systematic sampling patterns, with CIPC and 3-CA concentrations of 14-1667  $\mu\text{g g}^{-1}$  and 4.7-38  $\mu\text{g g}^{-1}$  respectively, in the first 1-cm layer of the concrete flooring. Grains (30.0 grams) were placed in glass containers of diameter 5 cm and height 1 cm. Trials (six weeks and three months) were conducted where six batches of duplicate samples exposing grains either to the headspace or the concrete surface were randomly positioned in six places. The spacing

for the trial in this store was limited so samples were placed 50 cm from the walls at the front, middle and back of the store. A wooden and mesh frame was used to protect the grains from rodents. The samples were extracted and analysed by HPLC UV/VIS and GCMS. The natural environmental factors (temperature and humidity) were not monitored because potato storage in this building had ceased.

The wheat samples were found to be cross contaminated with CIPC and no 3-CA was detected. The contamination process was independently influenced by: (I) the headspace of the store and (II) contact with contaminated concrete. The magnitude of cross-contamination in the 6 weeks and 3 months trials was greater in the samples exposed to the headspace of the store (Tables 4.4 and 4.5). The duration of storage influenced the magnitude of contamination in grains exposed to the headspace, with increasing CIPC concentrations for longer storage periods (3 weeks: 0.28-0.34  $\mu\text{g g}^{-1}$ ; 6 months: 0.22-0.56  $\mu\text{g g}^{-1}$ ), whereas, the samples in contact with the concrete (3 weeks: 0.10-0.24  $\mu\text{g g}^{-1}$ ; 6 months: 0.01-0.20  $\mu\text{g g}^{-1}$ ) were not affected by storage period. The magnitude of contamination in the wheat samples in contact with the concrete surface was not influenced by the CIPC levels in the concrete. The levels of CIPC in the concrete were higher at the front of the store, therefore higher concentrations in the wheat located at the front were expected. However, this was not observed and may be explained in terms of the locations of the samples and the surface areas of the grains. The samples were positioned at the corners of the building underneath shelves which spanned the periphery of the building. The residual CIPC in the concrete at the periphery of the building may be of the same magnitude due to restricted access of CIPC to these secluded areas. Therefore, the same magnitude of cross contamination was observed in the samples.

There was a disadvantage in using containers with a 5 cm diameter because a small surface area of grains was exposed to the concrete surface, hindering maximum cross-contamination. However, the design of using four small containers in a square (10 cm  $\times$  10 cm) was advantageous in that the degree of contamination in a small area of concrete was determined. Comparisons of the respective paired wheat samples on the concrete (6 weeks and 3 months) for each location showed no significant difference in the magnitude of cross-contamination, suggesting that the CIPC levels in the concrete 10 cm apart may be the same. Overall, it was evident that the headspace and the concrete surface in a contaminated store were integral in the route of cross-contamination of grains. Therefore, decontamination strategies will have to be considered to deal with both the headspace and the concrete surface.

Table 4.4 CIPC concentrations ( $\mu\text{g g}^{-1}$ ) in wheat samples collected from the 6 weeks route of cross contamination trial in store A.

Concentration $\mu\text{g g}^{-1}$ in wheat samples		
Sample Number	Exposed to the headspace of the store	In direct contact with the concrete surface
1	0.343	0.237
2	0.290	0.096
3	0.344	0.148
4	NA	NA
5	0.280	0.157
6	0.292	0.212

NA: Not applicable, sample was not retrieved.

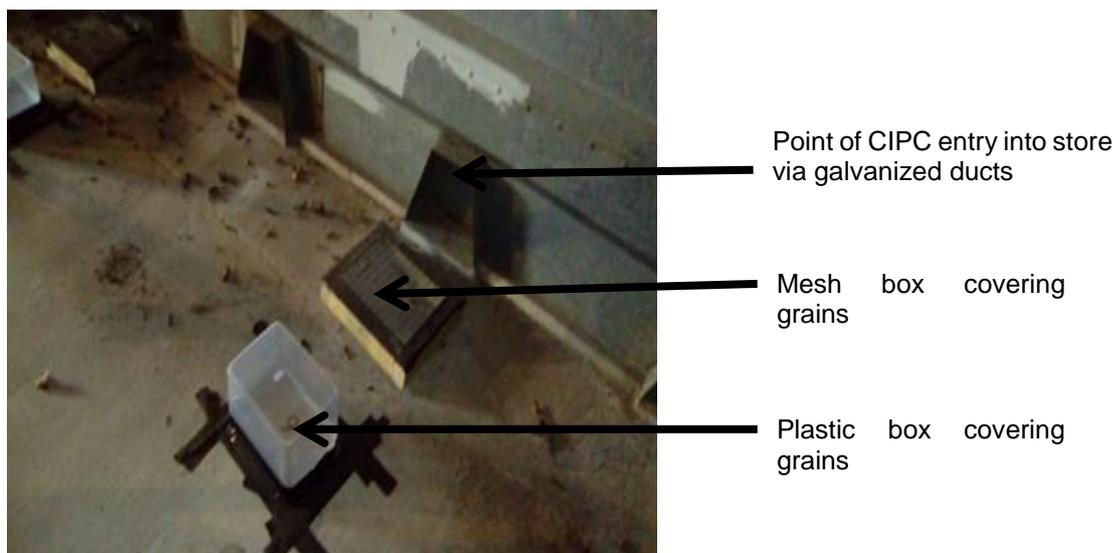
Table 4.5 CIPC concentrations ( $\mu\text{g g}^{-1}$ ) in wheat samples collected from the 3 months route of cross contamination trial in store A.

Concentration ( $\mu\text{g g}^{-1}$ ) in wheat samples		
Sample Number	Exposed to the headspace of the store	In direct contact with the concrete surface
1	0.561	0.201
2	0.242	0.013
3	0.224	0.142
4	NA	NA
5	0.256	0.167
6	0.240	0.024

NA: Not applicable, sample was not retrieved.

#### 4.4.2. The degree and route of CIPC cross contamination of grains in commercial stores: cross contamination trial in commercial store B: Preliminary assessment

Commercial store B was fogged with CIPC for at least five seasons, with the last application in 1990. Galvanized steel ducts were used to introduce CIPC into the store, with ducts 2 and 4, and occasionally duct 6 used as the point of CIPC entry (Figure 4.3). The store was not filled to its maximum capacity (200 tonnes) and therefore only three ducts were used to apply CIPC. The distribution of CIPC was previously determined, with concentrations between 0.58 and 304  $\mu\text{g g}^{-1}$  in the top four centimetres. The four locations where CIPC in the concrete flooring had been determined were selected for the cross-contamination study. Duplicate samples of non-organic wheat (130 g) were placed in close proximity to the cored positions in the concrete flooring. The grains were layered on the surface of the concrete flooring and were covered with either a mesh or an upturned plastic box (Tritan™ plastic containers {copolyester that is not manufactured with BPA (bisphenol compounds)} of size length 27 cm  $\times$  20 cm width  $\times$  17 cm height) (Figure 4.7). The plastic box samples were sealed to the flooring with duct tape (Gaffer, UK) to prevent air interactions with the headspace of the store, whereas the mesh box samples were subject to air interactions. The trial was conducted for seven months after which the samples were retrieved, extracted and analysed by HPLC UV/VIS and GCMS. The natural environmental factors (temperature and humidity) were not monitored because potato storage in this building had ceased.



*Figure 4.7 Wheat samples on the surface of the concrete flooring of commercial store B. Samples are exposed (mesh box) or unexposed (plastic box) to the atmosphere of the store.*

The preliminary route of cross-contamination trial demonstrated that the magnitude of cross contamination was influenced by the CIPC concentration levels in the adjacent concrete (Table 4.6). The most contaminated concrete surface ( $304 \mu\text{g g}^{-1}$ ) had the highest concentrations in the grains ( $25 \mu\text{g g}^{-1}$  and  $111 \mu\text{g g}^{-1}$ ). The magnitude of contamination in the grains was greater with the combined influence of the atmosphere and direct contact with contaminated concrete. Grains affected by both atmosphere and contact with concrete had higher CIPC concentrations relative to their counter-part samples that were isolated from the atmosphere. This was observed, for example, in the vicinity of duct 2 where grain samples that were equidistant from this duct had values of  $4.3 \mu\text{g g}^{-1}$  (exposed to atmosphere) and  $0.53 \mu\text{g g}^{-1}$  (not exposed to the atmosphere) (position 4, Figure 4.3 Table 4.6). CIPC was blown across the store from duct 2 and it can be assumed that the CIPC levels in the concrete in the vicinity of the exposed and unexposed samples were the same. It can therefore be assumed that the level of contamination was due to atmospheric influence. The heterogeneity of CIPC distribution in the concrete flooring, in a case where the exposed and unexposed grain samples were aligned linearly with respect to the CIPC point of entry into the store, may be the cause of the difference in the concentration in the grains. Grain samples, for example, that were aligned linearly to duct 2 (position 3, Figure 4.3 and Table 4.6) had values of  $43 \mu\text{g g}^{-1}$  (exposed to atmosphere) and  $17 \mu\text{g g}^{-1}$  (not exposed to the atmosphere). Higher levels of CIPC are more likely to be present in the concrete that is closest to the point of CIPC entry, where the exposed samples were located, as is the case of grains in position 3. Overall, consistently higher levels of CIPC, by factors of 2.5 and 8 approximately, were observed in grains exposed to the concrete and atmosphere compared to levels in grains exposed only to concrete. Subsequent investigations into the effect of the atmosphere on the cross contamination were conducted by eliminating direct contact with the contaminated concrete. No 3-CA was found in the preliminary trial samples.

Table 4.6 CIPC concentrations ( $\mu\text{g g}^{-1}$ ) in grains that were in contact with the surface of CIPC-contaminated concrete for 7 months and either exposed or not exposed to the atmosphere (Douglas et al. 2019).

Position in store	Total CIPC concentration in core ( $\mu\text{g g}^{-1}$ ) closest to sample	CIPC concentrations in grains ( $\mu\text{g g}^{-1}$ )	
		Mesh Box (exposed)	Plastic Box (not exposed)
1	0.58	0.25	0.079
2	304	111	25
3	216	43	17
4	10.5	4.3	0.53

#### 4.4.3. Degree and route of cross contamination trial in commercial store B: Subsequent assessment.

Further investigation into the route of cross contamination in commercial store B was conducted following the initial trial. In this trial, modified glass beakers were arranged in five experimental designs to study the route of cross contamination attributed to: (I) dislodged dust particles; (II) direct contact with the concrete flooring and (III) the headspace of the store. In design A, two modified beakers without bases were joined together with a piece of sieve cloth (355  $\mu\text{m}$ ) fixed between them. The sieve cloth provided support for a layer of wheat thus preventing direct contact with contaminated concrete surfaces while the open ends of the beakers allowed air interactions with the headspace of the store and the headspace above the concrete surface (Figure 4.8 A). Design B allowed the effects of air interaction above the concrete surface to be studied while restricting: (I) air interactions in the general headspace of the store and (II) direct contact with contaminated concrete flooring. In this design, a piece of sieve cloth was fixed to a beaker without a base, providing support for a layer of wheat, on top of which an enclosed beaker was inverted, sealing the grains from the headspace of the store (Figure 4.8 B). Glass beakers with bases were used in designs C and D to prevent direct contact of grains with contaminated concrete surfaces. Grains in design C were exposed to the headspace of the store (Figure 4.8 C). Air interaction with the headspace of the store was restricted in design D by a clock glass that was sealed with Blu tack (Figure 4.8 D). In design E, the grains were in direct contact with the concrete surface and restricted from headspace interactions in the store (Figure 4.8 E). The adjoined and single containers had the same 20 cm headspace height. The trial, using the five designs, was executed in the vicinity of each of the four cored positions. Designs A and B (and C and E) were arranged horizontally to the assessed core while D was aligned vertically. The distances of A, B and C from the centre of the core were 20, 20 and 15 cm, respectively (Figure 4.9 A). Designs C and E were 45 cm from A and B, forming a rectangular pattern in the vicinity of the core (Figure 4.9 A). Wooden and mesh traps (120 cm  $\times$  30 cm  $\times$  30 cm) were placed around designs A and B to protect the grains from rodents (Figure 4.9 B).

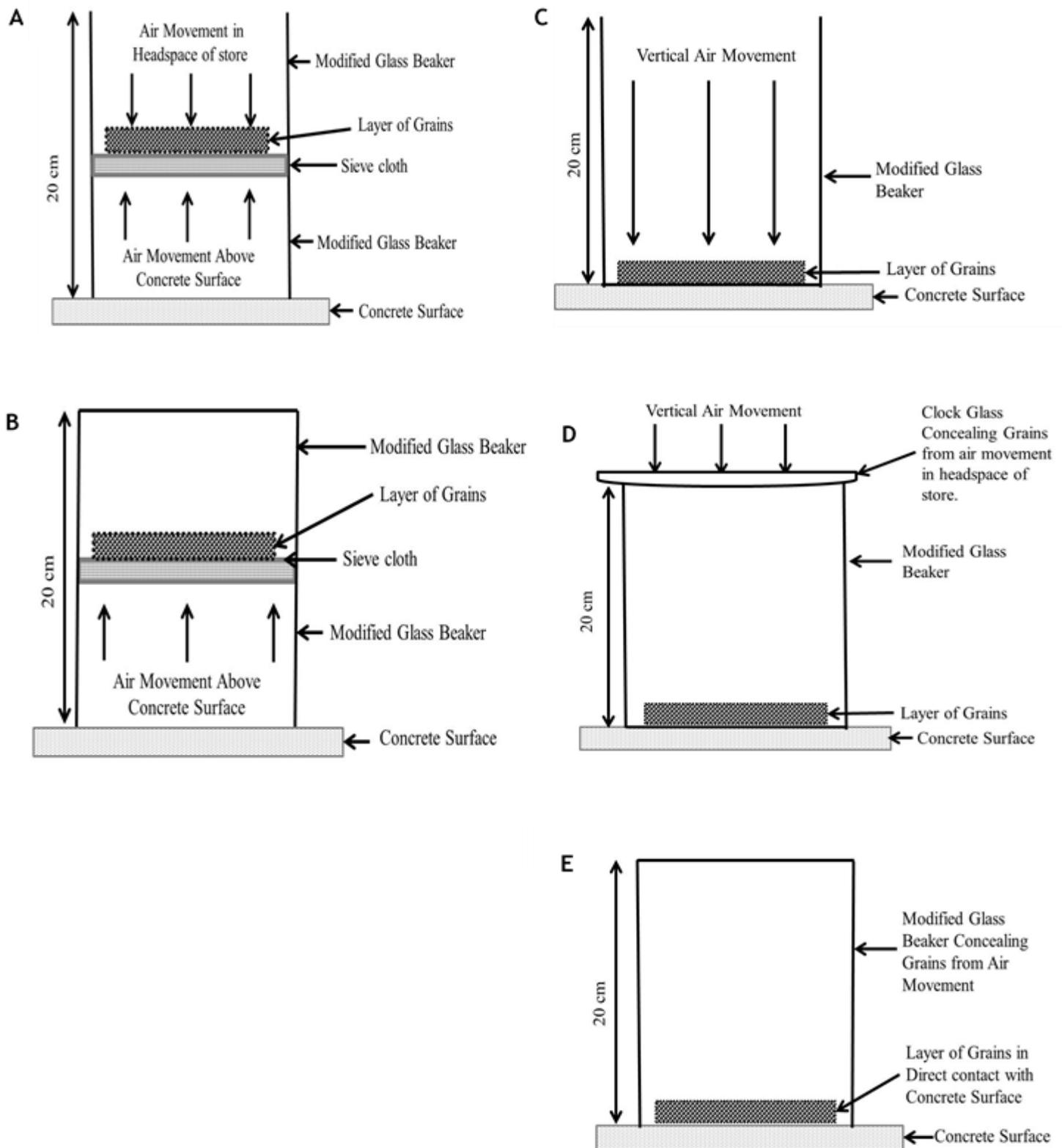
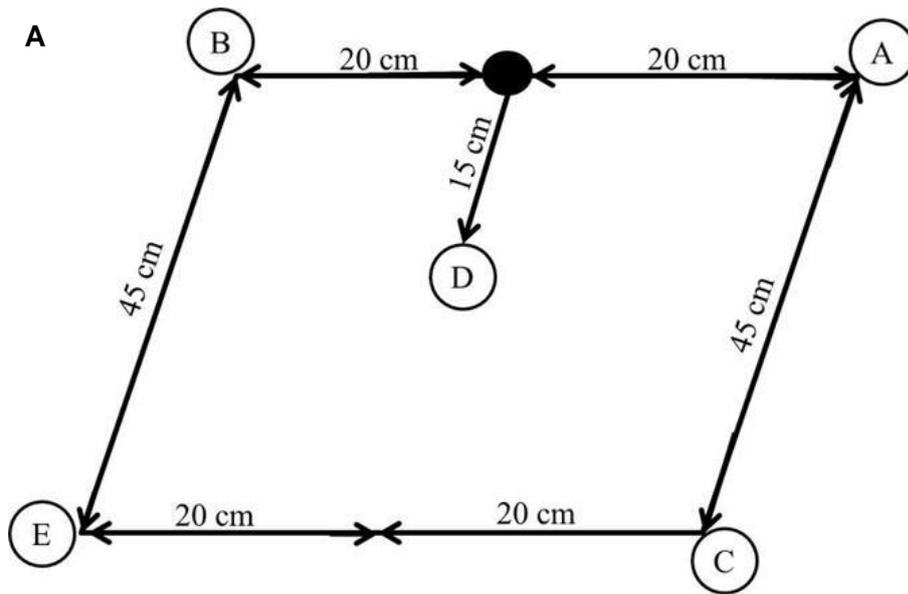


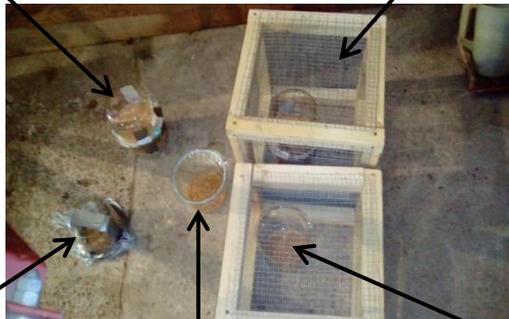
Figure 4.8 Full experimental design to investigate the route of CIPC cross contamination in commercial potato store B (Douglas 2019).



**B**

Grains not in contact with concrete and exposed to headspace above concrete.

Grains not in contact with concrete and exposed to headspace of store and headspace above the concrete.



Grains in contact with concrete and exposed to headspace above concrete.

Grains not in contact with concrete and not exposed to headspace of store.

Grains not in contact with concrete and exposed to headspace of the store.

Figure 4.9 Diagrams illustrating: (A) the spatial arrangement of the five experimental designs around a previously analysed core and (B) the arrangement in the actual store trial (A reproduced from Douglas 2019).

The information gathered from this experimental setup is summarised below, taking into consideration the different environmental conditions that contributed to the route of cross-contamination.

**(A) The possible effect of dust on the route of cross-contamination of grains.**

The dust that accumulated on the surface of the clock glasses is a possible source of cross contamination and therefore determination of the CIPC concentrations in dust samples was vital in this study. The concentrations in the dust samples were expressed as  $\mu\text{g mL}^{-1}$  because it was not feasible for the weight of the dust to be measured. However, this value is an indication of the possible contribution of the dust to the degree of cross-contamination. The LOD and LOQ values for the dust were determined using the LOD and LOQ values of the instrument response. The LOD ( $0.001 \mu\text{g mL}^{-1}$ ) and LOQ ( $0.004 \mu\text{g mL}^{-1}$ ), with respect to the instrument response, were previously evaluated using  $0.01 \mu\text{g mL}^{-1}$  CIPC solution.

The dust that accumulated on the clock glasses in the vicinity of the point of CIPC entry into the store, positions 2 to 4, had CIPC residues as confirmed by HPLC UV/VIS analysis (Table 4.7). CIPC was absent in the sample at position 1 that was remote from the point of CIPC entry. The point of CIPC entry seemed to influence the magnitude of CIPC in the dust and concrete flooring. The influence of cross contamination at CIPC entry points to the store may be more pronounced since the accumulation and deposition of CIPC in the flooring and roof are more evident at these points. This suggests that both the headspace and dust particles may have attributed to the cross contamination of grains in designs A and C.

Table 4.7 Concentration of CIPC in accumulated dust (Douglas et al. 2019).

Position in store	CIPC concentration in concrete flooring ( $\mu\text{g g}^{-1}$ )	Average CIPC concentration in sequential washes ( $\mu\text{g mL}^{-1}$ )
1	0.58	0.00
2	304	0.018
3	216	0.015
4	10.5	0.014

**(B) The effect of the headspace and physical contact with contaminated surfaces on the route of cross-contamination.**

The influence of the different environmental conditions on the route of cross-contamination was calculated in relation to the increase in CIPC content above the MRL. The MRL ( $0.01 \text{ mg kg}^{-1}$ ) was used as a constant factor to calculate the increase in CIPC content. The increase in content was calculated for each position for the respective setup A-E. An example of the calculation, using concentration values from positions 1 and 2 in setup A, is as follows: In experimental design setup A position 1, the CIPC concentration ( $\mu\text{g g}^{-1}$ ) in the grain was equal to  $0.026 / 0.01 =$  factor of 2.6 increase. In position 2, a factor of 260 increase ( $2.6 / 0.01$ ) was calculated (Figure 4.10). The influence of both direct and indirect contact with the concrete surface contributed to the cross-contamination of grains. The effect of both the headspace of the store and the headspace above the concrete was accounted for in design setup A, where an increase in CIPC content in grain ranged from a factor of 2.6 – 260 times the MRL. Design setup B and C clarified which atmospheric route dominated, with results indicating that the headspace above the contaminated concrete is responsible for the majority of the atmospheric transfer of CIPC to grains. The increase in CIPC content in grain in B, where only the concrete headspace interacted with the stored grain, ranged from a factor of 1.1 – 101 times the MRL. In comparison to C, where only the store headspace interacted with the stored grain, the values were much lower, ranging from 1.7 – 16 times the MRL (Table 4.8). The risk of cross-contamination of grain at elevated levels was also confirmed in designs A and B. The importance of these routes and the robustness of the experimental set-up were confirmed in experimental design D, where there was no evidence of contamination. Design D was sealed from both the concrete flooring and the atmosphere. The highest concentration of CIPC in grain, resulting in increases in CIPC

content ranging from 7.8 – 180 times the MRL, were observed in design E. In design E, grains were sealed from the atmosphere but were in direct contact with the concrete flooring, confirming that a build-up of CIPC vapour in the confined space, in addition to direct contact with the contaminated concrete, resulted in a relatively high level of contamination. This study confirmed that direct contact with the concrete is the most important factor in the route of cross-contamination of grain in stores. No 3-CA was found in the full trial samples.

These observations are different from the preliminary study where the exposure to the atmosphere brought about a more significant enhancement in contamination relative to exposure to the concrete alone. Several factors may have contributed to this including: (1) the plastic boxes used in the preliminary study may have been porous to CIPC vapour, resulting in poor retention of vapour, (2) elevated CIPC vapour in the atmosphere caused by restricted air movement during the 7 months trial, resulted in increased contamination or (3) dispersal of contaminated dust particles caused by excessive disturbance in the store led to residues in dust eventually ending up on the grains and (4) the cross contamination process was influenced by natural environmental factors (temperature and humidity) in the store. Overall, the results suggested that the most important environmental factor in the route of cross-contamination in stores was physical contact with the concrete surface.

The information obtained from this study indicated that cross contamination was feasible regardless of the CIPC levels in the concrete, suggesting that remedial strategies are required to decontaminate the entire structure of buildings with a history of CIPC use.

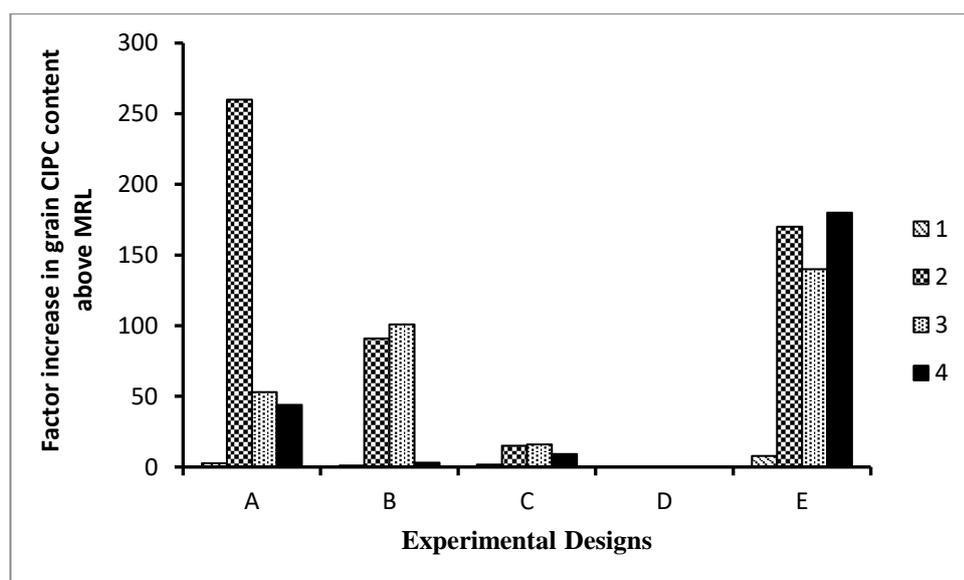


Figure 4.10 Increase in grain CIPC content above the MRL within the five experimental designs at four locations in a commercial store (Douglas et al. 2019).

**(C) Risk associated with storage of grains on contaminated concrete in commercial store B.**

The concentrations obtained in the cross contaminated samples for both trials were vital for comparisons pertaining to risk assessment. A risk assessment can be calculated using the concentration levels of CIPC in the concrete flooring. An assessment for this store was calculated using the CIPC concentration levels at position 3 (126  $\mu\text{g g}^{-1}$ ) and then a comparison was made to the actual concentrations obtained in the wheat samples that were in the vicinity of this concrete for both trials. The risk assessment calculated gives a value of 0.29  $\text{mg kg}^{-1}$ ; 29x higher than the MRL of CIPC in wheat (Douglas *et al.*, 2019). Based on the actual CIPC concentrations in the grain, in the vicinity of concrete at position 3, for the preliminary trial (7 month duration) and the full experimental trial (3 month duration), it was deduced that: (I) the heterogeneity of CIPC distribution in the flooring can cause the actual concentrations in grain to be higher than the calculated risk assessment value. (II) The total concentration of CIPC in the concrete flooring influenced the magnitude of contamination in grains, indicated by an increase in magnitude, with higher CIPC concrete levels (10.5 – 304  $\mu\text{g g}^{-1}$ , positions 2-4) relative to position 1 with a lower concentration (0.58  $\mu\text{g g}^{-1}$ , Table 4.8).

Table 4.8 CIPC concentrations ( $\mu\text{g g}^{-1}$ ) and factor increase in CIPC content above the MRL (in parentheses) in grains that were in the environment of a commercial store for 3 months (Douglas *et al.* 2019).

Position	CIPC conc. in concrete flooring ( $\mu\text{g g}^{-1}$ )	CIPC Concentration ( $\mu\text{g g}^{-1}$ )				
		A	B	C	D	E
1	0.58	0.026 (2.6)	0.011 (1.1)	0.017 (1.7)	0.00 (0)	0.078 (7.8)
2	304	2.6 (260)	0.91(91)	0.15 (15)	0.00 (0)	1.7 (170)
3	216	0.53 (53)	1.02 (102)	0.16 (16)	0.00 (0)	1.4 (140)
4	10.5	0.44 (44)	0.030 (3)	0.092 (9.2)	0.00 (0)	1.8 (180)

**4.4.4. Qualitative analyses of CIPC in cross contaminated wheat using GCMS.**

CIPC cross contamination in grains was confirmed using GCMS (Figure 4.11). Contaminated wheat gave spectral patterns that were consistent with the expected CIPC spectrum (213/215 m/z: parent ion; 153/154 m/z: m-chlorophenyl isocyanate; 171/173 m/z: free acid formed from isopropyl residue; 127/129 m/z: chloraniline) as outlined on the NIST database: (<http://webbook.nist.gov/cgi/cbook.cgi?Name=chlorpropham&Units=SI&cMS=on#Mass-Spec>)

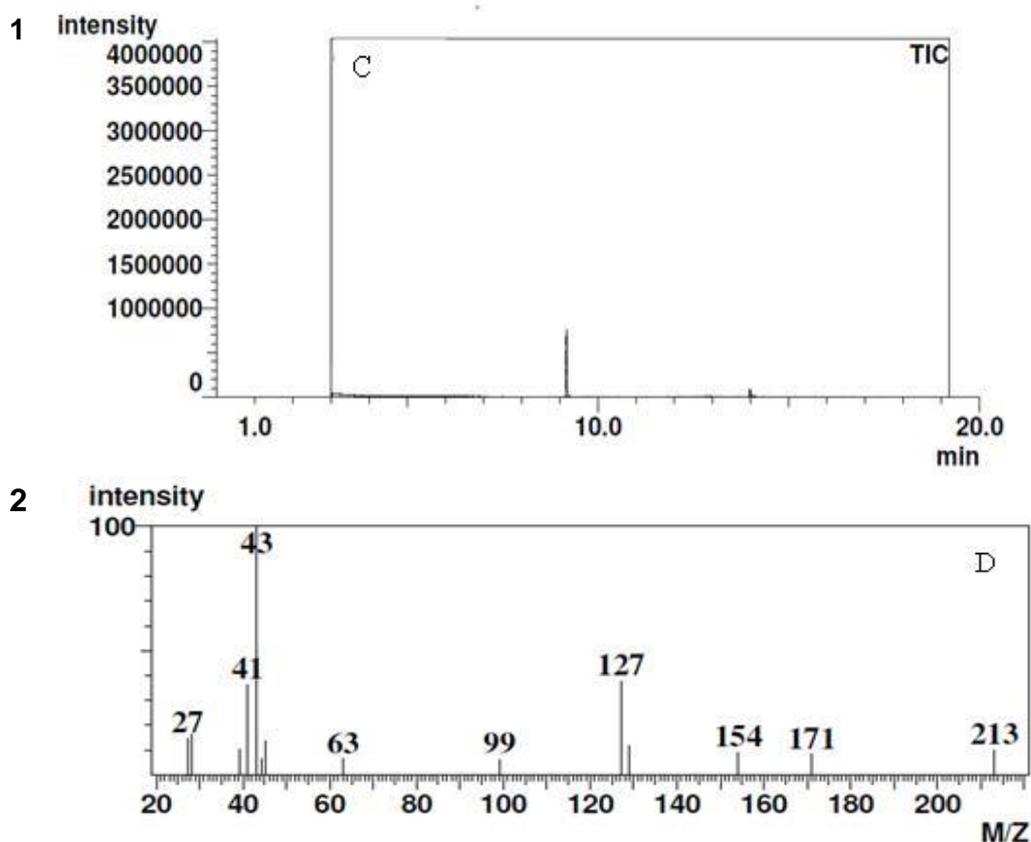


Figure 4.11 GCMS chromatograms and mass spectra obtained at a retention time of 9.1 minutes for a non-organic wheat sample exposed to a store environment and cross contaminated with CIPC (1 & 2) (Douglas et al. 2019)

#### 4.4.5. Quality Control

The reproducibility of the extraction and processing methods were assessed using a cross-contaminated sample from a trial. A contaminated sample was homogenised by manual mixing and split into three portions, subsequent to extraction and analysis by HPLC UV/VIS. The procedure for processing (manual mixing) prior to analysis was sufficient for sample homogenization and the method was precise, as indicated by the similar CIPC concentrations obtained in the triplicate analyses (mean =  $0.21 \mu\text{g g}^{-1} \pm 2.59\%$  RSD,  $n=3$ ). A CIPC-free clock-glass that was not exposed to the store environment was sequentially washed with acetonitrile and the collected washings analysed by HPLC UV/VIS. This sample was a negative control and used for comparisons with clock-glasses that were exposed to the store environment, thus confirming the presence of CIPC in the accumulated dust. Instrument performance was ensured prior to starting the analyses and routine analysis of procedural blanks and spiked samples ( $4.0 \mu\text{g g}^{-1}$ ), with each batch of analysed samples, ensured the absence of interfering substances and satisfactory recovery of CIPC (>95%).

## 4.5. Decontamination strategies

### 4.5.1. The effect of a sealant to prevent cross contamination of grains in contact with the concrete floor of a commercial store.

Two sections of a commercial potato store were thoroughly cleaned prior to the experiment. One section was painted (sealed) with a xylene based sealant and the other remained unpainted (unsealed). Wheat grains (100 g) were placed on the surfaces of the sealed and unsealed concrete and covered with a Tritan™ plastic container (Figure 4.12). The experiment was conducted in replicates of six (grains in boxes 1 to 6 were in contact with the unsealed concrete and boxes 7 to 12 were in contact with the sealed concrete)(Figure 4.13). The grains remained on the surface of the concrete for three weeks.



Figure 4.12 Grains in contact with the concrete surface and sealed from the atmosphere of the store.

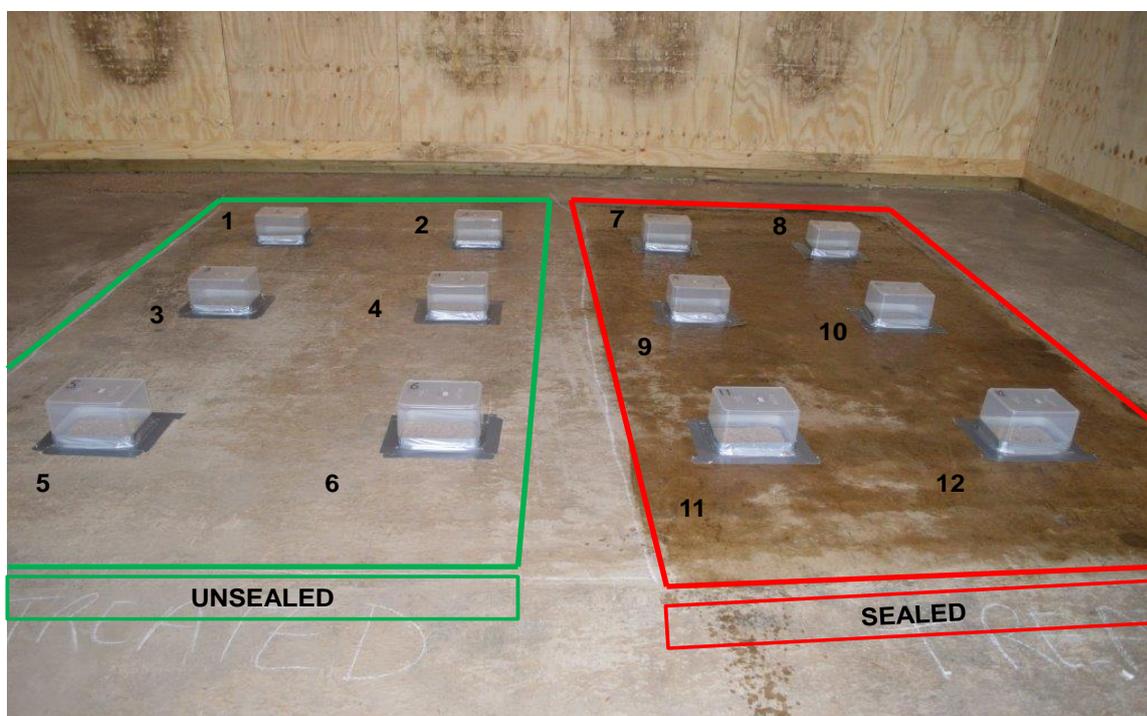


Figure 4.13 Grains in contact with the sealed and unsealed concrete flooring of the store

The CIPC concentration values for grains in contact with both sealed and unsealed concrete were in the range 0.01-0.10  $\mu\text{g g}^{-1}$  and 0.02-0.10  $\mu\text{g g}^{-1}$ , respectively (Figure 4.14). The variations in the values for the grains in contact with unsealed concrete suggested that CIPC cross contamination was not uniform and that this may be due to the heterogeneity of CIPC

distribution in the concrete. The values obtained for the grains in contact with sealed concrete suggested that: (I) the sealant was ineffective in preventing cross contamination, (II) cross contamination of the grains was not uniform and that again, this may be due to the heterogeneity of CIPC distribution in the concrete and (III) CIPC from the atmosphere was penetrating the plastic containers, contributing to the cross contamination. This trial was conducted prior to the full trial on routes of cross contamination. The sealant experiment has provided an insight into the method of sealant application to the concrete and type of containers used for the trials. Improvements in the application of the sealant to the concrete and the type of sealant can be considered for future experiments.

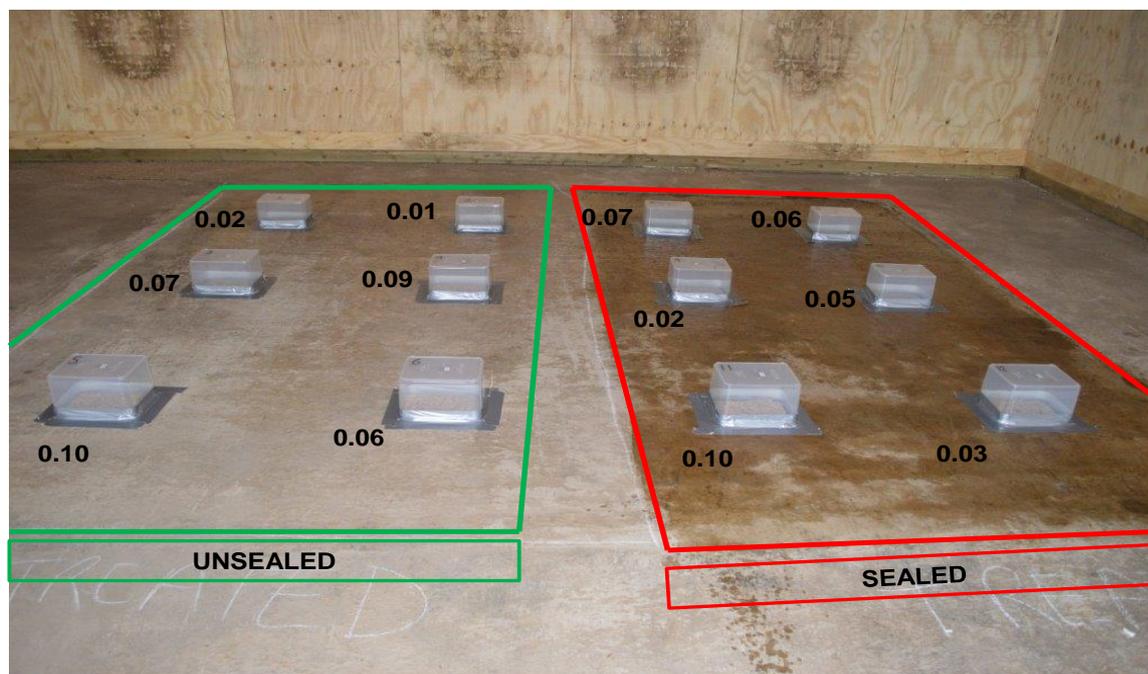


Figure 4.14 CIPC concentrations ( $\mu\text{g g}^{-1}$ ) in the grains on the sealed and unsealed surface of the concrete flooring of the store

#### 4.5.2. The chemical interaction of decenone with CIPC.

The ability of 3-decen-2-one to bind or degrade CIPC was explored to determine if this chemical could be used as a potential decontaminant. 3-decen-2-one is a constituent of the product SmartBlock. SmartBlock is a sprout suppressant applied to potatoes to maintain their quality and can be applied by itself or in combination with CIPC for effective sprout control. Research has shown that accumulated residues of CIPC on the walls and fans of contaminated stores were effectively removed with the application of SmartBlock in a non-combined form (personal communication John Immaraju EAPR, 2016). This observation was based on the physical disappearance (visible inspection) of CIPC residues on the surfaces of the store's infrastructure. The mechanisms involved in the removal process were unclear and require exploring. A preliminary study of the interaction of 3-decen-2-one with CIPC and concrete at the application temperature of SmartBlock (200 °C) in a non-combined form was investigated. This was conducted in collaboration with Götz Bucher; School of Chemistry, University of Glasgow.

The interaction was investigated with and without concrete at a temperature of 200 °C for 30 minutes under argon.  $^1\text{H}$  NMR spectroscopy was used to examine the composition of the interaction mixtures. A computational method, density functional theory, was used to further study the interaction. The potential reaction mechanisms and the most stable experimental complex formed are shown in Figure 4.15 and Figure 4.16, respectively. The results showed that 3-decen-2-one was unable to degrade CIPC, instead complexes were formed where a non-covalent complex involving a N-H...O hydrogen bond was the most stable. There was no evidence for the products of the Michael-type addition reaction which is shown in Figure 4.15.

The most stable complex, as calculated at the M06-2X/cc-pVTZ level of theory, is shown in Figure 4.16 where the length of the N-H...O hydrogen bond is calculated as 1.95 Å. The N-H...O bond is weak, relative to a covalent bond, making the reaction reversible. In conclusion, 3-decen-2-one may be ineffective as a decontaminant for CIPC on concrete. The complexes formed from the reaction, however, were unlikely to change the properties of CIPC present on building materials; preventing the formation of 3-CA. Therefore, 3-decen-2-one could be an alternative solvent for CIPC application in stores.

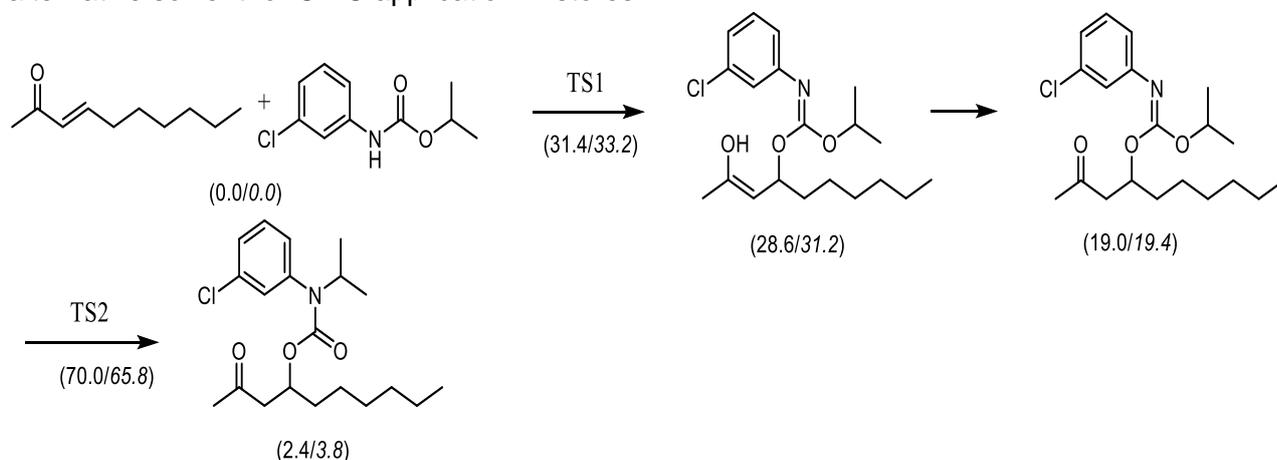


Figure 4.15 Michael-type addition of CIPC to 3-decen-2-one, as optimised at the M06-2X/cc-pVTZ level of theory. The numbers given represent the relative Free Energies in kcal / mol (precursors = 0.0 kcal / mol).

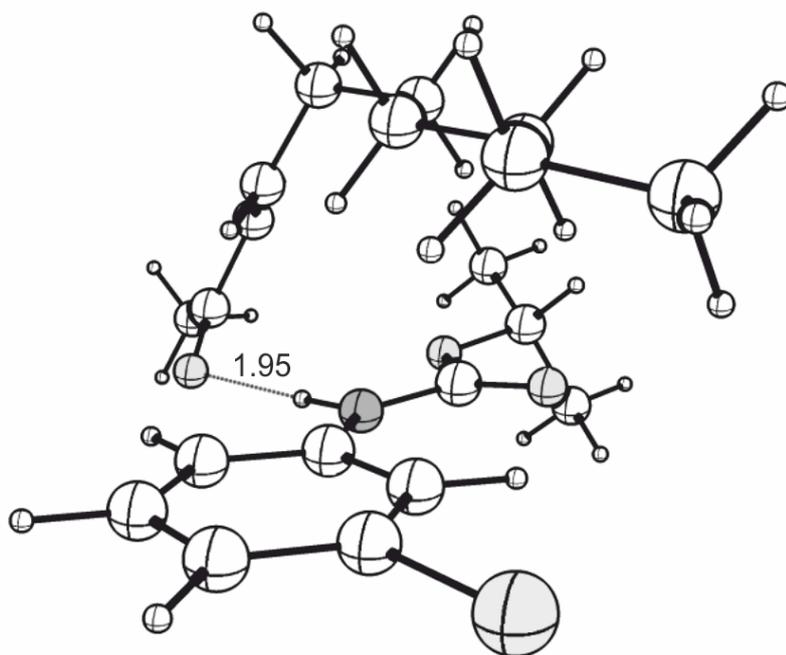


Figure 4.16 Optimised geometry (M06-2X/cc-pVTZ) of the most stable conformer of a 1:1 complex of CIPC and 3-decen-2-one. The N-H...O hydrogen bridge is indicated by a dashed line (distance in Å).

## 5. DISCUSSION

### 5.1. Extraction and analytical methods for agricultural chemicals used on concrete and wood surfaces.

Research relating to the application of agricultural chemicals onto concrete and wood surfaces is focused on pesticide wash off experiments and mortality tests for insects after exposure to surfaces treated with insecticides. Although the methods used in these papers were not applicable to analytical method development for CIPC, they provided an insight into the persistence of pesticides on concrete surfaces and the physical characteristics of concrete in terms of alkalinity and porosity, invaluable for future experimental design for this project.

Concrete is a common building material used for constructing floors in food processing plants, warehouses and grain storage facilities (Arthur, 1994). Concrete structures are continually exposed to chemicals in the form of emulsifiable concentrate and wettable powder formulations (Arthur, 1994; Trask et al., 2014). Studies have illustrated the ability of concrete to retain pesticides (Jiang et al., 2014) and to hydrolyze and rapidly break down applied insecticides (Arthur, 1994). Collins et al. (2000) used concrete and galvanized steel panels as test surfaces to study organophosphate breakdown. The concrete panels were weathered outdoors for three months to avoid the potential effect of the alkalinity of fresh concrete on the organophosphates. In addition, the steel panels were soaked in saturated salt solution overnight to age them. Fenitrothion was shown to maintain repellence against the barklice (*Liposcelis bostrychophila*) (Enderlein) for 24 weeks on steel but only 12 weeks on concrete, due to absorption in the pores of the concrete which reduced the efficacy of the chemical (Collins, Nayak and Kopittke, 2000). It was therefore concluded that the porosity of the surface also determines the efficacy of pesticides. Bong et al. (2013) have also concluded that the alkaline nature of concrete is likely to slow down the effect of an insecticide. Therefore, it is important to employ curing or aging techniques to surface materials (concrete and steel) prior to laboratory experiments. The effect of concrete alkalinity on chemicals was taken into consideration for the selection of material used in this study. The aggregate and reconstituted concrete blocks selected for this study were cured by the manufacturers as part of their quality control measure.

Only one published article was found for CIPC analysis in building material, particularly in concrete and wood (Boyd and Duncan, 1986). Boyd & Duncan (1986) used a Soxhlet extraction followed by a flame ionisation detection (GC-FID) method for the analysis of CIPC in concrete and wood. However, the Soxhlet method (16-18 hours) was time consuming and GC-FID detection is less sensitive for CIPC compared to other methods such as HPLC UV/VIS and GC MS (Mohammed, Flowers and Duncan, 2014). The only relevant HPLC UV/VIS method previously developed is for CIPC in potato extracts by Khan et al. (2008, unpublished). This method was used as the basis for analysis and adjustments were explored to optimise the method in concrete and wood.

A few published articles were found for chemical analysis in wood. These were focused on wood preservation where chemicals were used to prevent fungal and pest attacks, with no relevance to analytical methods required for this project.

### 5.2. The fate of chlorpropham in potato stores

Chlorpropham, like most other plant treatment agents, is applied to crop surfaces, resulting in retention of residues on the surface (Berchtold et al., 2013). During application of CIPC in stores, the chemical is finely atomized in order to achieve a uniform distribution, with regular deposition on the target surface. However, loss can occur due to drift of vapours from the point of application, causing exposure to non-target surfaces (Smith and Bucher, 2012). Non-target fates of CIPC in stores include loss to the environment, particularly the atmosphere, soil, waterways and fabric of the store (Boyd and Duncan, 1986; Smith et al., 2013; Douglas et al.,

2018a). The fate and distribution of chlorpropham applied to stored potatoes is well studied, with various researchers reporting on the residues on peeled and non-peeled potatoes (Corsini, Stallknecht and Sparks, 1979; Hajslova and Davidek, 1986; Camire et al., 1995; Beaver et al., 2003; Park, 2004; Campbell et al., 2010; Khan et al., 2012; Mohammed, 2012; Frazier and Olsen, 2014). Residual CIPC on potatoes is dependent on the application rate and storage temperature, with recent research conducted using application rates of 12-14 g per tonne for potatoes for the fresh market (held at a storage temperature of 3-4°C) showing that 23 – 25% of input CIPC was retained as a residue on tubers after storage (Briddon, Saunders and Seamark, 2015). In comparison to potatoes destined for processing, where 23-26 g per tonne CIPC was applied (held at a storage temperature of 7-9°C), 5 - 10% of input CIPC was retained (Briddon, Saunders and Seamark, 2015). The migration of CIPC into potato tubers was studied under controlled ventilation conditions for up to 6 months at 10 °C (Coxon and Filmer, 1985). <sup>36</sup>Cl or <sup>14</sup>C labelled CIPC treated potatoes, analysed by autoradiography, showed little penetration beyond the peel layer even after storage for 6 months. There were no identifiable degradation products in the extracts, although there was evidence of bound non-extractable residues (Coxon and Filmer, 1985). Since negligible concentrations penetrate the peel layer and between 5-25% of applied CIPC is retained on the surface of potatoes, it may be assumed that the remaining applied CIPC is lost to the fabric and headspace of the store. The accumulation of CIPC residues in the concrete walls and flooring of a potato store were in the range 130-290 mg kg<sup>-1</sup> and 2050-9470 mg kg<sup>-1</sup>, respectively (Boyd and Duncan, 1986). Recent studies conducted by Douglas et al. (2018a, 2018b) confirmed the loss of CIPC to the fabric of stores, particularly to concrete. The magnitude of contamination was confirmed in research stores and commercial stores (Douglas et al., 2018b). Prior to the Douglas et al. (2018a, 2018b) studies, there was limited information pertaining to CIPC loss to stores and the implications in terms of cross-contamination of other commodities in contact with potato stores. This research has enabled a better understanding of the possible risk of cross-contamination to non-potato crops in contact with buildings with a history of CIPC use.

### 5.3. Decontamination

Although no published research exists pertaining to CIPC degradation and concrete, useful information was available on the removal of CIPC and 3-CA from other environments, including water. In a recent CIPC review, it was suggested that titanium dioxide (TiO<sub>2</sub>) may be an option to remove CIPC from store environments (Paul, Ezekiel and Pandey, 2016). Various studies showed that 3-CA and 2-CA, in aqueous solutions, were degraded with titanium dioxide (TiO<sub>2</sub>-P25; 80% anatase and 20% rutile), with optimisation of the kinetic reactions using oxyhalogens (ClO<sup>3-</sup>, BrO<sup>3-</sup> and IO<sup>3-</sup>) (Choy and Chu, 2007, 2008; Chu, Choy and So, 2007). The robust methods developed during this project can be used to quantify CIPC, 3-CA and 2-CA, thus monitoring the effect of TiO<sub>2</sub> on the degradation process. An investigation of the reaction of titanium dioxide (TiO<sub>2</sub>-P25; 80% anatase and 20% rutile) with CIPC in an inert solvent such as acetonitrile might provide some insight into how the two could potentially react on concrete, leading to research on self-cleaning concrete and decontamination of CIPC, 2-CA and 3-CA using TiO<sub>2</sub> in cementitious systems being explored.

Photocatalysis is an effective and inexpensive tool for the removal of organic and inorganic pollutants from water, with the technique reaching industrial level in several countries (Devipriya and Yesodharan, 2005). Successful photocatalytic degradation of pesticides in aqueous solutions has been reported (Qamar, Muneer and Bahnemann, 2006; Verma and Dixit, 2012). The photocatalytic kinetics of the pesticides triclopyr and daminozid in an aqueous suspension of titanium dioxide were successfully shown, where the photo-oxidation process was monitored using GCMS analysis (Qamar, Muneer and Bahnemann, 2006). The degradation kinetics were studied under different conditions such as reaction pH, substrate and catalytic concentration, different types of TiO<sub>2</sub> and in the presence of different electron acceptors (hydrogen peroxide, potassium bromate and ammonium persulphate) (Qamar, Muneer and Bahnemann, 2006). Similarly, the photocatalytic degradation of the insecticide, chlorpyrifos, was successful in an aqueous phase using TiO<sub>2</sub>, where 90% degradation of the pesticide was observed (Verma and

Dixit, 2012). Although triclopyr, daminozid and chlorpyrifos are pesticides belonging to the groups chloropyridinyl, diazo and organophosphates respectively, their degradation by TiO<sub>2</sub> provides useful information in terms of methodologies that can be adapted for CIPC.

Carbamates (including carbofuran and carbaryl) are photocatalytically oxidized to carbon dioxide in the presence of titanium dioxide using artificial and solar light (Konstantinou and Albanis, 2003). The photocatalytic mechanism of carbamate pesticides (oxamyl, carbaryl, carbofuran and benzofuran) in the presence of TiO<sub>2</sub> has been illustrated. The intermediates in the degradation are of two types: (I) hydroxylated products and derivatives and (II) products of cleavage or cyclization of the side chain. Photocatalytic decomposition also occurs through cyclisation of the chain and/or posterior cleavage of the carbamate function. Oxidized aliphatic compounds (aldehydes, acids, etc.) and finally carbon dioxide, nitrate and sulfate are produced from the breakdown of amide function C–N bonds via hydroxylation (Konstantinou and Albanis, 2003). Since CIPC belongs to the carbamate group, it may be feasible for it to be degraded by TiO<sub>2</sub>. This interaction and mechanism of degradation is an interesting area for further investigation and something we hope to explore in the future.

The application of TiO<sub>2</sub> photocatalysis to concrete technology in relation to enhanced aesthetic durability and depollution properties, achieved by incorporating TiO<sub>2</sub> into cement has been extensively studied (Folli et al., 2012; Hassan et al., 2012). New technologies where methods are explored for the preparation of TiO<sub>2</sub> for incorporation into heat resistant sealants were reported (Gerasimova et al., 2013). However the combination of these technologies for CIPC decontamination have not been explored therefore, the potential of TiO<sub>2</sub> cement and TiO<sub>2</sub>-containing sealants to degrade CIPC may be feasible and requires further research. The effect of TiO<sub>2</sub> on the degradation of CIPC can also be explored by exploiting the physical properties of the chemical. The photocatalytic degradation of pesticides by TiO<sub>2</sub> and TiO<sub>2</sub> pillared purified clays was investigated by Abdennouri et al. (2011). The adsorption performance and photocatalytic activities using 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxypropionic acid (2,4-DP), as model organic pollutants, were studied. The results showed that degradation of the pesticides was enhanced by photocatalysis, with efficiency increasing with Titanium content in the pillared clay (Abdennouri et al., 2011). The influence of clay minerals on the hydrolysis of carbamate pesticides, including CIPC, has been studied. The hydrolysis of CIPC was inhibited by montmorillonite, probably because of its strong adsorption onto the clay mineral (Wei et al., 2001). Similarly, chemically activated halloysite successfully adsorbed CIPC and 3-CA, described by a pseudo-second order kinetic model (Szczepanik et al., 2014). Clay minerals have been used in the catalysis industry because they can catalyse reactions including cracking, elimination and condensation. The ability of certain clays to bind CIPC and 3-CA is of interest and can be exploited for removal of these chemicals from contaminated surfaces or water. The adsorptive property of halloysite and montmorillonite, coupled with TiO<sub>2</sub> in the form of pillared clay, may be useful for trapping and degrading CIPC and 3-CA, with possible application to contaminated surfaces and water. This area of research therefore requires further investigation and would result in a promising novel technology if successful.

The application of ozone to the headspace and surfaces of stores is a possible strategy for decontaminating CIPC and 3-CA. Although no research literature could be found on the degradation of CIPC or 3-CA using ozone, information pertaining to the application of ozone on pesticide degradation and 2-CA was obtained. Ozone was effective in reducing residues of the pesticides fenitrothion and deltamethrin on wheat grains with a 67.5, 88.1 and 89.8% reduction in deltamethrin after exposure to ozone for 60, 120 and 180 minutes, respectively. Similarly, there was a decrease in fenitrothion (66.7%) concentration following treatment after 180 minutes (Savi, Piacentini and Scussel, 2015). 2-CA degradation in water by ozonation, as well as by photolysis and radiolysis in the presence of ozone, was also studied (Winarno and Getoff, 2002). The most efficient degradation of 2-CA was achieved with the synergistic effect of radiolysis and ozone, followed by the photolysis/ozone combination and then pure ozonation (Winarno and Getoff, 2002). Again, it may be feasible to degrade CIPC and 3-CA with ozone, providing new areas of research to be explored.

## 6. CONCLUSIONS

### 6.1. Development and validation of analytical methods

Qualitative (GCMS) and quantitative (HPLC UV/VIS) methods were successfully developed for the confirmation of CIPC and its metabolite, 3-CA, in concrete and grain. Robust HPLC UV/VIS methods were developed and validated for single and dual analysis of CIPC and 3-CA, enabling options for analysis of both chemicals. A HPLC UV/VIS method was assessed for the quantification of chloroaniline isomers.

The developed methods were used to assess: (a) the degree of CIPC contamination in research and commercial potato stores; (b) the degree of CIPC cross-contamination of grains in commercial stores and (c) the effectiveness of sealants to prevent cross-contamination of grains in a commercial store.

### 6.2. Persistence and distribution of CIPC and 3-CA contamination in potato stores

The HPLC UV/VIS, HPLC PDA and GCMS methods successfully determined the persistence and distribution of CIPC and 3-CA contamination in the concrete flooring of potato stores. The presence of both chemicals (CIPC and 3-CA) in the stores was confirmed with GCMS, thus ensuring the robustness of the HPLC UV/VIS methods. The methodologies used to collect, process, extract and analyse samples were efficient in terms of: (a) ease of coring and removing intact layers subsequent to sectioning; (b) minimal loss of sample during the rigorous crushing process (3-9% loss) (c) small portions of concrete required for processing (4.3 diameter × 1cm height); (d) single extraction using one gram of sample was sufficient for quantification (>90% CIPC residues in first extract); (e) high recoveries of CIPC (> 95%) and 3-CA (> 95%) in spiked samples; (f) absence of interfering substances that may affect the analytical procedure; ensured by quality control measures and (g) comprehensive and reproducible results generated from analysis (mean =  $9.7 \mu\text{g g}^{-1} \pm 3.49 \text{ \%RSD}$  for triplicate analysis of a store sample).

The depth distribution study confirmed: (a) that concrete was pervious to CIPC and (b) the degree of penetration may have been dependent on the physical composition of the concrete. CIPC residues >90% were deposited in the top 1-cm layers in all stores except store B which had 47%. The accumulation of CIPC residues in the flooring of the stores was influenced by other factors in addition to the physical composition of concrete. This was evident from the total distribution study in both research and commercial stores. These factors were: (a) the quantities of applied CIPC; (b) the point of CIPC entry into the store and (c) the type of circulatory system used. The magnitude of contamination was increased with higher quantities of applied CIPC and the concentrations were more likely to be higher in areas closest to the point of CIPC entry into the store. The degree of contamination in stores was influenced by circulation causing heterogeneity of CIPC distribution in the concrete flooring (systematic sampling ranging from  $65\text{-}778 \mu\text{g g}^{-1}$  and random sampling ranging from  $14\text{-}1667 \mu\text{g g}^{-1}$ ). CIPC was persistent in all stores to a depth of at least 3 cm and this was irrespective of the last application. The persistence of 3-CA was also evident in the stores, particularly in the commercial stores. The 3-CA concentrations were also variable in the flooring and persisted, irrespective of the last application. In store A, for instance, 3-CA concentrations were  $4.74\text{-}38 \mu\text{g g}^{-1}$  (18 years since last application). Overall, CIPC and 3-CA were persistent in commercial stores with histories of 16 and 25 years since the final application of CIPC. A HPLC UV/VIS method confirmed the absence of isomers of 2-CA and 4-CA in commercial store concrete, thus eliminating the risk of cross contamination with these chemicals. The risk of possible 3-CA and CIPC cross contamination of other crop commodities stored on the surfaces of contaminated concrete is evident from the persistent and pervasive nature of both chemicals. This study provides invaluable information for decontamination strategies since it provides an indication of the depth of concrete that would require removal or treatment to allow stores to be re-used.

### **6.3. Degree and route of CIPC and 3-CA cross contamination of grains in commercial potato stores**

The degree and route of cross contamination of grains was examined in commercial stores with histories of 16 and 25 years since the final application of CIPC. The study revealed that cross contamination of grains was feasible irrespective of the CIPC levels in the concrete flooring and provided evidence that the headspace in the general store, the headspace above the concrete flooring and dislodged CIPC-contaminated dust particles in a store environment are all important routes of cross contamination. The duration of storage influenced the magnitude of cross contamination, with an increase in magnitude for longer storage periods. The magnitude of cross contamination was increased in the vicinity of the point of CIPC entry into the store because accumulation of residues in the concrete flooring and dust were higher in these areas. Therefore, the heterogeneity of CIPC distribution in the concrete flooring may influence the magnitude of cross contamination, with an increase in magnitude at higher levels of CIPC in the flooring. Overall, it was concluded that storage of grains, and other commodities with MRLs set at the LOQ for CIPC, are at risk of cross contamination in buildings where CIPC has previously been applied. It is important to note that grain samples stored in commercial stores during the trial period were not cross-contaminated with 3-CA although this chemical was detected in the concrete flooring. The information gathered from this study is useful for (I) decontamination strategies and (II) recommendations pertaining to the re-use of potato stores for other commodities whose MRLs are set at the LOQ for CIPC.

### **6.4. Decontamination strategies**

The effect of a xylene-based sealant to prevent cross contamination in a commercial store was examined and from this, useful information from the study can be considered for other sealant trials. The sealant was ineffective in preventing cross contamination of grains in direct contact with the concrete flooring. The sealant experiment has provided an insight into the method of sealant application to the concrete and type of containers used for the trials. The xylene sealant may be successful if applied more effectively but this requires further investigation. It was suspected that CIPC penetrated the plastic containers used in a trial in this study. Therefore, glass containers were used in a subsequent trial. Improvements in the application of the sealant to the concrete and the type of sealant can be considered for future experiments.

Computational and chemical methods were successfully used to study the interaction of 3-decen-2-one with CIPC. Complexes formed between 3-decen-2-one and CIPC, in the presence of concrete, were confirmed. The most stable complex with a N-H...O bond illustrated that the reaction was reversible due to the weakness of this bond relative to a covalent bond. It was therefore concluded that 3-decen-2-one was ineffective as a decontaminant for CIPC contaminated concrete. However, the inability of the complexes to alter the properties of CIPC present on concrete and to prevent production of 3-CA suggests that 3-decen-2-one may be an alternative solvent for application of CIPC in stores.

### **6.5. Further research and development needs**

The presence of CIPC and 3-CA in the building materials and atmosphere of potato stores is problematic, causing cross contamination of non-potato crops with MRLs at the limit of detection, stored in buildings previously treated with CIPC. Their persistence is a significant problem as they were identified in commercial stores where, in one case, the last CIPC application was 25 years prior to analysis. There are two fundamental methods to overcome these problems: (I) The use of chemicals to decompose both the CIPC and 3-CA into non-toxic compounds and (II) Cleaning the store and sealing all surfaces to prevent CIPC and 3-CA egress. A combination of both techniques may also be feasible.

A trial using a xylene-based sealant to retain CIPC was unsuccessful; however, the information obtained from this preliminary sealant study is useful because future trials can be conducted to include: (I) methods to enable careful sealing of the flooring (where there is proper interaction

between the concrete and sealant), (II) when measuring the effectiveness of treatments on concrete, the use of glass containers as opposed to plastic to prevent penetration of CIPC from the headspace of the store and (III) application of alternative sealants incorporating degradation chemicals/compounds such as TiO<sub>2</sub>.

A thorough literature review was conducted for possible remedial strategies involving chemicals that could be employed for removal of CIPC and 3-CA. Invaluable information was retrieved which can form the basis of further research/preliminary experimental trials, with novel applications including: (I) the use of TiO<sub>2</sub> in the form of cement and sealants to prevent accumulation of CIPC residues on surfaces, (II) the intercalation of TiO<sub>2</sub> into clays (montmorillonite and halloysite) and the application of this complex as a barrier to CIPC and 3-CA-contaminated surfaces in existing contaminated stores and (III) the use of ozone to eliminate CIPC and 3-CA from the store atmosphere and surfaces. All of these have the potential to go some way towards allowing cereals or other non-potato crops to be successfully stored in previously-treated potato stores.

This study has highlighted the possible means whereby grains stored in buildings treated with CIPC can become cross contaminated. The robust analytical methods developed in this project will be fundamental in the decontamination strategies used for CIPC because they can be used to monitor the degradation process by allowing quantification and identification of parent compound and by products.

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## 8. PUBLICATIONS/CONFERENCE ABSTRACTS

- Douglas, L. (2019) Understanding the persistence, transformation and fate of CIPC (Chlorpropham) in commercial potato stores to help guard against cross-contamination. PhD thesis.
- Douglas, L., MacKinnon, G., Cook, G., Duncan, H., Briddon, A. and Seamark, S. (2019) The risk of chlorpropham cross-contamination of grain in potato stores. *Food Control* 98, 1-8.
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- Douglas, L., MacKinnon, G., Cook, G., Duncan, H., Briddon, A. and Seamark, S (2017). The degree of CIPC cross contamination in commercial potato stores. 20th Triennial Conference of European Association for Potato Research, Versailles, France July 9-14, 2017.

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