Investigation into the partitioning of Lindane between air and dust in indoor environments

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Dedication

This work is dedicated to my exceptionally selfless parents who have provided endless support and encouragement throughout this research. I love you Mom and Dad.

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I would like to thank the Almighty God for enabling the successful completion of this project.

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Abstract

The investigation of harmful semi volatile organic compounds (SVOC) in the indoor environment is important because on average people spend over 90% of their time indoors. Lindane, an SVOC which was widely used in the UK until 2004, adsorbs to house dust. House dust acts as a reservoir for such contaminants which are remitted by desorption into the air over time. A method for measuring Lindane air concentrations in a vial using SPME without the use of water or any solvent was developed in order to carry out Lindane adsorption and desorption tests. Dynamic tests were carried out to determine adsorption and desorption coefficients as well as equilibrium time. Adsorption and desorption constants (k_1 and k_2 respectively) were determined by fitting results from the dynamic adsorption tests to an existing two compartment model described in chapter 2, using the statistical analysis software SPSS (vs16). These dynamic tests were carried out for two size fractions (<20µm and >45µm<63µm) and whole dust samples to determine the effect of size fraction on adsorption. For the >45µm to <63µm, $k_1 = 0.568h^{-1}$ and $k_2 = 0.047h^{-1}$, (standard error 0.119 and 0.030 respectively), for the <20µm fraction, $k_1 = 1.686h^{-1}$, $k_2 = 0.125h^{-1}$ (standard error 1.888 and 0.324 respectively), and the whole dust $k_1 = 2.587\ h^{-1}$, $k_2 = 0.288\ h^{-1}$ (standard error 0.514 and 0.113 respectively). Static tests were carried out at equilibrium to establish an adsorption isotherm and obtain partition coefficients for different size fractions. The adsorption constants K_a were $4.2 \times 10^{-4} mh^{-1}$, $7.67 \times 10^{-5} mh^{-1}$, and $3.03 \times 10^{-3} mh^{-1}$ respectively. The desorption constants K_d were $0.125h^{-1}$, $0.047h^{-1}$, $0.288h^{-1}$. The partition coefficients K_p were $4.8 \times 10^{1} \mu gm^{-2}$, $4.08 \times 10^{1} \mu gm^{-2}$, $1.05 \times 10^{2} \mu gm^{-2}$, for the <20µm, >45µm<63µm, and whole dust respectively. The higher K_p value for the smaller <20µm fraction compared to the >45µm<63µm fraction, suggests that Lindane adsorbs more strongly to smaller dust size particles. This is significant because it means that the inhalable dust fractions which fall within the <20µm fraction, will have higher concentrations and therefore could potentially be more harmful as the get into the lungs. A possible explanation for the higher K_a value for the whole dust fraction over the two other smaller fractions could be because whole dust is a more complex mixture containing more fibrous substances that may have stronger affinities for Lindane than dust e.g. carpet fibres.

Contents

Abbreviations

GC	Gas Chromatograph
GC-MS	Gas chromatograph-mass spectrometer
Lind	Lindane
PAN	Pesticides Action Network
PCNB	Pentachloronitrobenzene
RF	response factor
SVOC	semi volatile organic compound
TCMX	Tetrachloro-m-xylene
VOC	volatile organic compound

Notation of Symbols

A_{as}	Peak area of the analyte
A_{is}	Peak area of the internal standard
A_s	Sink projected surface area (m^2)
C	concentration of the pesticide molecules in air (μgm^{-3})
C_{as}	Concentration of the analyte in solution (gml^{-1})
C_e^*	equilibrium concentration of the pesticide molecules in air (μgm^{-3})
C_{is}	Concentration of the internal standard in solution (gml^{-1})
C_R^*	reduced equilibrium concentration ratio
C_{sat}^*	air phase concentration corresponding to saturated conditions (μgm^{-3})
k_1	adsorption rate constant (h^{-1})
k_2	desorption rate constant (h^{-1})
K_a	adsorption coefficient (mh^{-1})
K_{BET}	Brunauer-Emmett-Teller constant
K_d	desorption coefficient (h^{-1})
K_L	Langmuir coefficient ($\mu g^{-1}m^3$)
K_p	partition coefficient (m)
M_{se}^*	equilibrium adsorbed phase concentration (μgm^{-2})
M_{so}	monolayer capacity on surface of unit mass of sink (μgm^{-2})
S	number of adsorption sites
S_o	number of vacant sites

S_1	number of occupied sites
t	time (h)
V	volume occupied by adsorbed molecules (m^3)
θ	fraction of surface covered by molecules
X_o	mass of Lindane measured in air at time zero (µg)
$X(t)$	mass of Lindane at any given time (µg)

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Chapter One

1 Introduction

1.1 Indoor air contaminants

Households are exposed to very harmful contaminants e.g. pesticides that are present in indoor air (Brown 2003; Lewis et al. 1999; Lewis et al. 1994; Savage 1989). Studies (Lewis et al. 1994; Simcox et al. 1995) have found that concentrations of SVOCs are up to a hundred times higher in household dust than those found in outdoor surface soil. Some studies have measured indoor air concentrations of organochlorine pesticides in the range of <0.013 to 4600 ngm^{-3} (Roßkamp et al. 1999; Schenk et al. 1997).

On average, people spend more time indoors than outdoors (Chapin 1974; Savage 1989; Dorre 1997; Newton et al. 2001; Leech et al. 2002; Brown 2003; Brasche and Bischof 2005). Thus the quality of indoor air becomes a critical determinant of occupants' comfort and health (Savage 1989; Lewis et al. 1994; Brown 2003; Salvato et al. 2003). While this is the case, the need for energy conservation has resulted in the drive to reduce heat loss from buildings, one of the results of which has led to a decreased air exchange rate (ACH) in buildings (Spalding 1999; Jones 1999). The implications have been that contaminants in indoor environments stay longer over time resulting in relatively higher concentrations.

Generally, indoor air contaminants are classed under two categories; Volatile Organic Compounds (VOC) and Semi-Volatile Organic Compounds (SVOC). VOCs are commonly present as ingredients in household products such as paints, varnishes and

adhesives. SVOCs, on the other hand, are found in insecticides, household cleaning agents, wood preservatives and flea control pesticides (Butte 2004). Whilst the majority of VOC indoor contaminants have been investigated in great detail (Levin 1987; Wallace 1996; Bouhamra and Elkilani 1999; Brown 2002; Huss-Marp et al. 2004; Jørgensen 2007), investigations into SVOC indoor contaminants have been very limited (Walker et al. 1994; Simcox et al. 1995; Watt and Colston 2003). Investigations into VOC concentrations in indoor air have found high concentrations whilst the limited SVOC concentration assessments have found significantly lower concentrations in air.

The difference can be attributed to the properties of VOCs and SVOCs. Indeed, several studies have shown that SVOCs have low vapour pressures (10^{-2} to 10^{-8} kPa) (Daisey 1999) and high boiling points ranging between 260^{o}C - 400^{o}C (Butte 2004). VOCs on the other hand have significantly higher vapour pressures and much lower boiling points ranging between 50^{o}C - 260^{o}C (Butte 2004). The main route for exposure to VOCs is inhalation because the VOCs are mostly present in the vapour phase. On the other hand, there are many other routes of exposure to SVOCs which include inhalation of respirable properties, ingestion (for example children playing with dust and putting their hands in their mouth), and dermal contact (Lewis et al. 1994; Roßkamp 1999; Wilson et al. 2001; Watt and Colston 2003). The above properties characterize the behaviour of VOCs and SVOCs and are, in fact, the underlying reason for VOC's being found in large concentrations in indoor air, whereas SVOCs tend to remain in the sorbed phase on solid material which makes it difficult to detect in indoor air. A previous study showed concentrations in indoor air and predictions based on the vapour pressure of

these pesticides point to a risk of exceeding the acceptable daily intake (ADI) purely by intake through inhalation (Schenk et al. 1997).

Normally, in well ventilated indoor environments, the retention times for VOCs are typically short. This is due to the natural (or forced) exchange of stale contaminated indoor air with outdoor air. Given that VOCs are present in large concentrations in indoor air, they are easily carried along with the warmer stale air. This may explain why it is advisable that a space recently painted or varnished should be vacated by humans even though it is well ventilated. This is because of the fact that the VOCs present in paint and varnish are often retained in high concentrations for a short period in the air. This means that high concentration of VOCs present in the air decline in proportion to the air renewal rate. Human indoor exposure to VOCs immediately after application can result in acute exposure (ATSDR 2001a), which, if prolonged, will cause unconsciousness and possibly death (ATSDR 2001a). This is especially the case where indoor ventilation is poor (ATSDR 2001a).

Although both VOCs and SVOCs bind to surfaces in the indoor environment (e.g. wood, dust and glass) however, VOCs when compared to SVOCs form a much weaker molecular bond with the adsorbent or surface (Wilke et al. 2004). Driven by either concentration gradients or temperature gradients, the adsorbed molecules are continuously adsorbed and desorbed between the indoor surface(s) and surrounding air (Ruthven, 1984). This molecular transfer phenomenon is responsible for the extended retention times of SVOCs indoors when compared to VOCs (Ruthven 1984). For instance a house that had previously been treated with the insecticide permethrin (an

SVOC) three years earlier was found to have relatively high residual concentrations (with majority on surfaces and less in air) (Gebefuegi and Kettrup 1995). Consequently, household occupants are exposed to SVOCs for longer periods when compared to VOCs, albeit in lower concentrations. This is referred to as chronic exposure (ASTDR n.d.; U.S. EPA, n.d.), and this underpins the need for detailed studies to be carried out in the area of SVOC contamination in the indoor environment.

SVOCs are adsorbed by the skin, lungs, and gastrointestinal lining. The liver, kidneys, blood, lungs, nervous system, immune system and gastrointestinal tract can be harmed by long-term exposure to pesticides such as Lindane (ATSDR 2001b, 2005). The presence of pesticides (in dust) for respiratory exposure and ingestion depends on particle size. Smaller dust particles are more likely to be respired and the larger particles may be ingested. Therefore the redistribution of SVOC indoors is a function of the size of the house dust particles with which they are associated. This is why it is important to be able to estimate the potential exposure to dust associated pollutants in relation to particle size. Although studies in the US and Germany (Lewis et al. 1999) have associated pesticide concentrations with dust fractions, no particular study has been carried out for Lindane concentration in household dust with relation to size fraction. More so, no studies on pesticide concentration in household dust fractions on the one hand and on the other in relation to Lindane have been carried out for the UK. This is why this research is significant in allowing the extent of exposure to Lindane and the attendant effects to be gauged in the UK. In this regard this research analyses UK household dust size fractions for human exposure to Lindane.

1.2 Requirements for improved SVOC determination in indoor environments in modern times

The drive to improve SVOC contamination assessments has never been greater. Apart from the sustained drive to reduce heat loss in buildings which has inevitably led to lower air exchange rates and therefore higher SVOC contaminants in the indoor environment, the health implication is another important reason for improving SVOC contamination assessments. Though there are complications associated with measurement of airborne concentration such as the need for onsite visits by professionals to collect air samples, source strength, room ventilation, temperature (Gebefuegi et al. 1979; Levin and Hahn 1986; Schweinsberg et al. 1993), indoor air has continued to be the main medium for SVOC contamination assessments (U.S. EPA 1999).

Studies on SVOCs in the United States and Germany (Starr et al. 1974; Seifert and Schmahl 1987; Schlitt et al. 1993; Schenk et al. 1997; Lewis et al. 1999; Berger-Priess et al. 2002; Rudel et al. 2003) have established that household dust acts as reservoir (sink) for SVOCs. SVOCs are continuously adsorbed and desorbed on dust in the indoor environment. However a state of equilibrium is reached when the rate of adsorption equals the rate of desorption.

Indoor air concentration measurements of SVOC are common despite the attendant difficulties. However the difficulties that have arisen from the attempts to measure SVOCs have brought about the need to develop appropriate techniques to measure the concentration of SVOCs adsorbed/desorbed unto/from dust with reasonable accuracy.

Dust has a large surface area and is ubiquitous in households, and this has a major impact on the concentration of the contaminant in the indoor air space. The implication is that it reduces peak air contaminant concentrations but increases retention times for the contaminant in the system thereby leading to long term exposure (Berger-Priess et al. 1997). It has been suggested that these 'sink' effects of dust may be the reason for the negative health effects reported by indoor environment occupants even in situations where the airborne contaminant concentration is insignificant (Berger-Priess et al. 1997).

As a result of the inherent restrictions with indoor air SVOC measurements, the use of dust in contamination assessments presents a better alternative, as dust samples are easy to obtain, have a high surface area and are omnipresent in the household. Thus, the need to investigate the contribution of household dust to the SVOCs concentration in indoor air is imperative, especially given that it will now be possible to determine the concentration of SVOCs in the air from dust particles instead of air.

Indeed, dynamic and static studies of possible relationships between pesticide concentrations in air and dust have been undertaken (Schnelle-Kreis et al. 2000; Pedersen et al. 2002). As a first stage in the modelling process, this research will concentrate on static equilibrium studies. Such a model could have immense impact on the building industry. House owners or potential house buyers would be able to make more informed choices with the availability of a simpler way to predict pesticide levels in indoor air i.e. via dust analysis. The cost implication of having professionals come to collect air samples would be greatly reduced as the occupants could easily collect the

dust samples which would be sent for analysis. The added information obtained from concentration measurements in dust allows for more straightforward means of predicting SVOC concentrations in air through SVOC adsorption isotherms.

1.3 Scope of research

This section outlines the general aim and objectives of this research and indicates the relevant chapters in which these are addressed and fulfilled.

1.3.1 Aims

1. Determination of the partition coefficient through dynamic and static equilibrium studies, of the insecticide Lindane between air and dust in samples spiked with known Lindane concentrations.
2. Determination of the effect of size fraction of dust samples on the partitioning of Lindane between air and dust by partition coefficient, adsorption and desorption constants through static equilibrium and dynamic studies of Lindane concentrations on different size fractions (<20µm and >45µm<63µm and whole samples) of dust and air in samples spiked with known pesticide concentrations
3. Determination of the adsorption and desorption rate constants through both dynamic and static studies of Lindane concentrations in whole and size fractioned dust.
4. Fitting experimentally derived adsorption data to an appropriate sorption model.
5. Comparing rate constants from mass balance model with physical sorption coefficients from physical sorption models
6. Develop a simple method to measure SVOCs air concentrations in small vials without the use of water or any solvents.

1.3.2 Work plan

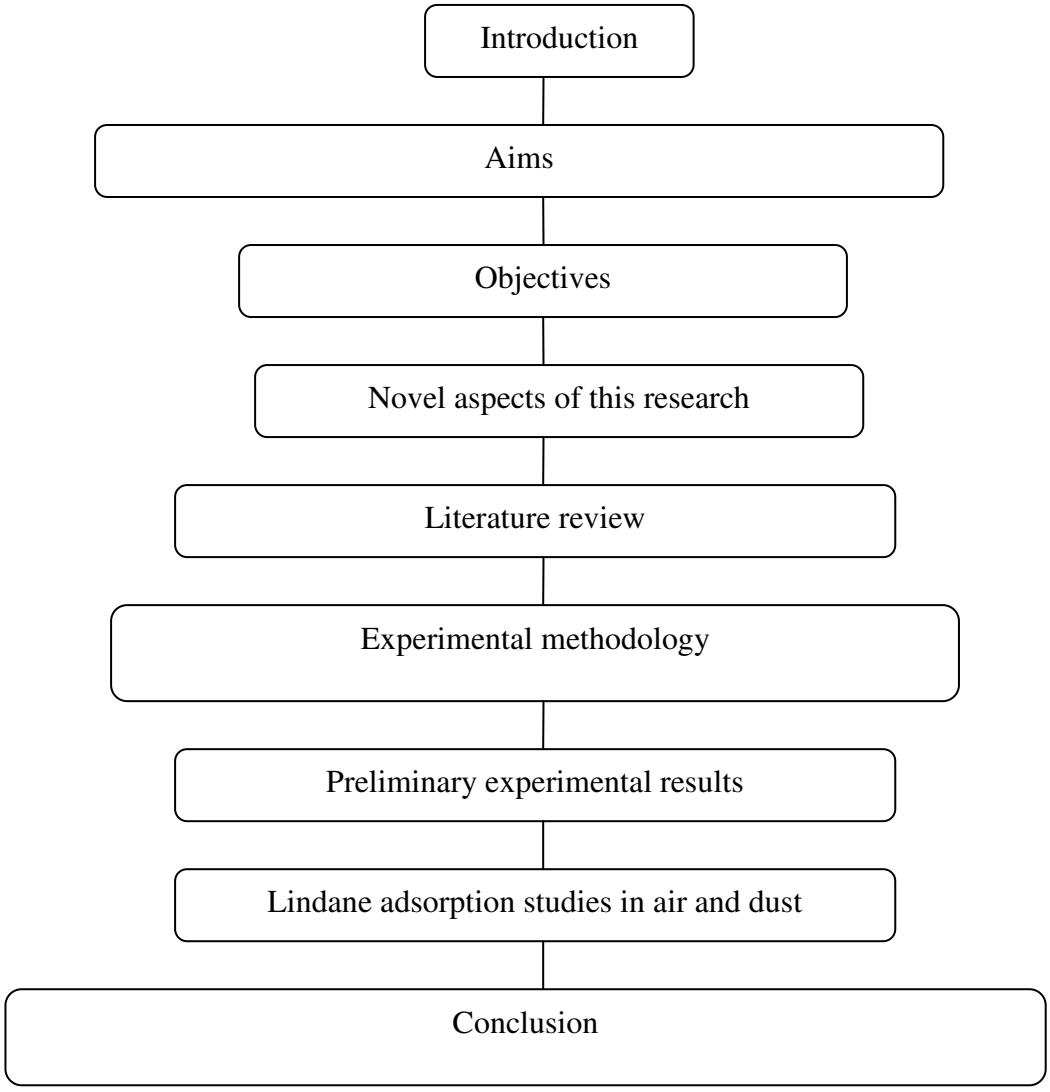
The following objectives provide a framework for the proposed tasks which were undertaken to attain the above aims.

1. Review common pesticides banned in the UK to determine the pesticide to be investigated in detail (Chapter 2)
2. Review of dust components and its size fractions in order to understand its interactions with pesticides in particular pesticide distribution in dust size fractions (Chapter 2).
3. Review of mathematical models used for adsorption/desorption processes between air and dust (Chapter 2).
4. Devising a methodology through adapting existing experimental protocols in literature to this research. This is achieved by reviewing protocols for sampling and analysis of air and dust followed by preliminary testing of existing and subsequently adapted protocols (Chapters 2, 3 and 4).
5. Dynamic tests to measure change in air and dust concentrations over time in order to establish an equilibrium time as well as obtain adsorption and desorption rate constants for dust size fractions as well as whole dust samples (Chapters 4 and 5)
6. Measurement of corresponding concentrations in air and dust at equilibrium in order to establish an adsorption isotherm and obtain a partition coefficient between air and size fractioned dust samples as well as air and whole dust samples (Chapters 3, 4 and 5).

1.4 Novel aspects of this research

The relationship of Lindane concentrations in different dust size fractions and corresponding air concentrations is investigated. The partition coefficients of different size fractions as well as whole dust samples are then compared. Prior to this research, this aspect of indoor air and dust contamination has not been investigated.

1.5 Structure of research



Chapter Two

2 Literature review

2.1 Summary

This chapter identifies the need to investigate hazardous pesticides and more specifically Lindane in indoor air and dust. Smaller size fractions of dust are available for inhalation. It appears there is a relationship between dust size fractions and pesticide concentrations and thus the need to investigate the effect of size fraction on dust. When unsettled from floors or surfaces, smaller dust sizes may enter the air and thus contribute to a larger pesticide concentration in air than may have been previously measured by a professional when testing for air concentration of a contaminant in a household.

2.2 Pesticides in the indoor environment

Pesticides are substances used for controlling or eliminating insects, pests, and other organisms that are threats to plants and animals, and are used both indoors and outdoors. Traces of pesticide found on dust in homes emanate from prior indoor applications of pesticides and migration of pest control laden dirt from agricultural fields, playgrounds and lawns amongst others (Paustenbach et al. 1997; Roßkamp et al. 1999).

Specifically, pesticide application in the indoor environment include flea and pest control for pets, disinfectants, bathroom and kitchen cleaners, head lice treatment and wood worm and fungal wood treatment. Remedial wood worm treatment in homes is usually very extensive owing to the large proportion of wood-based furniture and fixtures used in building construction, which include but are not limited to roofing, doors and furniture. The wood is treated with pesticides to protect it from fungal and insect attack. As a result, a typically designed home with wooden furniture and fixtures would, therefore, expose its occupants to potentially chronic levels of pesticide. For this reason, it is important to be able to ascertain the level of indoor insect and fungal pesticide contamination.

However, the exact formula, application, and quantities of pesticides vary from country to country due to a number of factors, most important of which is the severity of pest or organism problems, which is usually influenced by climatic conditions. This is one of the reasons that countries have different safety regulations regarding the use of pesticides. For example, some pesticides currently in use in the United Kingdom are banned in the United States (Harrison 1998).

Also, the type and concentration of pesticides in homes may be different for a variety of reasons. For example, in countries where safety legislation restricts the use of certain pesticides to trained professionals only, the levels and types of pesticides found in homes would be different from homes in countries with no restrictions. Consequently, greater concentrations of these pesticides in household dust are found in geographical regions where pesticide application is not restricted to professional use compared to

regions where regulation is enforced. Thus, the level of pesticide concentration and extent of use may determine the duration of the contaminant in the air.

Certain pesticides can remain indoors for a very long time, in some cases for as long as twenty years after application (Gebefuegi and Kettrup 1995; Roßkamp et al. 1999). This is why traces of some harmful pesticides that were previously in use, but have been banned for some time now, may still be found indoors. Thus indoor contaminant investigations on pesticides that have been banned many years ago are important. Table 2.1 comprises a list of organochlorine pesticides that have been banned in the United Kingdom since 1981.

Table 2.1

UK banned organochlorine pesticides

Pesticide	Ban date
Lindane	2004
Aldrin	1991
Endrin	1991
Heptachlor	1984
Chlordane	1981
Dieldrin	1981
Hexachlorobenzene	1981

Source: Adapted from PAN UK (2007), HSE (2004)

Table 2.1 lists seven banned organochlorine pesticides in the UK of which Dieldrin and Lindane were the main insect eradication pesticides for wood (Howell 1998). Although both have been banned, as mentioned previously they may still be present in the indoor environment. In the particular case of the UK, the use of Lindane as a wood insecticide was more widespread than Dieldrin (Richardson 1993). Additionally, Lindane was also widely used for other purposes indoors such as the treatment for head lice and flea

control making Lindane a choice for investigation on banned pesticides for this research.

2.2.1 Lindane as a problem in the indoor environment

Lindane is a dangerous organochlorine pesticide which has been proven to cause health hazards. Lindane was developed in the 1940's where relatively hazardous chemicals were acceptable (Harvey 2000) however as shown in Table 2.1, a complete ban did not come into effect till 2004 (HSE 2004).

It has harmful effects on the nervous system and is a suspected human carcinogen that has been linked with breast cancer and birth defects (IARC 1987). Lindane has also been linked with aplastic anaemia (a blood disorder), kidney damage and endocrine disruption (CDC 2003). As far back as 1998, it was concluded in a European Union report that there was no safe limit of exposure for Lindane. The UK Lindane Campaign Group was very active in pressing the government to introduce a complete ban on Lindane.

Apart from the wide spread use of Lindane, its harmful effect, which was aptly demonstrated in 2000 with the death of a little girl who had ingested a small quantity of Lindane is another motivation for its choice for this research. Contrary to scientific studies on the dosage of Lindane per unit weight of a child, the amount ingested in this case was considerably less than the 'lethal dose' but was potent enough to kill the child (PAN UK 2002). This has further confounded many indoor air specialists and other health and safety practitioners about the safe dose of Lindane given the levels of Lindane found in most households. Prior to the ban, there were over 147 products in the UK market with Lindane as the active ingredient (HSE 2001; 2004; 2006). Some

common ones include Doff Ant Killer, Murphy Gamma BHC Dust, Doff Gamma BHC Dust, Doff Weevil Killer, Doom Ant and Insect Powder, Fumite Lindane Generator (PAN UK 1999). A cross-section of these products is presented in Table 2.2 which details the application method and rate of these and the percentage of the active ingredient Lindane.

Table 2.2

Cross section of banned Lindane based biocide products

HSE Number	Product Name	% Active ingredient (Lindane)	Application Method	Application Rate
4571	Doom moth proofer aerosol	1	Surface spray	For the control of moths: spray fabric for 10-15 seconds per square metre every 6 months for the control of carpet beetles and woolly bears: spray fabric for 25 seconds per square metre every 2 months
4572	Doom flea killer	1	Surface spray	Apply a 25 second spray per square metre
3641	Kingston dual purpose fluid	6.9	Spray	Dilute 2 litres of concentrate with 25 litres of water (to give 0.51% w/w gamma-hch and 1.02% w/w tributyltin oxide) then spray onto timber surface at at a rate of 1 litre diluted formulation per 4-6 square metres
3736	Pc-i	0.5	Coarse spray	4 litres per square metre (depending on wood) 16 grammes active ingredient per square metre
3051	Wilco wood preservative brown	0.5	Brush and spray	One or two coats as required 6-8 square metres per litre
3006	Timber preservative solvent based fungicidal insecticide 30	0.8	Brush, spray and dip	5 litres treats 150-200 square feet
4641	Supergrade wood preserver	0.12	Brush, spray and dip	Small timbers: apply at a rate of 1 litre of product to 4 square metres of wood surface by brush, spray or injection re-apply once. When dipping, immerse timber in product for 3 minutes large timbers: apply at a rate of 1 litre of product to 4 square metres of wood surface by brush, spray or injection re-apply twice. When dipping, immerse timber in product for 10 minutes
3170	Vacsol mwr concentrate 2203	1.4	Industrial impregnation	Dilute 1 part of concentrate with 2 parts of petroleum distillate/white spirit before use
4713	Fumite lindane generator size 10	59.4	Smoke generator	Generator size 10 contains 21 gm (ai) and will treat 85 cubic metres
4465	Wax polish	0.18	Cloth	Apply as required
3129	Aqueous fungicide - insecticide concentrate	4.5	Brush and coarse spray	Dilute 1 part concentrate with 9 parts water five litres per 20 square metres
3138	Protim wb12	6.75	Brush, spray and dip	Dilute concentrate 1:9 with water

Source: Adapted from the U. K Health and Safety Executive (HSE 2001; 2004)

As shown in Table 2.2, the percentage of active ingredient varies from 0.12% to 59.4%. In addition some of these products were for use by amateur as well as professional applicators which could mean that application rates were not adhered to for people erroneously assuming they would get better results if they applied larger quantities. This suggests that Lindane is likely to be present in many large quantities in households and thorough investigations into Lindane as an indoor air contaminant need to be carried out.

Despite the well-documented harmful effects of Lindane, very few attempts have been made to quantify its presence in UK homes. In two UK based studies, Lindane was only tentatively identified in dust (Santillo 2003) and found in 7% of the target sample of homes in the other study (Coldwell and Corns 2001) despite the evident wide spread use of Lindane in UK homes before it was phased out in 2004 (HSE 2001; 2004; 2006).

Such attempts at developing a technique to reliably measure Lindane concentration in households will be beneficial to the building industry. This is particularly the case since the past use of pesticides in households and therefore the evaluation of the level of concentration of pesticides indoors affect on the quality of the indoor environment and hence indoor comfort. Furthermore, UK legislation has in 2007 introduced home information packs as mandatory requirements for home owners trying to sell their homes (Directgov c2007), and so establishing simple and relatively inexpensive tests to measure pesticide contamination would enable incorporation into these packs. In the 2001 study by Coldwell and Corns, information on known pesticide use in households was collected via a questionnaire that was sent out to participants. Coincidentally, households in which

Lindane was found had reported non-known use of Lindane. This could be because the pesticides where applied by previous residents or indeed at construction stage. It would therefore be beneficial for past pesticide applications by both professional and amateurs to always be documented and incorporated into these home information packs.

Similarly there might be a need for a study of this nature to transcend the indoor use of Lindane given its wide use in outdoor activities such as in agriculture and horticulture as is evident in a pesticide use survey carried out by the Central Science Lab in 1998. (Harvey 2000). This implies that other environmental media such as farms and garden sheds can harbour Lindane contaminants, which can find their way into homes through foot track in.

2.2.1.1 Properties of Lindane

Lindane is the common name for the gamma isomer of hexachlorocyclohexane (γ-1 2,3,4,5,6-hexachlorocyclohexane). It belongs to the organochlorine (OC) pesticide class which are known to be highly toxic and persistent in the environment. It is a white crystalline solid which is stable in heat, air, light, carbon dioxide and strong acids. Technical grade hexachlorocyclohexane contains mainly five isomers whose mixture was largely used as an inexpensive pesticide but as gamma isomer was shown to be the only isomer with strong insecticidal properties, it was purified from the mixture and commercialised under the name Lindane. Its chemical formula $C_6H_6Cl_6$ and its CAS registration number is 58-89-9. Its structural formula is shown in Figure 2.1.

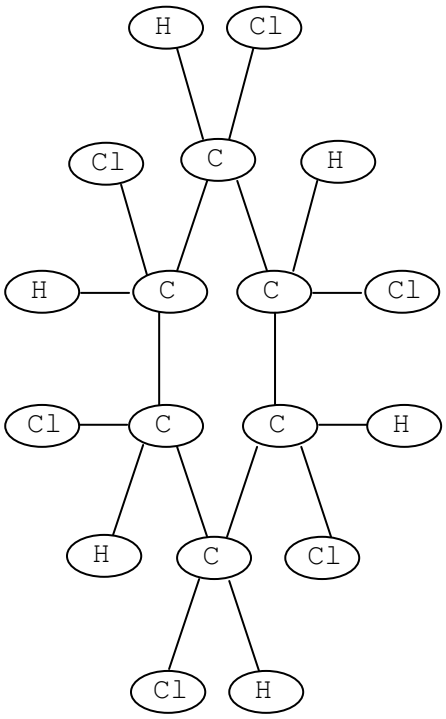


Figure 2.1 Chemical structure of Lindane.
Source: Lindane (2002).

As illustrated in Figure 2.1, the chemical structure of Lindane consists of six atoms each of chlorine, carbon and hydrogen atoms. Its relative molecular mass is 290.8, and compounds with such high molecular masses tend to have low vapour pressures and high boiling points.

Lindane is a white crystalline solid and is odourless in its pure form. It has a vapour pressure of 0.434×10^{-5} kPa (3.26×10^{-5} mmHg) at 20°C, and a boiling point of 323°C and thus falls into the SVOC category. It undergoes vaporization and condensation cycles and can be found in far-off regions where it is not used, such as the Arctic.

2.3 Characterisation of household dust

It is important to characterise dust into different components. This owes to the fact that the relative sizes of dust components can help explain the variances in Lindane concentrations in dust fractions.

2.3.1 Components of house dust

Household dust can be defined as a "complex mixture of biologically derived material (animal dander, fungal spores etc), particulate matter deposited from indoor aerosol, and soil particles brought in by foot traffic" (U.S. EPA 1997, p. 334). Further examples of dust constituents include food crumbs, synthetic fibres, fingernail filings, oil soot, ash, human and animal skin and hair.

In particular, soil is a constituent of household dust and in fact makes up a large proportion of the dust and Lindane has been shown to have close affinity for organic soil material compared to inorganic material (Mills and Biggar, 1969; Baluja et al.; 1975; Wahid and Sethunathan, 1980; IPCS 1991). Therefore household dust containing significant levels of soil (e.g. through foot track in) with high organic content, would tend to retain Lindane more strongly and over a longer period. This can be an important factor in predicting the resulting Lindane air concentration in homes.

Household dust falls into a wide range of different particle sizes, ranging from <2.5µm to over 2mm (Morawska and Salthammer 2003; Lewis et al. 1999). When dust is size fractioned wood chips, sand and stones are found in the larger fractions, whilst smaller

fractions are represented by food crumbs, fungal spores and pollens (Morawska and Salthammer 2003). The constituent materials may affect how Lindane is sorbed. Indeed a number of researchers have found that higher pesticide concentrations predominate in smaller size fractions (Lewis et al. 1999; Walker et al. 1999). This is important given that smaller size particles of dust are inhalable (<10µm), respirable (<2.5µm) and ingestible, posing greater risks for human health.

2.3.2 Dust size fractioning and size distribution

Varieties of dust size fractionating methods (Lewis et al. 1999; Pedersen et al. 2002) are available including sieving and fluidised bed dust tube methods. However dry sieving has been compared to the other fractionating methods and found to be relatively simple and has no adverse effects on efficiency of recovery (Pedersen et al. 2002). Another study also used the sieving method in addition to a fluidised bed fractionating technique (Lewis et al. 1999). The dust was collected from professional cleaning companies who had used commercial vacuum cleaners to collect the dust. The dust was fractioned step wise first using a sieve followed by an air classifier. The fractionating process involved screening the dust sample at the >500 µm to remove larger particles that might plug the separation equipment. The resulting fraction was then separated into two fractions <25µm and 25µm – 500µm using an air classifier which separates dust particles on the basis of their aerodynamic diameter. After this, the 25µm – 500µm sample was then sieved to produce five different fractions using a sieve shaker (Ro Tap). The size fractions are represented in Figure 2.2. The <25µm fraction was further processed in an air classifier made up of a fluidised bed aerosol generator (FBAG) to divide it into 4µm -25µm and <4µm fractions. The dust recovery efficiency from the FBAG was very low at 7%. It was assumed that the bulk of the dust was lost to the walls of the

walls of the apparatus or remained in the FBAG. Following the dust size fractioning, the resulting dust size fractions were weighed. The weight size distributions of dust size fractions in the study are presented in Figure 2.2.

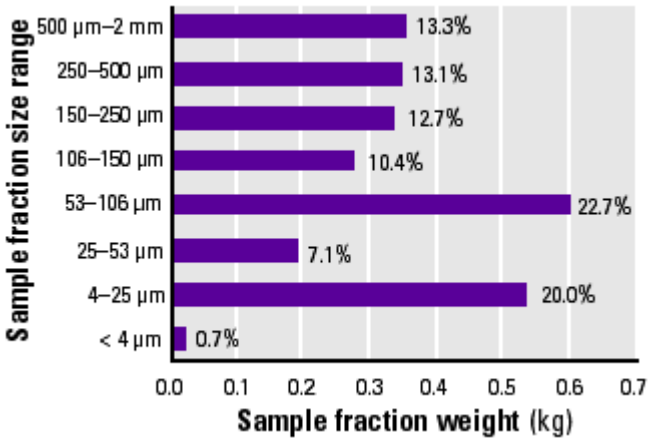


Figure 2.2 Weight of separated dust fractions and percent of total coarse (< 2 mm) dust weight for each size fraction.
Source: Lewis et al. 1999

Following size fractioning the size distribution and characteristics of dust can be verified using the Scanning Electron Microscopy technique (SEM) (Gebefuegi and Kettrup 1995; Lewis et al. 1999). The SEM enables the dust particles to be viewed on a microscopic scale and thus their nature may be determined, for example, fibrous and porous properties may be identified. This can help explain the properties of dust size fractions which enhance adsorption of contaminants. In addition the magnified images of the dust particles enable the operator to measure individual particle dimensions which are then used to verify the particle sizes in the different fractions. To this end this research will employ the scanning electron microscopy technique to investigate constituents of different dust size fractions

2.4 Indoor SVOC concentrations

This section reviews literature in which SVOC concentrations that have been found in house dust measurements as well as air.

2.4.1 SVOC concentrations in dust

Overseas studies have reported indoor dust organochlorine pesticide concentrations spanning orders of magnitude (Fortune et al. 1999; Rudel et al. 2003; Schenk et al. 1997). In a US study, Rudel et al., 2003 measured amongst other compounds, pesticide concentrations in indoor air and dust. Again, the volunteers for test homes were recruited on the basis of self reported pesticide usage. There had been reported cases of breast cancer in a lot of the test homes sampled. They reported dust pesticide concentrations in the range of ($<2 \times 10^{-4} - 0.228$) mgg^{-1} of dust. A similar trend was observed with a previous study with chloropyrifos, trans-permethrin and cis-permethrin being the most abundant (Fortune et al. 1999).

In a German study a maximum Lindane concentration of $9 \times 10^{-3} mgg^{-1}$ of dust was found (Rosskamp et al. 1999). The indoor use of Lindane as a biocide in Hylotox 59, a wood preservative had been banned eleven years before the study was conducted in 1999. This study compared concentration levels of Lindane in the air of attics, newly converted attic apartments or apartments situated immediately under attics which had known history of Hylotox 59 treatments. Sampling attic dust is useful, since settled dust in attics is likely to be preserved from weathering, and thus can indicate past exposure of occupants to the contaminants associated to the dust (Dahlgren et al. 2003; O'Connor and Sabrsula 2005; Hensley et al. 2007). They found that the attics had

higher concentrations of Lindane than the apartments immediately below them and converted attics. High concentrations in apartments below the attics were attributed to the possibility of air exchange between the air and the rooms as well as direct use of the biocides in the apartments.

Fortune et al. (1999) analyzed aged household carpeting to determine the distribution of pesticide residues between dust, carpet and pad compartments. Like other studies, volunteers were also selected on the basis of self reported pesticide usage as well as individuals about to change their carpets. Lindane was found in two of the eight homes at concentrations of $3.4\mu gm^{-2}$ and $0.53\mu gm^{-2}$. Another finding was that Lindane was present in the finer dust particles i.e. <150µm, but absent in the larger coarse particles. This suggests that the smaller particles have a higher affinity for Lindane. This would be further investigated in this research.

Their results were similar to some others found in literature. Camann and Buckley 1994 reported detected values of cis and trans permethrin at maximum concentrations of $1.75\mu gg^{-1}$ and $0.8\mu gg^{-1}$ respectively. Chloropyrifos at $0.56\mu gg^{-1}$, bendiocarb at $0.36\mu gg^{-1}$ methoxychlor at $0.59\mu gg^{-1}$ and alpha and gamma chlordane at $0.4\mu gg^{-1}$ and $0.46\mu gg^{-1}$ respectively (the dust was sieved to <150µm). A range of concentration of pesticides in indoor dust reported in various studies is presented in Table A1 in the appendix. It shows that permethrin, diazinon, chloripyrifos, bendiocarb and gamma-chlordane were the most abundant.

2.4.2 SVOC concentrations in air

As mentioned previously, overseas studies have reported indoor air concentrations of organochlorine pesticides in the range of $<1.3 \times 10^{-8}$ to 9.3×10^{-4} mgm^{-3} (Roßkamp et al. 1999; Levin and Hahn 1986; Schenk et al. 1997). As is the case with organochlorine pesticides dust levels, there is also insufficient information on measured air concentrations of OCPs in the UK. There is clearly a need to be able to relate the dust concentration to the air concentration.

2.5 Adsorption theory and modelling techniques

Adsorption is the process by which a substance leaves one phase, to accumulate on the surface of another phase. In the present context, pesticides leave the indoor air phase to accumulate on a solid phase, dust. Over time the reverse processes, desorption, occurs. Here, the pesticides leave the dust to re-enter into the indoor air thereby contributing to elevated indoor air concentrations. The adsorption and desorption cycle continues and eventually reaches equilibrium. At this stage, desorption rate from the sink into air will equal the adsorption rate from the air to the sink. The figure below describes the adsorption and desorption closed system.

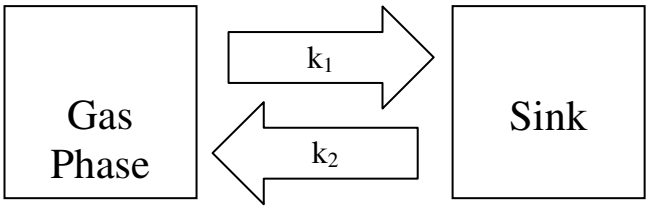


Figure 2.3: Mass balance two compartment model

Equilibrium relations can often describe this phenomenon and are generally unique to the adsorbate-adsorbent system being considered (in this research Lindane-dust). These equilibrium relations are referred to as adsorption isotherms when reported for isothermal conditions at atmospheric pressure (Axley 1991; Ruthven 1984).

The equilibrium concentration value of the pesticide molecules C_e^* in the free phase (air) is related to the equilibrium concentration value of the pesticides in the adsorbed phase, dust, M^*_{Se} and the thermodynamic state of the system defined by temperature, T, and gas phase pressure, P, and the fraction of surface covered by the molecules θ, can be represented generally thus:

$$M^*_{se} = \theta(C_e^*, T, P) \quad \text{---------- (1)}$$

There are a number of adsorption isotherm equations to describe the adsorptive and desorptive behaviour of gas molecules with solid surfaces the most common of which are Linear, Langmuir, BET, and Freundlich isotherms.

The **Linear model** is the simplest form.

$$M^{*}_{se} \cong K_P C^{*}_e \quad \text{---------- (2)}$$

Where the single parameter, K_p is a temperature-dependent coefficient also known as the partition coefficient (Ruthven 1984, Slejko 1985). It is generally appropriate for cases of adsorption of gases at very low concentrations on homogeneous surfaces with ample sites available for adsorption.

The **Langmuir model** considers the fact the sites available for adsorption are limited (Ruthven 1984, Slejko 1985). In mathematical terms the Langmuir model is derived thus:

S = number of adsorption sites, S_1 = number of occupied sites, S_o = number of vacant sites where $S_o = S - S_1$

At equilibrium, the rate of desorption is assumed to be proportional to occupied sites S_1

Therefore,

Desorption rate $= K_d S_1$ ---------- (3)

Also the rate of adsorption is assumed to be proportional to the bare surface S_o and C^{*}_e

Adsorption rate = $K_a S_o C^{*}_e$ ---------- (4)

At equilibrium, adsorption and desorption rate are equal,

Therefore,

$K_d S_1 = K_a S_o C^{*}_e$ ----------(5)

or since $S_o = S - S_1$

$K_d S_1 = K_a (S - S_1) C^{*}_e$ ----------(6)

$K_d S_1 = K_a S C^{*}_e - K_a S_1 C^{*}_e$

$K_d S_1 + K_a S_1 C_e^* = K_a S C_e^*$

$S_1(K_d + K_a C_e^*) = K_a S C_e^*$

$$\frac{S_1}{S} = \frac{K_a C_e^*}{K_d + K_a C_e^*} \text{ ----------(7)}$$

Now, θ = fraction of surface covered

$$\theta = \frac{S_1}{S} \text{ ---------- (8)}$$

and $\frac{S_1}{S} = \frac{M^*_{se}}{M_{so}}$

where M_{so} = monolayer capacity on surface of unit mass of sink

M^*_{se} = equilibrium adsorbed phase concentration ($\mu g m^{-2}$)

$$\Rightarrow \theta = \frac{K_a C_e^*}{K_d\left(1 + \frac{K_a}{K_d} C_e^*\right)} \text{ ---------- (9)}$$

Denoting $K_L = \frac{K_a}{K_d}$

Where K_L is the temperature dependent Langmuir adsorption coefficient

$$\therefore \theta = \frac{K_L C_e^*}{\left(1 + K_L C_e^*\right)} \text{ ---------- (10)}$$

Also in terms of equilibrium adsorbed phase concentration M^*_{se}

$$\theta = \frac{M^*_{se}}{M_{so}} = \frac{K_L C_e^*}{\left(1 + K_L C_e^*\right)} \text{ ---------- (11)}$$

$$M^*_{se} = M_{so} \frac{K_L C_e^*}{\left(1 + K_L C_e^*\right)} \text{ ---------- (12)}$$

At low vapour phase concentrations $(C_e^* \to 0)$, $M^*_{se} \to M_{so} K_L C_e^*$

At high vapour phase concentrations $(C_e^* \to \infty)$, $M_{se}^* \to M_{so}$

The Langmuir model is non-linear as K_a is a function of C_e^*

Linear assumption- occupied sites very small proportion of available sites $\theta << 1$

$$\theta = \frac{K_a C_e^*}{K_d + K_a C_e^*} \text{----------(12)}$$

$$\theta K_d + \theta k_a C_e^* = K_a C_e^*$$

$$\theta K_d = K_a C_e^* - \theta K_a C_e^*$$

$$\theta K_d = K_a C_e^* (1 - \theta) \text{----------(13)}$$

$\theta << 1$

$$\theta K_d = K_a C_e^* \text{----------(14)}$$

or $M_{se}^* K_d = K_a C_e^*$

Sink projected surface area A_s

$$A_s K_a C_e^* = A_s K_d M_{se}^*$$

$$\frac{A_s M_{se}^*}{A_s C_e^*} = \frac{K_a}{K_d} = K_L (= K_p) \text{----------(15)}$$

Linearised Langmuir

$$\frac{A_s dM_{se}^*}{dt} = k_1 CV - k_2 A_s M_{se}^* \text{----------(16)}$$

At equilibrium $\frac{dM_{se}^*}{dt} = 0,\ C = C_e^*,\ M_{so} = M_{se}^*$

Therefore, $0 = k_1 C_e^* V - k_2 A_s M_{se}^*$

$$k_1 C_e^* V = k_2 A_s M_{se}^* \text{---------- (17)}$$

$$A_s K_a C_e^* = A_s K_d M_{se}^* \text{----------(18)}$$

Comparing Equations (17) and (18),

$$k_1 C_e^* V = A_s K_a C_e^* \text{ ----------(19)}$$

$$\Rightarrow k_1 = \frac{A_s K_a}{V} \text{ ---------- (20)}$$

and $\Rightarrow k_2 A_s M_{se}^* = A_s K_d M_{se}^*$ ----------(21)

$$k_2 = K_d \text{ ---------- (22)}$$

Langmuir's expression as in Equation (12)

$$M_{se}^* = M_{so} \frac{K_L C_e^*}{\left(1 + K_L C_e^*\right)}$$

$$M_{se}^* + K_L M_{se}^* C_e^* = M_{so} K_L C_e^*$$

$$\frac{M_{se}^*}{M_{so} K_L M_{se}^*} + \frac{K_L M_{se}^* C_e^*}{M_{so} K_L M_{se}^*} = \frac{M_{so} K_L C_e^*}{M_{so} K_L M_{se}^*}$$

$$\frac{C_e^*}{M_{se}^*} = \frac{C_e^*}{M_{so}} + \frac{1}{M_{so} K_L} \text{ ---------- (23)}$$

Compared to the equation

$$y = mx + c \text{ ---------- (24)}$$

$$\Rightarrow y = \frac{C_e^*}{M_{se}^*}, m = \frac{1}{M_{so}}, c = \frac{1}{K_L M_{so}}$$

This Langmuir model approximates the linear model at very low concentrations of adsorbate in the gas phase (when $K_L C_e^* << 1$). Following this approximation the Langmuir model can be expressed as $M^*_{se} \cong K_P C_e^*$

$$\frac{M^*_{Se}}{C_e^*} \approx \frac{M_{So} K_L}{1} \text{ ---------- (25)}$$

Combining equation (2) and (25) gives,

$$\frac{M_{se}^{*}}{C_{e}^{*}} \approx K_P \approx M_{So} K_L \text{ ---------- (26)}$$

$$\therefore K_P \approx M_{So} K_L \text{ ---------- (27)}$$

The **BET** model provides for multilayer adsorption that may occur in physical adsorption although unlikely to occur indoors as the concentration is usually very low. It is expressed as follows:

BET: $$M_{se} \cong \frac{M_{So} K_{BET} C_R^*}{(1 - C_R^*)(1 - C_R^* + K_{BET} C_R^*)} \text{ ---------- (6)}$$

where K_{BET} is the BET constant related to the energy of adsorption, M_{so} (the same as in Langmuir model), the surface concentration when there is complete coverage by a single monolayer, C_{sat}^* is the air phase concentration corresponding to saturated conditions, and $C_R^* = (\frac{C_e^*}{C_{sat}^*}) << 1$ is the reduced equilibrium. Previous research has found the BET model to be reliable in the range of reduced concentrations of $0.05 < (\frac{C_e^*}{C_{sat}^*}) < 0.35$ (Ruthven 1984). Therefore, if $\frac{C_e^*}{C_{sat}^*}$ for Lindane does not fall in this range, the BET model will not be considered further in the research.

2.5.1 Test Chamber Experiments

Various test chamber experiments have been conducted to investigate the adsorption and desorption rates of VOCs to and from sinks. In these studies test chambers usually comprise of a glass chamber with a sink (e.g. carpet) placed at the bottom of the chamber. The test can either be dynamic or static. Previous dynamic studies have involved measuring the concentration of VOCs in air and dust at intervals over time (Jørgensen 1999; Tichenor et al. 1991; Axely 1991). There is usually an initial flow of the compound of interest and purified air into the chamber. After a given time the flow of the contaminant compound is stopped and only purified air flows through the chamber. There is usually an outlet through which the concentration of the compound in the chamber air at any given time can be measured. The relationship between the concentration in air and concentration measured in sinks are then modelled based on available adsorption isotherm equations. An adsorption isotherm for Lindane in air and dust has not been reported in literature. A wide variety of tests can be conducted in test chamber experiments on sorption. Tichenor et al. (1991) investigated the effect of VOC concentration and the temperature of the system on sorption behaviour. They found that at elevated temperatures of 350^{o}C the adsorption rate and desorption constants were significantly higher than at 230^{o}C.

Elkilani et al. (2003) investigated sorption of volatile organic compounds on carpet fibres. They conducted test chamber experiments to study the decay of VOC concentration under controlled conditions. They were conducted in dynamic state. Two test chamber experiments were conducted, one in the presence of carpet flooring and one without. Each experiment contained a single source of VOC in a Petri dish. The

experiments showed that the carpet represented a sink thereby lowering the maximum VOC concentration observed in the chamber. Also the presence of the carpet resulted in prolonged elevation of the VOC concentration in the test chamber.

Berger-Preiss et al. (2002) investigated the indoor exposure to permethrin in rooms with wool textile floor coverings (wool rugs). The concentrations of permethrin in wool fibres, house dust and air-borne particles were monitored. The concentrations in dust were the highest ranging from $<1 \mu g g^{-1}$ – $659 \mu g g^{-1}$. The concentrations in wool fibres ranged between <1 - 245µg permethrin per gram of wool fibre. The concentration in air-borne particles was lowest ranging between <1 - $6 \mu g m^{-3}$. An approximate value of the partition coefficient of $0.009 g m^{-3}$ would describe the adsorption process. Their observed statistical correlations show that the concentration level of permethrin in the air may be caused by a few wool fibres suspended in the air.

Gebefuegi and Kettrup (1995) investigated the accumulation of SVOCs on material surfaces, which include textiles and dust particles containing textile fibres. Their results indicate that settled particles such as house dust may be used for monitoring purposes as indicators of the presence of SVOCs. They also suggest that house dust may be used for sampling SVOCs in order to estimate the whole body exposure. They put forward that dermal exposure is possible through skin contact with contaminated textiles and dust particles.

Small chamber studies showed that adsorption of SVOCs to textile from air occurs over a period of time. They compared results from previous works of SVOC concentrations in air to concentrations of SVOCs adsorbed on textile surfaces. Concentrations in

textiles were significantly higher. For Lindane they found 8mgkg^{-1} on the fibre surface when the concentration in air was 1.6μgm^{-3}. This gives an approximate value for the partition coefficient of 5gm^{-3}. For an average air concentration of pentachlorophenol of 0.6μgm^{-3} an amount of 32mgkg^{-1} was adsorbed on the cotton fibre surface within 48hours in the chamber studies giving a partition coefficient of 53.3gm^{-3}. In another study of pentachlorophenol in air and dust, a partition coefficient of 3.68 x 10^{-4}gm^{-3} approximately was found (Schnelle-Kreis et al. 2000).

2.6 Extraction of Lindane from dust

It was important to ensure that the dust samples used in these experiments were lindane free prior to commencement of any dosing. Therefore preliminary an extraction technique was employed to identify the presence or absence of Lindane in the dust samples. Various extraction methods are possible including ultrasonic, Soxhlet, and microwave assisted extraction amongst others. The Soxhlet extraction technique which is the most robust technique was employed in this research.

Soxhlet extraction has been used to extract SVOCs from solid matrices such as soil and dust. Soxhlet extraction involves placing the SVOC containing solid matrix into a cellulose thimble which is then placed into the main chamber of the Soxhlet extractor. This chamber is connected to a round bottom flask which is placed in a heating mantle. The extraction solvent in the flask is heated to reflux and then travels up the distillation arm and floods into the main chamber with the thimble. The chamber then slowly fills and some of the analyte will dissolve into the solvent. The chamber is emptied with the help of the side arm and the cycle repeats. The Soxhlet extraction method is typically thought to be a relatively more exhaustive method with higher recovery rates of the

analytes. The length of extraction and hence interaction of the sample with the extraction solvent is typically between 16 to 24 hours.

It should be noted that an important consideration during extraction, collection and storage of organochlorine compounds is the septa. The vials in which samples are collected are sealed with a crimp top which is lined with a septum. The choice of septa is very important when dealing with organochlorine compounds like Lindane especially in small concentrations as such compounds can attack and react with certain types of septa for example rubber. This research adopts the Teflon/Silicone septa with the Teflon side always facing the sample as it is inert and as such will not react with vapours, liquid or solid forms of organochlorine compounds.

2.7 Solid Phase Micro Extraction (SPME) Measurement of SVOC Concentration in Air

The SPME technique employed in this research is an extraction procedure that is used to measure concentration levels of compounds in gaseous, liquid or solid samples. It involves immersing a phase-coated fused silica fibre into a sample or headspace above a sample. Compounds of interest adsorb to the phase and are then thermally desorbed in the injection port of the gas chromatograph. The amount of analyte adsorbed by the fibre is directly proportional to the amount of compound in the sample. The SPME process is illustrated in Figure 2.4 below.

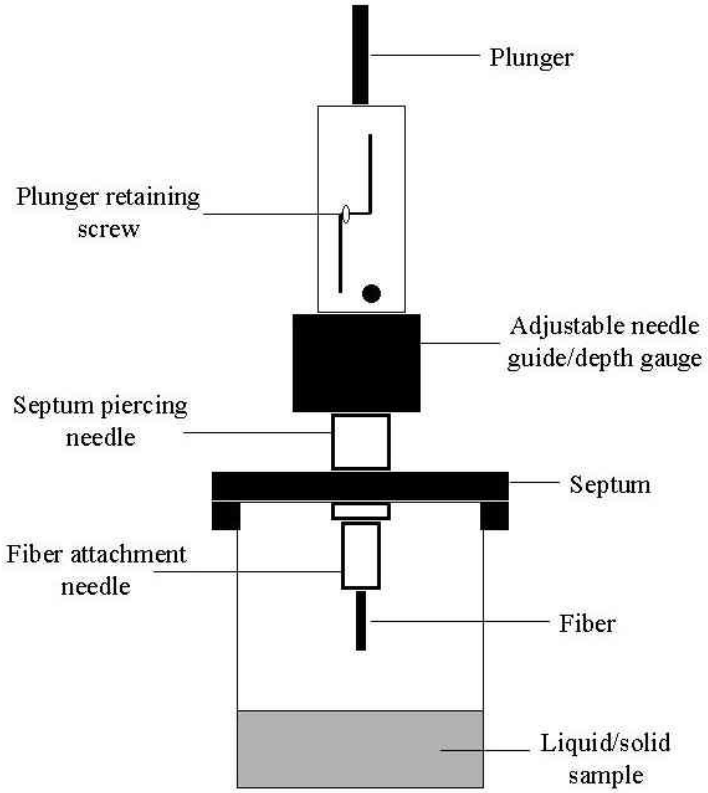


Figure 2.4 SPME system.
Source: Galipo et al. (c2002).

A coated fused silica fibre which is coated with a polymer is bonded to a stainless steel plunger and installed in a syringe-like holder. The plunger moves the fused silica fibre into and out of a hollow needle. To operate it, the needle is used to pierce the septum that seals the sample vial. The plunger is then depressed to expose the fibre to the headspace above the sample. Organic analytes adsorb to the polymer coating on the fibre. After a defined period, the fibre is drawn back into the needle, and the needle is withdrawn from the sample vial. Desorption of the analytes from the fibre for GC analysis then follows by introducing the needle into the GC injector, and depressing the plunger again such that the adsorbed analytes are thermally desorbed and delivered to the GC column. In SPME, the amount of analyte adsorbed by the fibre depends on the thickness of the polymer coating and on the distribution constant for the analyte.

Extraction time is determined by the length of time required to obtain precise extractions for the analytes of interest. The distribution constant generally increases with increasing molecular weight and boiling point of the analyte. Sensitivity can be improved by changing the type of polymer coating on the fibre, or the coating thickness, to match the characteristics of the analytes of interest. In general, volatile compounds require a thick coating, and a thin coating is most effective for adsorbing/desorbing semi volatile analytes (Supelco, 2004).

2.8 Analytical methods

Semi volatile organic compounds (SVOCs) in solid and gaseous matrices are typically analysed using gas chromatography. Gas chromatography is an analytical technique which can separate, identify and quantify compounds introduced into it. Other methods available include liquid chromatography, assay, and thermo gravimetric analysis. The standard protocol EPA Method 8081b (U.S. EPA 2000b) suggests the use of gas chromatography, for organochlorine pesticides (a class of SVOCs) as it is fast, and typically offers better separation.

2.8.1 Gas chromatography

Gas chromatography is a separation technique which involves passing a sample into an injection port in which volatilization of the sample occurs. The sample is then swept through a separating column by a mobile phase (an inert gas), into a detector. The compounds in the sample are separated due to differences in the partitioning behaviour

between the mobile gas phase and the stationary phase in the column. Figure 2.5 shows a schematic diagram of a GC.

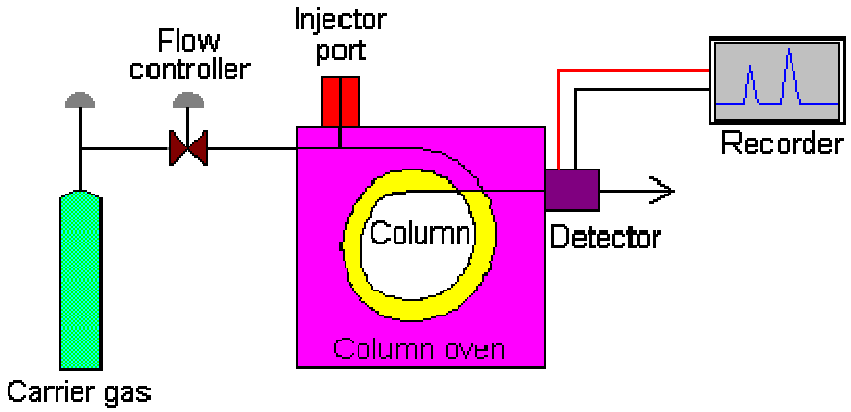


Figure 2.5 Schematic of a Gas Chromatograph.
Source: GC Schematic diagram (1997)

Typically, a GC consists of an injection port consists of a septum through which a syringe needle is inserted to inject the sample. It is important that the injection port is maintained at a temperature high enough to volatilize the compounds in the sample. These are then swept through the column and interact differently with the column and finally reach the detector at different times based on the affinity of the stationary phase for each compound. When the compound reaches the detector, an output referred to as a 'peak' is generated (see Figure 2.6).

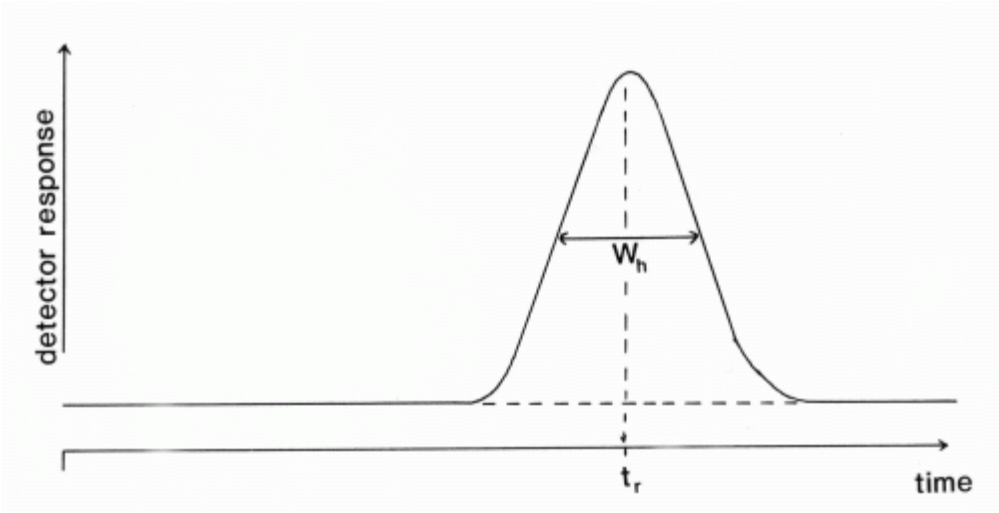


Figure 2.6 Schematic of a GC Peak.
Source: Chromatographic Peak (c2006)

As partitioning behaviour is dependent on temperature, the column is contained in a thermostat controlled oven. Samples consisting of a range of compounds with different boiling points are separated typically by starting at a low temperature and increasing the temperature over time to elute higher boiling point compounds. The length of time it takes for the compounds to be detected by the detector and create an output known as a peak is termed the retention time. This is typically the mode of identification of the analytes in gas chromatography coupled with ordinary detectors. Gas chromatography/mass spectrometry however, offers a more specific identification as is explained below.

2.8.2 Gas chromatography/Mass Spectrometry

As shown in Figure 2.7, GC-MS involves coupling a GC with a mass spectrometer detector. The volatilised specimen from the GC enters an ionisation chamber. High

voltage electrons are then made to collide with the analyte molecules which are then shattered into well defined fragments. Each fragment is charged and travels on to the accelerator as an individual particle. In the acceleration chamber the charged particle's velocity increases due to the influence of an accelerating voltage. Only one mass accelerates sufficiently to reach the detector for each given value of voltage. The accelerating voltage varies to cover a range of masses so that all fragments reach the detector.

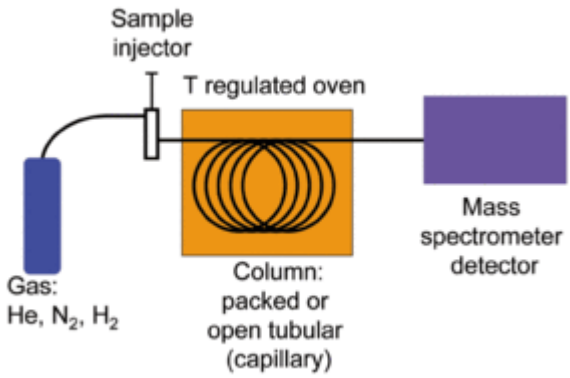


Figure 2.7 Schematic of a GC-MS.
Source: Gas chromatography mass spectrometry schematic (2006)

The charged particles travel in a curved path towards the detector. When an individual charged particle collides with the detector surface, several electrons (also charged particles) emit from the detector surface. These electrons then accelerate towards a second surface, generating more electrons, which bombard another surface. Each electron carries a charge. Eventually, multiple collisions with multiple surfaces generate thousands of electrons which emit from the last surface. The result is an amplification of the original charge through a cascade of electrons arriving at the collector. At this point the instrument measures the charge and records the fragment mass as the mass is proportional to the detected charge.

The MS instrument produces the output by drawing an array of peaks on a chart, which is referred to as the mass spectrum (see Figure 2.8). Each peak represents a value for a fragment mass. A peak's height increases with the number of fragments detected with one particular mass.

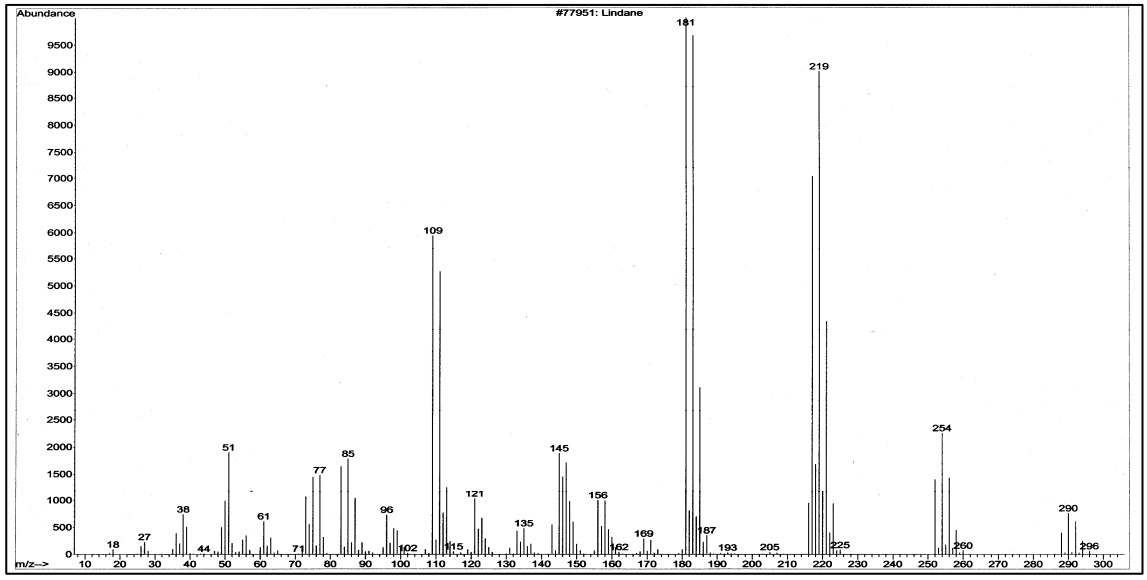


Figure 2.8 Lindane mass spectrum.
Source: Cutter et al. (n.d.)

2.8.2.1 Gas Chromatography terms

The following section explains some terms used.

The **Method blank:** is used to assess and document contamination resulting from the analytical process. According to recommended guidelines by the US Environmental Protection agency, for a method blank to be acceptable for use with accompanying samples, the concentration should not be higher than the method detection limit or five percent of the measured concentration in the sample (U.S. EPA, 1992). However this research adopted the most stringent guidelines due to the level of accuracy required for sensitive SVOC analysis. Therefore whenever an analyte was found in any blank

sample, reagent, GC column, SPME fibre or vial rinsate, the contaminated medium would be decontaminated until there was no longer traces of the analyte. Specifically in the case of syringes and SPME fibres, they would be rinsed and thermally desorbed respectively. This implies that between every run, a method blank for the SPME fibre was run to ensure there was no carryover of the analyte still adsorbed unto the fibre. Also for liquid injections using a syringe, each time a solution of a different concentration was to be analysed, the syringe was thoroughly rinsed out with the solvent, and then a blank solvent would be injected to ensure there was no carryover. Also periodically a blank solvent was injected between two injections of the same concentration to ensure there was no carryover on the GC column from the previous run.

A **Surrogate:** is used to monitor the performance of a method. Surrogates are added to all samples where appropriate, method blanks and calibration solutions. When the surrogate peak area obtained from the GC-MS analysis of samples, blanks, spikes or calibration standards, differs by more than 50 per cent, the procedure has to be re-examined to identify the reason for the variation and reanalyzed. Tetrachloro-m-xylene, referred to henceforth as TCMX, was adopted as the surrogate for this research as recommended by the EPA method 8081b for the analysis of SVOCs (U.S. EPA, 2000b).

An **Internal standard** is a compound that is added to samples, calibration standards and blanks prior to analysis in order to quantify the analyte or analytes of interest. The solutions of the samples and standards are prepared such that the concentration of the internal standard is constant in all samples. The ratio of area of the internal standard

peak to the area of the analyte in the sample is compared to the peak area ratio of the internal standard peak and analyte in the calibration. The concentration of the analyte is thus determined. Whenever an internal standard is used for quantitation, the area must not differ by more than fifty percent of the average area calculated during calibration (U.S. EPA, 1996). Pentachloronitrobenzene referred to henceforth as PCNB is employed as the internal standard as recommended by the EPA 8081b (U.S. EPA, 2000b).

2.9 Conclusion

The above is conclusive that Lindane was widely used in variety of forms and that it has been banned is an indication of its harmful effects. While the prevalent use in the various environmental media is widely acknowledged, the exact quantity and the process of contamination are yet to be fully understood. In particular, the partitioning of Lindane between air and dust need to be fully understood if it is to be effectively contained. Chapter three details the methodology employed to investigate Lindane partitioning between air and dust.

Chapter Three

3 Experimental methodology

3.1 Summary

In this chapter a methodology is devised through adapting existing standard (where available) and other author devised non-standard experimental protocols in literature to this research. This is achieved by initially reviewing protocols for sampling and analysis of air and dust followed by preliminary testing of existing and subsequently adapted protocols.

The different experimental procedures are described indicating the rationale for conducting the experiments as well as how literature and standard protocols have informed them. Also adaptations to the protocols are explained. Dust sample collection, preparation and analysis are described in this chapter. First the dust collection and then dust size fractioning procedures are described. This is followed by a description of the scanning electron microscope procedure for viewing dust particles on a microscopic scale. In order to quantify Lindane concentrations the gas chromatograph-mass spectrometer is used. Calibration of Lindane in the gas chromatograph-mass spectrometer is carried out and the procedure is explained here. This is followed by a description of the Soxhlet extraction technique coupled with a rotary evaporator for extracting Lindane from dust and preparing the resulting extract in readiness for GC-MS analysis. Finally the adsorption experiment to compare dust and air concentrations of Lindane is described.

3.2 Dust collection

This section explains the type and nature of dust sample data collected and the attendant processes. The samples were collected from randomly selected houses based on information obtained from the Environmental Health Department of Leicester City Council, age of house, type of house, and location. Ten houses fulfilled our selection criteria informed by the literature review out which only 3 households agreed to participate. This nevertheless depicts a thirty percent response rate.

3.2.1 Materials and method

A preliminary investigation of dust collection followed the ASTM D5438 -93 standard dust collection procedure (ASTM 1998) which entailed collection of dust from a stipulated $1m^2$ area. A cyclone vacuum was used to collect the dust. Carpets in three homes in Leicester, United Kingdom were used as the initial test sample. In each case, the dust collected resulted in very small portions of dust much less than 1g. As larger quantities are needed for reliable contamination measurements, it was decided to henceforth obtain dust from old vacuum bags sent in by householders from vacuum cleaners which had been collecting dust over time. So the dust used throughout this research was collected in this manner from vacuum cleaners which were generally used for vacuuming all parts of the house. The contents were then emptied into plastic bags and a portion of the dust was used for following experiments.

3.3 Dust size fractioning by sieving

A literature search depicted the suitability of sieving as a dust size fractioning method. In order to investigate the effect of dust size fraction on the adsorption/desorption of Lindane to and from dust, it was important to first establish a procedure to separate the dust into different size fractions. This experiment also aimed to quantify the mass distribution of dust size fractions in typical whole dust samples in order to understand adsorption phenomenon in whole dust as well.

3.3.1 Materials and method for dust sieving

A set of sieves [Endecott] was used in this experiment. Each clean empty sieve was weighed on an analytical balance. When each sieve was placed on the balance 20 seconds were allowed before the mass was noted to allow for cessation of fluctuation in the mass. The sieves were then stacked on top of each other in ascending order of size, with the largest size (150µm) topmost. A 5g portion of dust was weighed and placed in the topmost sieve. The whole stack was placed on a sieve shaker [Restech, AS200] and the topmost sieve was covered with a lid to prevent loss of dust during the sieving and shaking process. The stack was shaken for 15 minutes. On completion the stack was removed from the shaker. The topmost sieve (the largest sieve size) was carefully removed from the stack in a twisting motion to minimize loss of dust through possible spillage. The removed sieve was then weighed. The rest of the sieves where then removed and weighed as above in turn and in descending order.

The preliminary experiment suggested that after the topmost sieve had been taken off some dust may have been lost from the next sieve size on the stack during its exposure to air. Therefore, henceforth a lid was immediately placed on the new topmost sieve on the stack each time a sieve was removed for weighing. When all the weighing was complete the sieves where then washed and dried before the next use.

3.4 Microscopic analysis of dust size fractions

The nature of dust components was investigated by examining the different dust size fractions under a scanning electron microscope (SEM) [LEICA, 3430]. This would help understand possible differences in adsorption of pesticides to different size fractions.

3.4.1 Materials and Method for SEM analysis of dust

SEM is a technique used in the analysis of particle morphology and size. For this study, the particle sizes in the size fractions were verified by conducting dimensional analysis on the images of dust particles obtained from the scanning electron microscope. Minute portions of each dust size fraction obtained from the sieving, were gold plated to prevent charging during SEM analysis. This was done by placing the small portions of the dust from the different size fractions on individual slides and then placed in a gold plating machine [Edwards, S150B] until the process had been completed. These were then examined under the SEM which produced images of the individual dust particles. Length and width measurements were then obtained by manually measuring the constituent particles dimensions by ruler and then converting them using the corresponding scale.

3.5 Chemical analysis of Lindane in air and dust

This section sets out the methodology for identifying and quantifying Lindane in the two media this research is concerned with i.e. air and dust. This involves the calibration of Lindane in GC-MS, the extraction of Lindane from dust and the measurement of Lindane in air and corresponding air and dust concentrations as well as dynamic measurements of Lindane in air to determine the time it takes to reach equilibrium. These are set out in sections 3.5.1 to 3.6.2. The results and analysis from these experiments are later presented in chapters four and five.

3.5.1 GC-MS calibration for Lindane analysis

This set of experiments was to establish a calibration curve for Lindane in solution within the linear range of the GC-MS in order to calculate the concentration of Lindane in solution from the peak area obtained from the GC-MS following injection of the solution into the GC-MS. It was essential to establish a protocol that would ensure reproducibility of the analysis. These included devising a method to eradicate carryover contamination from previous runs. Results are presented in section 4.5.2 of chapter 4.

3.5.1.1 Materials and method

The gas chromatograph-mass spectrometer (GC-MS) described in chapter two is used to detect and quantify Lindane. A diagram of the GC-MS [Varian star, 3400CX] used in this research is shown in Figure 3.1a. For clear illustration, a schematic of a GC-MS is also presented in Figure 3.1b.

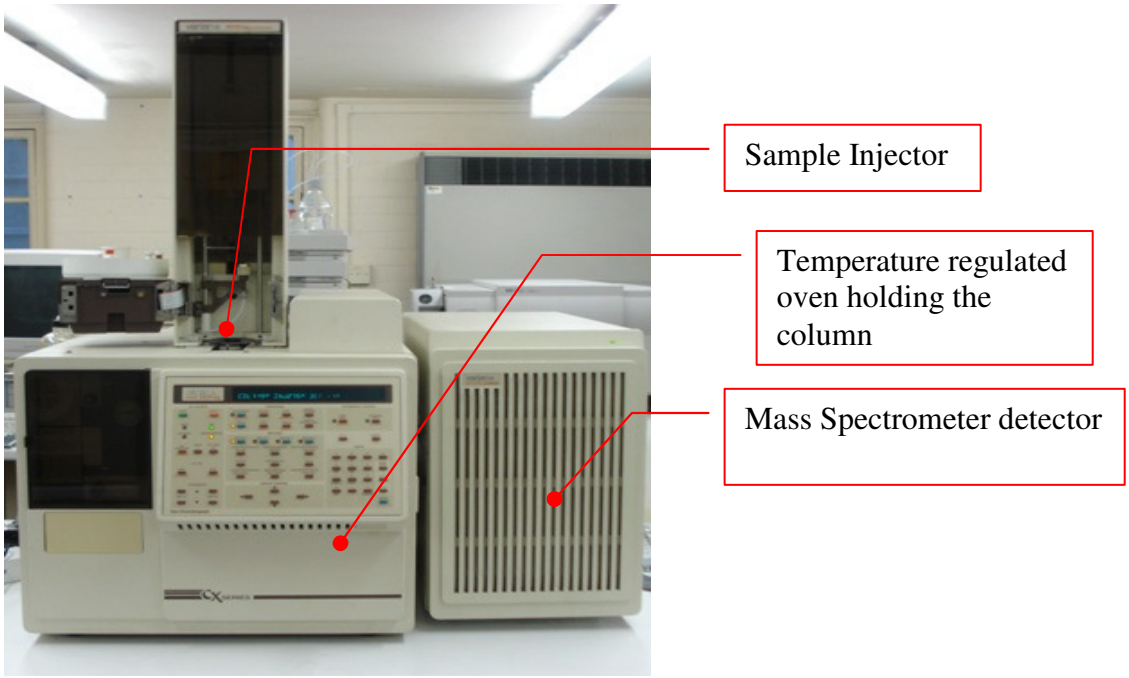


Figure 3.1a Gas Chromatograph coupled with a mass spectrometer (Varian star 3400CX) used in this research.

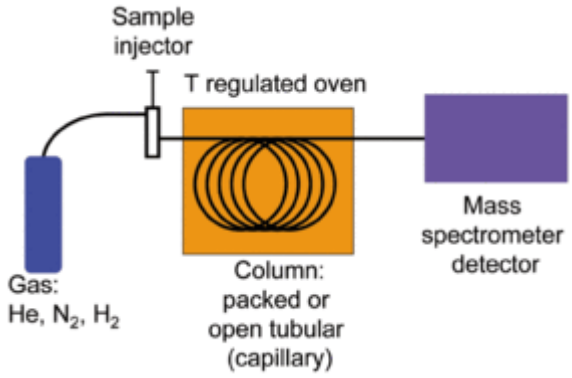


Figure 3.1b Schematic of Gas chromatograph coupled with a mass spectrometer
Source: Gas chromatography mass spectrometry schematic (2006)

The gas chromatograph/mass spectrometer (GC-MS) calibration was conducted to determine the relationship between the Lindane concentration introduced into the GC-MS and the response of the GC i.e. the peak area. This was to enable quantification and

confirmation of the known and unknown concentrations of Lindane. The conditions of the GC-MS were set up as follows:

Gas Chromatography (GC)	Varian STAR 3400CX	
Capillary column	BP-1 (SGE)	
Phase	100% methyl polydimethylsiloxane	
Dimensions	25 Length (meters)	
	0.25 I. D. (mm)	
	0.25 Film thickness (micrometer)	
Temperature Limits	Minimum – 100^{o}C	
	Maximum – 275^{o}C	
Oven	Liquid injections	SPME Injections
	120^{o}C for 1 min	100^{o}C for 2 min
	120^{o}C to 270^{o}C at 10^{o}C/min	100^{o}C to 270^{o}C at 20^{o}C/min
	270^{o}C for 0.5 min	270^{o}C for 3 min
Injector	Splitless, 275^{o}C	
Carrier gas pressure	Helium, 10 psi	
Injection volume	1 µl	
Mass Spectrometry (MS)	Varian Saturn 2000	
Trap Temperature	219^{o}C	
Manifold Temperature	100^{o}C	
Transfer line Temperature	275^{o}C	

The following describes the procedure used for preparation of all stock solutions from which all calibration standards would be prepared.

Preparation of a stock solution:

A stock solution is the initial solution prepared when the analyte is dissolved into a solvent and from which all other solutions of different concentration are then prepared. Individual stock solutions were prepared for the Lindane, Tetrachloro-m-xylene (TCMX) and Pentachloronitrobenzene (PCNB). An empty 120ml amber vial was weighed on an analytical balance and the mass was noted. The compound was then carefully added to the vial whilst it was on the balance until 0.1g of the compound had been added to the vial was then removed from the balance.

Preparation of the calibration solutions:

Using a pipette, 1ml of toluene was then added to the compound in the vial to dissolve it. After which 99ml of hexane was added using a measuring cylinder. This procedure was used for Lindane and TCMX. The resulting solutions were $1x10^{-3}gml^{-1}$ of each compound in hexane. For PCNB, the same procedure was repeated except that the mass of PCNB used was 0.4g. This therefore resulted in a stock solution of $4x10^{-3}gml^{-1}$. All further solutions of these compounds at lower concentrations were obtained from these initial stock solutions in a step wise manner by taking out a known volume from the stock solution and adding a volume of hexane required to obtain the new lower concentration.

Further lower concentrations were then obtained in a similar manner from the latest low concentration solution. For example to make up a solution of $1 \times 10^{-6} gml^{-1}$ of Lindane, 1ml of the $1 \times 10^{-3} gml^{-1}$ (stock solution) was drawn out using a pipette, then placed into an empty vial. This was followed by adding 99ml of hexane to the 1ml resulting in a 100ml solution at a concentration of $1 \times 10^{-5} gml^{-1}$. The next step was to remove a 1ml aliquot from the $1 \times 10^{-5} gml^{-1}$ solution and place this into an empty vial followed by adding 9ml to make up to 10ml resulting in the desired concentration of $1 \times 10^{-6} gml^{-1}$. This step wise dilution procedure is referred to as serial dilution. The stock solutions were kept refrigerated when not in use and replaced every six months.

The required concentration of the surrogate, TCMX, in each analysis sample was $5 \times 10^{-6} gml^{-1}$. To obtain this concentration a 5ml portion of the $1 \times 10^{-3} gml^{-1}$ TCMX stock solution was initially diluted down to in $5 \times 10^{-5} gml^{-1}$ of TCMX in hexane. For the calibration of Lindane for the GC-MS, five different concentrations ranging from $9 \times 10^{-6} gml^{-1}$ to $5 \times 10^{-7} gml^{-1}$ Lindane in hexane were prepared. Using the Lindane in hexane concentration at $5 \times 10^{-6} gml^{-1}$ as an illustration, 5ml of the $1 \times 10^{-5} gml^{-1}$ solution of Lindane in hexane was placed into an empty vial and then 1ml of the $5 \times 10^{-5} gml^{-1}$ solution of the surrogate TCMX in hexane was added. This was then made up to 10ml by adding 4ml of hexane. This resulted in a solution of concentration of $5 \times 10^{-6} gml^{-1}$ Lindane and $5 \times 10^{-6} gml^{-1}$ TCMX in hexane. A 1ml portion of this solution was then placed in an empty vial and then 10µl of the $4 \times 10^{-3} gml^{-1}$ PCNB stock solution was added using a syringe. This resulted in a final solution of $5 \times 10^{-6} gml^{-1}$ Lindane, $4 \times 10^{-5} gml^{-1}$ PCNB, and $5 \times 10^{-6} gml^{-1}$ TCMX in hexane. The same procedure was used to prepare all the four other Lindane concentrations in the calibration range, keeping the

final concentrations of the surrogate TCMX and the internal standard PCNB constant. All final solutions were then analysed in the GC-MS with each concentration analysis repeated five times as recommended by the EPA Method 8081b (U.S. EPA 2000b).

3.5.2 Extraction of Lindane from dust

In order to identify and quantify Lindane in dust it was necessary to firstly recover the analyte Lindane from the dust matrix. This procedure is referred to as the extraction procedure. The relatively robust Soxhlet extraction available during this research was investigated for reproducibility and efficiency. This was conducted by pre-dosing the pre-determined Lindane-free dust with a known amount of Lindane and then extracting the Lindane with the Soxhlet extraction procedure.

3.5.2.1 Materials and method for Soxhlet Extraction of Lindane from dust

1g of Lindane-free dust was placed in a vial. The dust was certified to be Lindane-free as a portion of it was extracted using the Soxhlet extraction method and analysed to ensure that the dust did not contain Lindane. The dust was then dosed with 10µl of $9 \times 10^{-6} gml^{-1}$ Lindane in hexane and the vial was then closed. After one minute, the dust was then transferred into an extraction thimble which was then placed into the extraction unit of the Soxhlet apparatus. A 1ml aliquot of the surrogate TCMX at a concentration of $5x10^{-5} gml^{-1}$ TCMX in Lindane was added to the dust after it had been placed in the extraction thimble. The Soxhlet extraction unit was then switched on and

set to 4 cycles per hour. The sample was extracted for 24 hours using hexane and acetone as the extraction solvents (vol/vol 1:1) (U.S EPA 1996a, 1998, 2000a, 2000b).

The round bottom flask which contained the sample extract was then carefully removed from the Soxhlet extraction unit and then connected to the rotary evaporator which was then switched on. The sample extract was then reduced to 1ml by the rotary evaporation process. The resulting solution was exchanged in hexane by adding 9 ml of hexane to the 1ml sample extract and this was again reduced to 1ml. This exchange procedure was then repeated. The resulting 1ml solution was transferred from the round bottom flask into an empty vial using a pipette. A 10µl aliquot of internal standard PCNB was then added to the 1ml of extract. This was then analysed in the GC-MS. The percentage of recovery of Lindane was then calculated.

The Soxhlet extraction unit was the washed and dried. Prior to reuse, the different parts of the unit were rinsed with hexane and the solution from the rinse was analysed by the GC-MS to check for any contamination from the previous run. If any of the compounds were detected the affected component of the unit was rewashed and dried and then retested. The units were only used if they were void of any contamination. In order to measure the effectiveness of the length of the extraction process and the extraction process itself, the same previously extracted dust sample was placed into a clean Soxhlet extraction unit and the Soxhlet process coupled with the rotary evaporation process was repeated to investigate if the previous extraction had completely removed all the Lindane.

The Soxhlet extraction of dust at the same concentration of $9x10^{-6}gml^{-1}$was repeated for a further three batches. The percentage of recovery of Lindane was then calculated for all batches.

Figure 3.2 Soxhlet Apparatus.

3.6 SPME method for measuring Lindane in air

As earlier indicated, the SPME is a method commonly used for the measurement of volatile organic compounds (VOCs) in indoor air. One of the many advantages of SPME is economic use of solvents.

3.6.1 Materials and method

In order to prevent the possible reproducibility problems, the method was standardised by using syringes [Hamilton, #1702] from the same manufacturer for all Lindane injections into the vial. Then 10µl of 6 x 10^{-6}gml^{-1} was injected into each of three 50ml vials giving a concentration of 1.4 x 10^{-7}gm^{-3} in each vial. The syringe was left in the vial to provide a seal to the septa to prevent any possible loss of analyte from the septa not self resealing. Another advantage of leaving the syringe in was to allow enough time for any possible residual drops of the solution on the syringe tip to remain within the closed system hence aiding reproducibility. These were then placed into a water bath and regulated at 25^{o}C. This was immediately followed by concentration measurement in the headspace using the SPME technique followed by GC-MS analysis. The peak area was noted. This procedure was repeated to test for concentration after 4, 24, 48 and 72 hours. The results are presented in section 4.5.4.1 in chapter 4.

3.6.2 Dynamic and static Lindane adsorption experiments

In order to investigate the relationship between air and dust concentrations of Lindane, it was necessary to obtain an adsorption isotherm. This is a plot of the amount of Lindane adsorbed unto dust versus the amount of Lindane in the headspace above the dust in a vial. A partition coefficient obtained from the adsorption isotherm would help in modelling any relationship between the air and dust concentrations of Lindane. This section describes the procedure.

An empty 50ml vial was weighed then 0.5g of Lindane-free dust was carefully placed into the vial. The vial was then closed and sealed tightly with a screw top. Liquid solutions of Lindane in hexane were prepared at five different concentrations. A 10µl aliquot of Lindane in hexane at a known concentration was then injected into the vial. The vial was then placed into a water bath to regulate the temperature at 25^{o}C. When equilibrium was reached, the headspace concentration was measured using the SPME fibre. A mass balance was then performed to determine the concentration of Lindane which had been adsorbed on the dust. An Adsorption isotherm was then plotted with the dust concentration of Lindane versus the air concentration.

3.7 Conclusion

The size and nature of dust size particles may have an effect on the partition coefficient between air and dust. Therefore sieving of the dust as well as Scanning electron microscopic analysis is employed in this research to examine dust particle size and morphology. GC-MS is employed as the analytical tool in the qualitative and quantitative analysis of Lindane in air and dust. For quantification to occur calibration of the GC-MS for Lindane in air and dust is necessary. Soxhlet extraction is used to extract the Lindane from the different media whilst the SPME technique was successfully adapted and used to measure the Lindane in vapour phase in vials. The data obtained are analysed in chapters four and five.

Chapter Four

4 Preliminary experimental results

4.1 Summary

Dust samples were size fractioned by sieving and dust particulate morphologies were examined. This was followed by the investigation via chemical analysis, of the amount of Lindane adsorbed on dust and desorbed into air. A method for Lindane Gas Chromatography-Mass spectrometry analysis was adapted from standard methods and gave good repeatability for the measurements. The relative standard deviations of the response factors which indicate linearity was 6.06% which is acceptable as it falls below the maximum acceptable relative standard deviation of 20% (U.S. EPA 1996b). The GC-MS calibration of Lindane in solution on the gave a graph with a correlation coefficient (R^2) value of 0.9967 which demonstrates good linearity across the calibration range of 5 x 10^{-7} gml^{-1} to 9 x $10^{-6}gml^{-1}$ Lindane in hexane. The Soxhlet extraction technique was used to ensure that the dust used in all experiments was Lindane-free prior to commencement of the experiments. A method for air concentration measurements using SPME was adapted. Calibration of the GC-MS for Lindane in air resulted in a graph with a correlation coefficient of 0.9114 which demonstrates acceptable linearity across the calibration range of 1 x $10^{-7}\mu gm^{-3}$ to 2 x $10^{-7}\mu gm^{-3}$. The outcomes of these analyses and conclusions drawn are presented. These results are essential precursors to the work undertaken in chapter five.

4.2 Dust collection

Dust collected from vacuum cleaners in the three randomly selected homes in Leicester were mixed together to yield a total of 10.2kg dust sample.

4.3 Dust size fractioning by sieving: Results and discussions

The route of human exposure to Lindane and pesticides in general adsorbed on dust is a function of the dust size to which they are attached. Smaller size particles are available for inhalation; larger particles are available for ingestion and dermal penetration. As described in chapter three, whole dust samples were separated into nine size fractions by sieving. Results of the mass distribution of the size fractions are presented in Tables 4.1 to 4.3.

Table 4.1

Mass and cumulative mass of separated dust fractions (batch a)

Size Fraction (µm)	Mass of empty sieve (g)	Sieve + dust mass (g)	Dust mass (g)	Dust mass %	Cumulative dust mass %
<5	84.907	84.909	0.002	0.04	-
10 - 5	115.544	115.546	0.002	0.04	0.04
30 - 10	110.096	110.161	0.066	1.32	0.09
63 - 30	109.286	110.280	0.994	19.93	1.40
75 - 63	108.777	109.328	0.551	11.05	21.33
90 - 75	108.547	109.481	0.933	18.72	32.38
106 - 90	109.521	110.440	0.919	18.44	51.11
150 - 106	110.423	110.821	0.398	7.99	69.54
>150	112.805	113.925	1.120	22.47	77.53
			4.986		100.00

In Table 4.1, the percentage mass of dust retained for each size fraction was calculated as follows:

% mass in size fraction = (Mass of dust in size fraction/Total mass of dust recovered) x 100.

Similarly, and to measure the mass of dust lost in the sieving process, the following calculations were undertaken and results from the first batch are used as an illustration:

For the size fraction >150µm, Dust weight = Weight of sieve containing dust - Weight of empty sieve = 110.4404g -109.5213g = 0.398g

Also,

Total mass of dust lost in sieving process = Initial dust weight - dust weight after sampling = (5.0 - 4.98554) g

= 0.01446g

% error = (0.01446/5)*100

= 0.29%

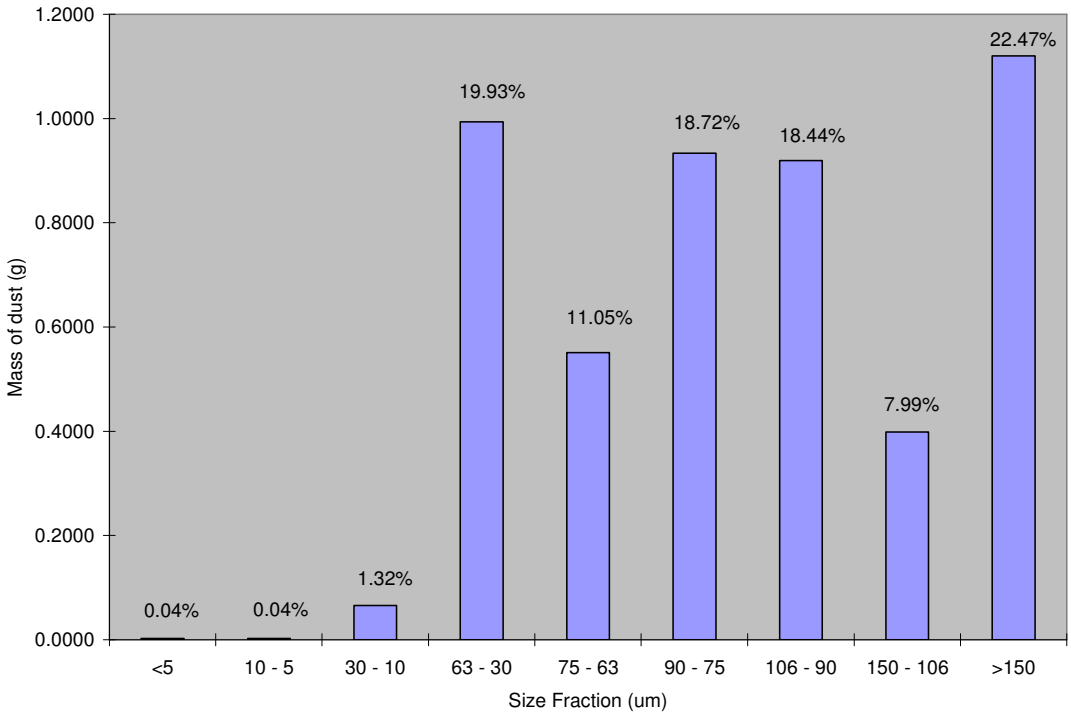


Figure 4.1 Weight of separated dust fractions and percent of total coarse (< 2 mm) dust weight for each size fraction.

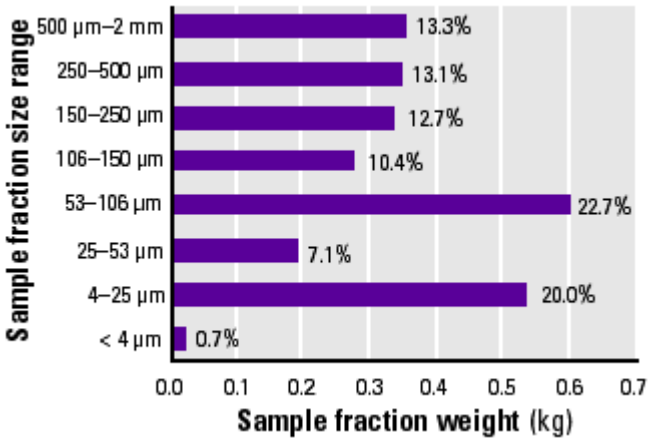


Figure 4.2 Weight of separated dust fractions and percent of total coarse (< 2 mm) dust weight for each size fraction. Source (Lewis et al. 1999).

Table 4.2

Mass and cumulative mass of separated dust fractions (batch b)

Size Fraction (µm)	Mass of empty sieve (g)	Sieve + dust mass (g)	Dust mass (g)	Dust mass %	Cumulative dust mass %
<5	84.9073	84.90994	0.00264	0.05	-
10 - 5	115.5442	115.5444	0.0002	0.00	0.05
30 - 10	110.0956	110.2561	0.1605	3.22	0.06
63 - 30	109.2863	110.7147	1.4284	28.63	3.27
75 - 63	108.777	109.4389	0.6619	13.27	31.91
90 - 75	108.5471	109.6621	1.115	22.35	45.18
106 - 90	109.5213	110.1359	0.6146	12.32	67.53
150 - 106	110.4225	111.1538	0.7313	14.66	79.85
>150	112.8051	113.0791	0.274	5.49	94.51
			4.98854		100.00

As shown in table 4.2 for batch b,

Total mass of dust lost in sieving process = Initial dust weight - dust weight after sampling = (5.0 - 4.98554) g

= 0.01446g

Therefore, % error = (0.01446/5)*100

= 0.29%

Table 4.3

Mass and cumulative mass of separated dust fractions (batch c)

Size Fraction (μm)	Mass of empty sieve (g)	Sieve + dust mass (g)	Dust mass (g)	Dust mass %	Cumulative dust mass %
<5um	84.9073	84.9083	0.001	0.0200377	-
10-5um	115.5442	115.5487	0.0045	0.0901695	0.02
30-10um	110.0956	110.1904	0.0948	1.8995712	0.11
63-30um	109.2863	110.0483	0.762	15.268705	2.01
75-63um	108.777	109.6932	0.9162	18.358514	17.28
90-75um	108.5471	109.5127	0.9656	19.348375	35.64
106-90um	109.5213	110.2147	0.6934	13.894121	54.99
150-106um	110.4225	110.9283	0.5058	10.135054	68.88
>150um	112.8051	113.8524	1.0473	20.985453	79.01
			4.9906		100.00

As shown in Table 4.3 for batch c,

Total mass of dust lost in sieving process = Initial dust weight - dust weight after sampling = (5.0 - 4.9906) g

= 0.00946g

% error = (0.00946/5)*100

= 0.19%

Dust was lost during the process when each sieve was being removed from the stack of sieves. This experiment tried to minimize such loss by taking extra care in removing the sieves using a twisting motion. Also each time a sieve was removed from the stack; a lid was placed on the topmost sieve.

The error ranged from 0.15% to 0.29%. This falls within the 2% maximum acceptable error according to the ASTM standard D422-63 (ASTM 1999).

4.4 SEM analysis of dust size fractions: Results and discussions

It was observed from the dust images from the scanning electron microscope that the size fraction >150µm were more fibrous in nature as would be expected. Figure 4.3 and Figure 4.4 respectively show SEM images of dust.

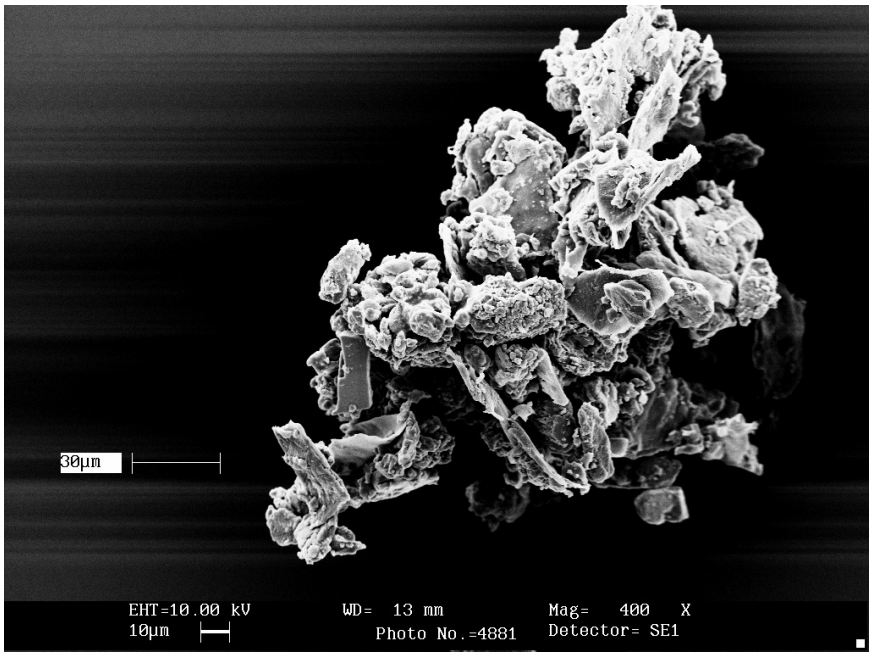


Figure 4.3 SEM image of dust (>30µm<63µm fraction).

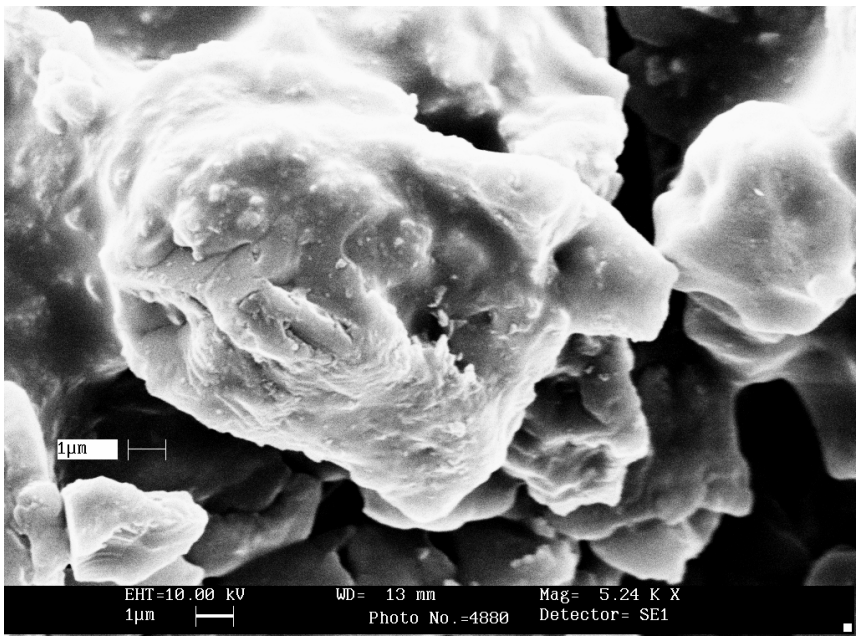


Figure 4.4 SEM image of dust (>106µm<150µm fraction).

The dimensional analysis of the dust sample used is presented in Tables 4.4

Table 4.4

Dust dimensional analysis for 150-106µm size fractions

scale factor 1mm =10.53	width (mm)	length (mm)	actual length (µm)	actual width (µm)	geometric mean (µm)
10.5	20	10	210.5	105.3	148.9
10.5	20	12	210.5	126.3	163.1
10.5	12	10	126.3	105.3	115.3
10.5	12	11	126.3	115.8	120.9
10.5	16	16	168.4	168.4	168.4
10.5	12	19	126.3	200	158.9
10.5	10	10	105.3	105.3	105.3
10.5	2	50	21.1	526.3	105.3
10.5	1	24	10.5	252.6	51.6
10.5	2	50	21.1	526.3	105.3
10.5	16	6	168.4	63.2	103.1

Table 4.5

Dust dimensional analysis for 63-32µm size fractions

scale factor 1mm =10.53	width (mm)	length (mm)	actual length (µm)	actual width (µm)	geometric mean (µm)
1.1	17	15	17.9	15.8	16.8
1.1	14	20	14.7	21.1	17.6
1.1	13	11	13.7	11.6	12.6
1.1	10	5	10.5	5.3	7.4
1.1	8	17	8.4	17.9	12.3
1.1	16	15	16.8	15.8	16.3
1.1	10	16	10.5	16.8	13.3
1.1	14	12	14.7	12.6	13.6
1.1	17	11	17.9	11.6	14.4
1.1	2	13	2.1	13.7	5.4
1.1	12	44	12.6	46.3	24.2
1.1	8	34	8.4	35.8	17.4
1.1	19	25	20	26.3	22.9
1.1	16	13	16.8	13.7	15.2
1.1	36	15	37.9	15.8	24.5
1.1	5	13	5.3	13.7	8.5
1.1	9	21	9.5	22.1	14.5
1.1	9	30	9.5	31.6	17.3
1.1	25	27	26.3	28.4	27.3
1.1	9	7	9.5	7.4	8.4
1.1	32	23	33.7	24.2	28.6
1.1	7	10	7.4	10.5	8.8
1.1	11	15	11.6	15.8	13.5

Table 4.6

Dust dimensional analysis for 90-75µm size fractions

scale factor 1mm =10.53	width (mm)	length (mm)	actual length (µm)	actual width (µm)	geometric mean (µm)
5.9	8	15	47.1	88.2	64.4
5.9	10	20	58.8	117.6	83.2
5.9	15	11	88.2	64.7	75.6
5.9	15	5	88.2	29.4	50.9
5.9	12	17	70.6	100	84
5.9	16	12	94.1	70.6	81.5
5.9	12	11	70.6	64.7	67.6
5.9	16	13	94.1	76.5	84.8
5.9	3	25	17.6	147.1	50.9
5.9	17	13	100	76.5	87.4
5.9	15	15	88.2	88.2	88.2
5.9	16	13	94.1	76.5	84.8
5.9	24	21	141.2	123.5	132.1
5.9	11	30	64.7	176.5	106.9
5.9	5	27	29.4	158.8	68.3
5.9	26	7	152.9	41.2	79.4
5.9	11	23	64.7	135.3	93.6
5.9	15	10	88.2	58.8	72
5.9	13	15	76.5	88.2	82.1
5.9	5	15	29.4	88.2	50.9
5.9	14	10	82.4	58.8	69.6
5.9	21	12	123.5	70.6	93.4
5.9	14	11	82.4	64.7	73
5.9	17	21	100	123.5	111.1
5.9	16	5	94.1	29.4	52.6
5.9	12	22	70.6	129.4	95.6
5.9	10	11	58.8	64.7	61.7
5.9	9	11	52.9	64.7	58.5
5.9	13	21	76.5	123.5	97.2
5.9	17	19	100	111.8	105.7
5.9	13	10	76.5	58.8	67.1
5.9	22	7	129.4	41.2	73
5.9	12	13	70.6	76.5	73.5
5.9	15	14	88.2	82.4	85.2
5.9	14	4	82.4	23.5	44
5.9	21	13	123.5	76.5	97.2
5.9	12	12	70.6	70.6	70.6
5.9	17	11	100	64.7	80.4
5.9	11	16	64.7	94.1	78
5.9	16	6	94.1	35.3	57.6
5.9	21	7	123.5	41.2	71.3
5.9	14	14	82.4	82.4	82.4
5.9	25	11	147.1	64.7	97.5
5.9	12	20	70.6	117.6	91.1
5.9	15	13	88.2	76.5	82.1
5.9	12	14	70.6	82.4	76.2
5.9	12	21	70.6	123.5	93.4
5.9	21	11	123.5	64.7	89.4
5.9	15	22	88.2	129.4	106.9

Table 4.6 (…Continued)

scale factor 1mm =10.53	width (mm)	length (mm)	actual length (µm)	actual width (µm)	geometric mean (µm)
5.9	13	12	76.5	70.6	73.5
5.9	13	15	76.5	88.2	82.1
5.9	18	14	105.9	82.4	93.4
5.9	17	13	100	76.5	87.4
5.9	16	14	94.1	82.4	88
5.9	22	9	129.4	52.9	82.8
5.9	17	11	100	64.7	80.4
5.9	15	20	88.2	117.6	101.9
5.9	24	13	141.2	76.5	103.9
5.9	6	28	35.3	164.7	76.2
5.9	18	10	105.9	58.8	78.9
5.9	13	20	76.5	117.6	94.9
5.9	20	16	117.6	94.1	105.2
5.9	22	10	129.4	58.8	87.2
5.9	13	10	76.5	58.8	67.1
5.9	12	13	70.6	76.5	73.5
5.9	13	17	76.5	100	87.4
5.9	15	14	88.2	82.4	85.2
5.9	9	34	52.9	200	102.9
5.9	13	11	76.5	64.7	70.3
5.9	4	25	23.5	147.1	58.8
5.9	19	11	111.8	64.7	85
5.9	15	15	88.2	88.2	88.2
5.9	17	13	100	76.5	87.4
5.9	11	14	64.7	82.4	73
5.9	18	12	105.9	70.6	86.5
5.9	16	9	94.1	52.9	70.6
5.9	2	23	11.8	135.3	39.9

Evidently, the SEM analysis showed the dust sieving technique to be sufficiently accurate. Thus, the different dust size fractions obtained using this technique were used in investigating the effect of dust size fraction on Lindane adsorption to dust.

4.5 Chemical analysis of Lindane in air and dust

4.5.1 Summary

This section presents results from the experimental investigation of dust contaminants and their chemical analysis. Each experiment is presented in the form of its aims, objectives, the results and discussions.

4.5.2 Analysis and discussion of GC-MS calibration results for Lindane

The results of the calibration are presented in the tables 4.7 – 4.10 below.

Table 4.7

GC-MS peak areas for calibration of Lindane at a concentration of 5×10^{-7}gml^{-1} Lindane in hexane

PCNB	TCMX	Lindane	Lind/PCNB	TCMX/PCNB	Response Factor
10228	3795	272	0.0266	0.3710	0.2659
11084	4077	290	0.0262	0.3678	0.2616
11769	4028	318	0.0270	0.3423	0.2702
			0.0266	0.3604	0.2659

Table 4.8

GC-MS peak areas for calibration of Lindane at a concentration of 2×10^{-6}gml^{-1} Lindane in hexane

PCNB	TCMX	Lindane	Lind/PCNB	TCMX/PCNB	Response Factor
8296	2719	821	0.0990	0.3277	0.2474
6801	2502	642	0.0944	0.3679	0.2360
8615	2994	888	0.1031	0.3475	0.2577
7415	2568	721	0.0972	0.3463	0.2431
10652	3516	1055	0.0990	0.3301	0.2476
7868	2840	785	0.0998	0.3610	0.2494
			0.0987	0.3468	0.2469

Table 4.9

GC-MS peak areas for calibration of Lindane at a concentration of 7×10^{-6} gml^{-1} Lindane in hexane

PCNB	TCMX	Lindane	Lind/PCNB	TCMX/PCNB	Response Factor
7224	2443	2294	0.3176	0.3382	0.2268
7705	2971	2499	0.3243	0.3856	0.2317
			0.3209	0.3619	0.2292

Table 4.10

GC-MS peak areas for calibration of Lindane at a concentration of 9×10^{-6} gml^{-1} Lindane in hexane

PCNB	TCMX	Lindane	Lind/PCNB	TCMX/PCNB	Response Factor
10856	3902	4726	0.4353	0.3594	0.2419
7556	3006	3486	0.4614	0.3978	0.2563
7401	3078	3412	0.4610	0.4159	0.2561
8997	3832	3009	0.3344	0.4259	0.1858
5122	2268	2425	0.4734	0.4428	0.2630
4363	2139	2161	0.4953	0.4903	0.2752
			0.4435	0.4220	0.2464

Where PCNB = Pentachloronitrobenzene (internal standard), Lind = Lindane TCMX = Tetrachloro-m-xylene (surrogate)

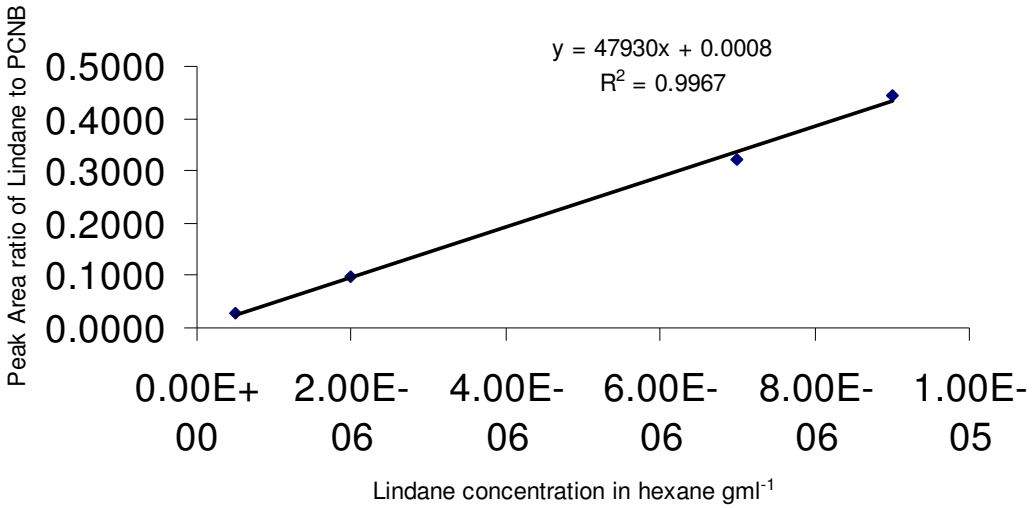


Figure 4.5 GC-MS Calibration graph for Lindane in hexane with PCNB as the internal standard ($y = 47930x + 0.0008$).

As shown in Figure 4.5 the equation of the calibration curve is:

$y = 47930x + 0.0008$, here y is the ratio of Lindane to internal standard PCNB and x is the concentration of Lindane in hexane.

In order to evaluate the linearity of the calibration curve, the correlation coefficient of the curve R as well as the response factor is investigated. The standard deviation of the response factor (RF) gives an indication of the linearity. If this is less than 20% then the use of the linear model is appropriate. The RF is calculated for the analyte relative to the internal standard at each calibration concentration as follows:

$$RF = \frac{A_{as} \times C_{is}}{A_{is} \times C_{as}}$$

where:

A_{as} = Peak area of the analyte

A_{is} = Peak area of the internal standard.

C_{as} = Concentration of the analyte in solution in (gml^{-1}).

C_{is} = Concentration of the internal standard in solution (gml^{-1}).

Table 4.11

Response factors at each Lindane calibration concentration

Lindane concentration in hexane (g/ml)	Response Factor
9×10^{-6}	0.2464
7×10^{-6}	0.2292
2×10^{-6}	0.2469
5×10^{-7}	0.2659
Average	0.2471
Standard Dev	0.0150
Relative Standard Dev	6.06%

For this calibration the relative standard deviation of the response factor is 6.06% which is below the maximum value of 20%. This calibration curve is therefore linear. The slope and intercept from the regression analysis match exactly the plot values. The R^2 value is 0.9967. This indicates linear reliability, the calibration curve can be assumed to be linear.

4.5.3 Lindane Extraction from dust: Results and discussion

4.5.3.1 Soxhlet extraction of Lindane from dust

Soxhlet extraction was carried out on four 1g dust samples which had been pre-dosed with 10µl of $9 \times 10^{-4} gml^{-1}$ of Lindane in hexane. A 1ml aliquot of the surrogate TCMX

at a concentration of 5 x 10^{-5}gml^{-1} in hexane was added to the dust whilst in the thimble prior to the start of the extraction. The results and calculations are presented below.

Table 4.12

GC-MS peak areas and their ratios for Soxhlet extractions of dust dosed with 10µl of 9 x 10^{-4}gml^{-1} Lindane in hexane (batch a)

PCNB	TCMX	Lindane	Lind/PCNB	TCMX/PCNB
7446	14428	2307	0.30983078	1.937684663
9827	17778	2896	0.29469828	1.809097385
7295	5971	1935	0.26525017	0.818505826
8349	7650	2452	0.29368787	0.916277398
Average			0.29086678	1.370391318

Table 4.13

GC-MS peak areas and their ratios for Soxhlet extractions of dust dosed with 10µl of 9 x 10^{-4}gml^{-1} Lindane in hexane (batch b)

PCNB	TCMX	Lindane	Lind/PCNB	TCMX/PCNB
10328	8943	3153	0.3052866	0.865898528
11894	10363	3241	0.27249033	0.871279637
9333	10486	2596	0.27815279	1.123540126
10048	8769	3214	0.31986465	0.872710987
Average			0.29394859	0.93335732

Table 4.14

GC-MS peak areas and their ratios for Soxhlet extractions of dust dosed with 10µl of 9 x 10^{-4}gml^{-1} Lindane in hexane (batch c)

PCNB	TCMX	Lindane	Lind/PCNB	TCMX/PCNB
10328	8943	3153	0.3052866	0.865898528
11894	10363	3241	0.27249033	0.871279637
9333	10486	2596	0.27815279	1.123540126
10048	8769	3214	0.31986465	0.872710987
Average			0.29394859	0.93335732

Table 4.15

GC-MS peak areas and their ratios for Soxhlet extractions of dust dosed with 10µl of 9 x 10^{-4}gml^{-1} Lindane in hexane (batch d)

PCNB	TCMX	Lindane	Lind/PCNB	TCMX/PCNB
10615	8650	3355	0.31606218	0.814884597
8981	9353	2358	0.26255428	1.041420777
9923	9263	2976	0.2999093	0.933487856
10823	9591	3226	0.29806893	0.886168345
14440	9940	3491	0.241759	0.688365651
Average			0.28367074	0.872865445

Using the equation of the calibration curve shown in Figure 4.5,

$y = 47930x + 0.0008$

where y is the ratio of Lindane to internal standard PCNB and x is the concentration of Lindane in hexane,

The concentration of Lindane on recovery from Soxhlet extraction for the first batch (Table 4.12) is given below:

where y = 0.2908, then x= 6.058 x 10^{-6} gml^{-1}

$$\therefore \%\,\text{recovery} = \left(\frac{6.058\times10^{-6}}{9\times10^{-6}}\right)\times100$$

$$= 67.3\%$$

The calculated efficiency values for the three other extractions are 68%, 65.6% and 57.4% for batches 2, 3 and 4 respectively. The percentage relative standard deviation of the efficiencies is 7.59% which indicates good repeatability. Although the extraction efficiencies are in agreement with acceptable recovery guidelines (EPA 1996a; ATSDR

2005), it was still necessary to investigate the reason for the unaccounted mass to determine if the procedure could be adjusted to improve the results. The emptied vial which had contained the Lindane-dosed dust was rinsed with hexane. The rinsate was then analysed by GC-MS to determine if any Lindane had been adsorbed by the vial walls. However no Lindane was detected which showed that the walls did not act as a sink.

In addition, the apparatus was rinsed with hexane to check if there was any Lindane left on the walls of the apparatus nothing was found. The Soxhlet extraction was then repeated for the same previously extracted dust sample to check if there was any Lindane left unextracted from the dust, but again no Lindane was found. It was therefore assumed that the Lindane was lost from the condenser in the Soxhlet apparatus to the air in the fume cupboard. It was also possible that some of the Lindane was lost to the headspace above the dust whilst it was in the vial. This would later be investigated in the Lindane air measurements.

The absence of Lindane in the repeat extraction of the same previously extracted dust sample showed that the period of extraction was sufficient. This led to the conclusion that the Soxhlet extraction was sufficient to ascertain the presence or absence of Lindane in dust sample. However, the large amount of Lindane unaccounted for as well as the long periods of extraction typical of the Soxhlet extraction made it necessary to adopt a mass balance system to calculate the amount of Lindane in dust from the mass measured in air and the initial amount injected into the vial.

4.5.4 SPME method for analysis of Lindane in headspace

4.5.4.1 Reproducibility and equilibrium time for SPME

Table 4.16

Time taken for vapour phase calibration standard at a concentration of 1.4 x 10^{-7}µgm^{-3} to reach equilibrium.

Time (h)	Peak Area		
	Batch 1	Batch 2	Average
0	2596	2054	2325.0
4	2602	2956	2779.0
24	2305	2541	2423.0
48	2312	2157	2234.5
72	2266	2259	2262.5

A graphical representation of the equilibrium trend is also shown in Figure 4.6 below.

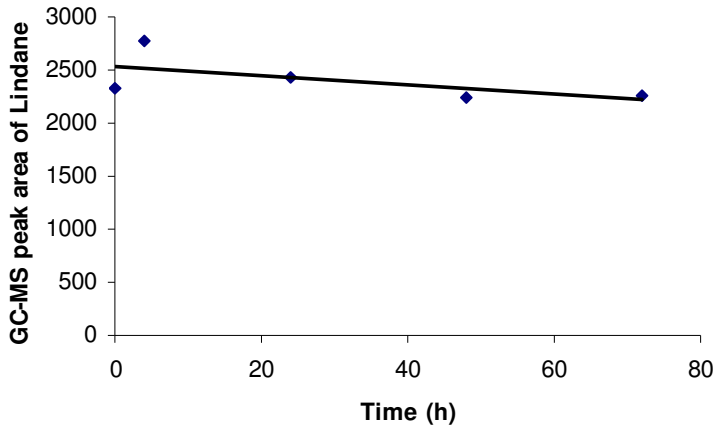


Figure 4.6 Graph illustrating time taken for 1.4 x 10^{-7}µgm^{-3} Lindane in headspace to reach equilibrium.

As is illustrated in Figure 4.6, the GC-MS peak area was fairly stable between 24 to 72 hours and varied only marginally (6.1%). It was therefore established that 24 hours was

sufficient equilibrium time. All subsequent readings for the vapour phase calibration standards were therefore taken after 24hours of injection into the vial.

4.5.5 Optimisation of SPME extraction time

The length of time the fibre stays in contact with the sample determines the amount of analyte that is adsorbed on the SPME fibre and subsequently desorbed in the GC-MS. A forty five minute SPME extraction time was initially used as is suggested for headspace analysis (Supelco 2004). The length of extraction time should be sufficient enough so that even at low concentrations the fibre remains in contact long enough to adsorb a quantity which will be detectable by the GC-MS. To this end, a longer extraction period of 1 hour was investigated at the lowest calibration concentration ($5 \times 10^{-11} gcm^{-3}$). This however gave no significant difference in peak area. Hence forty five minutes was adopted as the extraction time for all subsequent studies

4.5.6 Calibration of Lindane in air on GC-MS using SPME

In order to quantify unknown Lindane vapour phase concentrations in samples using the GC-MS, calibration was necessary. The vapour phase calibration standards used in this work ranged from $1 \times 10^{-7} \mu gm^{-3}$ to $2 \times 10^{-7} \mu gm^{-3}$. As mentioned in the methodology chapter, it is important to periodically verify the validity of the calibration and if the calculated concentration differs by over $\pm$15% from the concentration injected, a new calibration will have to be established and used for subsequent analysis. As a result two vapour phase calibration graphs are presented in Figure 4.7 and Figure 4.8, the latter being the newer recent calibration.

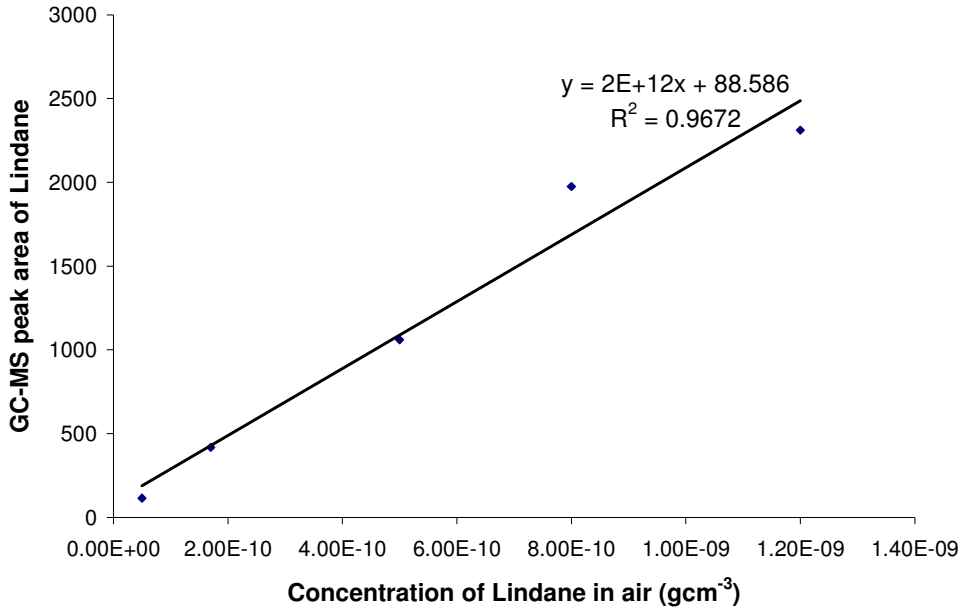


Figure 4.7 GC-MS calibration graph for Lindane in air using SPME.

As shown in Figure 4.7 the equation of the calibration curve is $y = 2 \times 10^{12}x + 88.586$, where y is the GC-MS peak area and x is the concentration in gcm^{-3}. The equation is used to calculate all further Lindane vapour phase concentrations within the calibration range.

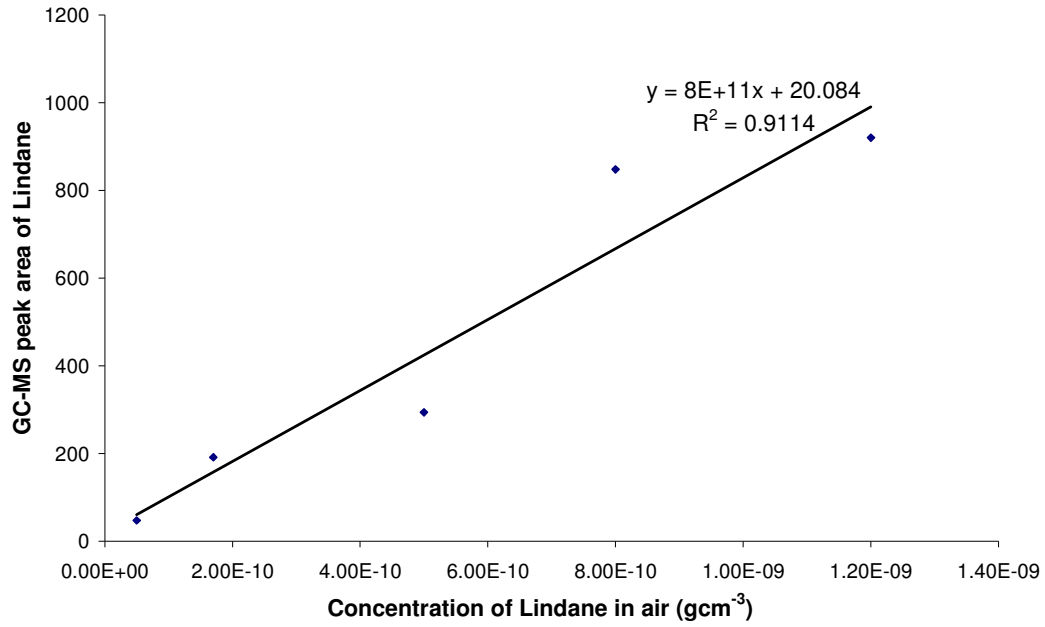


Figure 4.8 GC-MS calibration graph for Lindane in air using SPME (2nd calibration).

4.6 Conclusion

The methodology used for the measurement of Lindane in air has been shown to be adequate as the calibration produced a linear plot with a correlation coefficient of with R^2 values above 0.9 in both the initial and subsequent calibration. The GC-MS calibration plot of Lindane in solution also produced a linear plot with a R^2 value of 0.9967 indicating a robust technique. Amounts of Lindane were not accounted for during the Soxhlet extraction and were thought to be lost during the extraction procedure. Therefore further quantification of Lindane in dust would be obtained from mass balance calculations from air concentration measurements. Soxhlet extraction would therefore only be used to ensure that dust used in experiments were Lindane-free prior to the commencement of any Lindane dosing. The results from this chapter are used in subsequent adsorption experiments results of which are presented in chapter five.

Chapter Five

5 Lindane adsorption studies in air and dust

5.1 Summary

As indicated earlier, these results follow from the preliminary analysis in chapter 4. Dynamic tests were carried out to determine adsorption and desorption coefficients as well as equilibrium time. Adsorption and desorption rate constants (k_1 and k_2 respectively) were determined by fitting results from the dynamic adsorption tests to an existing two compartment model described in chapter 2, using the statistical analysis software SPSS (version 16).

Firstly, the dynamic tests were carried out for two size fractions (<20µm and >45µm to <63µm) and whole dust samples to determine the effect of size fraction on adsorption. For the <20µm fraction, $k_1 = 1.686h^{-1}$, $k_2 = 0.125h^{-1}$ (standard error 1.888 and 0.324 respectively), 45µm to <63µm, $k_1 = 0.568h^{-1}$ and $k_2 = 0.047h^{-1}$, (standard error 0.119 and 0.030 respectively), for the and the whole dust $k_1 = 2.587\ h^{-1}$, $k_2 = 0.288\ h^{-1}$ (standard error 0.514 and 0.113 respectively).

Secondly, static tests were carried out at equilibrium to establish an adsorption isotherm and obtain partition coefficients for different size fractions. The partition coefficients K_p were 4.8 x $10^1 \mu g m^{-2}$, 4.08 x $101 \mu g m^{-2}$, 1.05 x $10^2 \mu g m^{-2}$ for the <20µm, >45µm<63µm, and whole dust sample respectively. These higher partition coefficient value for the smaller <20µm compared to >45µm<63µm fraction suggests that the

Lindane adsorbs more strongly to smaller size fractions which. The whole dust sample has the highest partition coefficient which suggests that it acts as the strongest sink of the three samples. The adsorption constants K_a were 4.2 x $10^{-4}mh^{-1}$, 7.67 x $10^{-5}mh^{-1}$, and 3.03 x $10^{-3}mh^{-1}$ for the <20µm, >45µm<63µm and whole dust respectively. The desorption constants K_d were 1.25 x $10^{-1}h^{-1}$, 4.7 x $10^{-2}h^{-1}$, 2.88 x $10^{-1}h^{-1}$ respectively.

The linearised Langmuir model plot obtained by a linear regression of the plot of C_e^* / M_{se}^* against C_e^*, had R^2 values of 0.9505, 0.8611 and 0.983 respectively illustrating a good fit to the data.

The higher K_p value for the smaller <20µm fraction compared to the >45µm<63µm fraction, suggests that Lindane adsorbs more strongly to smaller dust size particles. This is significant because it means that the inhalable dust fractions which fall within the <20µm fraction, will have higher concentrations and therefore could potentially be more harmful as they get into the lungs. A possible explanation for the higher K_p value for the whole dust fraction could be because whole dust may contain fibrous substances that may have stronger affinities for Lindane than dust e.g. carpet fibres.

5.2 Results and discussion of dynamic adsorption studies for Lindane in air above dust

The results for dynamic adsorption studies for Lindane headspace above dust of size fractions >45µm<63µm, whole dust and <20µm are presented in Tables 5.1 to 5.3 respectively and in a graphical representations in Figures 5.2 to 5.4 respectively.

Table 5.1

Dynamic study of Lindane adsorption to dust (>45µm to <63µm fraction)

Time (h)	GC-MS Peak Area
0	8188
24	491
36	580
72	406
120	323
144	368

Using the initial Lindane vapour phase calibration equation obtained in section 4.5.6, $y = 2 \times 10^{12}x + 88.586$, where y is the GC-MS peak area and x is the vapour phase concentration, the concentration after 24, 36 and 72 hours are $2.01 \times 10^{-10}gcm^{-3}$ ($0.201ngcm^{-3}$), $2.46 \times 10^{-10}gcm^{-3}$ and $1.59 \times 10^{-10}gcm^{-3}$ respectively. The concentration remained relatively constant between 24 hours and 144 hours with values at $1.17207 \times 10^{-10}gcm^{-3}$ and $1.39707 \times 10^{-10}gcm^{-3}$ respectively. Thus an equilibrium time of 24 hours for Lindane between air and dust was adopted.

A two compartment model derived below describes the adsorption and desorption process to and from a sink. Figure 5.1 below illustrates the process with X being the amount of compound in the air and Y in the dust.

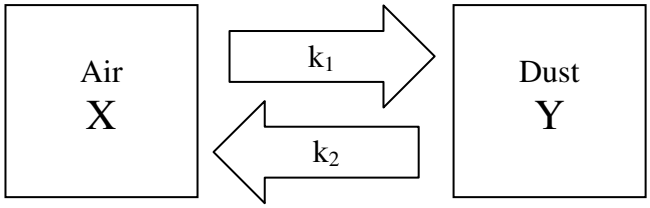


Figure 5.1 Illustration of Mass balance model for the Lindane adsorption-desorption system between air and dust.

The rate of change of the amount of Lindane in air in this closed system is represented by

$$\frac{dX}{dt} = -k_1 X + k_2 Y \quad \text{---------- (1)}$$

The value of adsorption rate constant k_1 and desorption rate constant k_2 indicates the affinity of the compound Lindane to the dust. This can be rewritten in the form

$$X(t) = \frac{X_o}{k_2 + k_1}\left(k_2 + k_1 e^{-(k_2 + k_1)t}\right) \quad \text{---------- (2)}$$

where:

X = mass of Lindane in air at time t,

X_o = Mass of Lindane in air at time zero,

k_1 = mass balance model adsorption constant,

k_2 = mass balance model desorption rate constant, t is the time at any point during the process.

Equation (2) is derived from Equation (1) as follows:

$$\frac{dX}{dt} = -k_1 X + k_2 Y$$

$$= -k_1 X + k_2 (X_o - X)$$
$$= -k_1 X + k_2 X_o - k_2 X$$

Integrating equation (1) from first principle,

$$\int_{X_o}^{X} \frac{dX}{-(k_1 + k_2) X + k_2 X_o} = \int_0^t dt \text{ ---------- (3)}$$

Therefore,

$$\therefore -\frac{1}{(k_1 + k_2)} \ln\left(-(k_1 + k_2) X + k_2 X_o\right)\Big|_{X_o}^{X} = \Big|_0^t \text{ ---------- (4)}$$

Substituting the upper and lower boundaries gives,

$$-\frac{1}{(k_1 + k_2)} \ln\left(-(k_1 + k_2) X + k_2 X_o\right) + \frac{1}{(k_1 + k_2)} \ln\left(-(k_1 + k_2) X_o + k_2 X_o\right) = t \text{ ------(5)}$$

Therefore,

$$-\frac{1}{(k_1 + k_2)} \ln\left(\frac{\left(-(k_1 + k_2) X + k_2 X_o\right)}{\left(-(k_1 + k_2) X_o + k_2 X_o\right)}\right) = t \text{ ----------(6)}$$

$$\frac{-(k_1 + k_2) X + k_2 X_o}{-(k_1 + k_2) X_o + k_2 X_o} = e^{-(k_2 + k_1) t} \text{ ----------(7)}$$

Expanded to give

$$\frac{-(k_1 + k_2) X + k_2 X_o}{-k_1 X_o - k_2 X_o + k_2 X_o} = e^{-(k_2 + k_1) t}$$

$$-(k_1 + k_2) X + k_2 X_o = -k_1 X_o e^{-(k_2 + k_1) t}$$

$$-(k_1 + k_2) X = -k_2 X_o - k_1 X_o e^{-(k_2 + k_1) t}$$

$$-(k_1 + k_2) X = -X_o\left(k_2 + k_1 e^{-(k_2 + k_1) t}\right)$$

Therefore,

$$X(t) = \frac{X_o}{k_2 + k_1}\left(k_2 + k_1 e^{-(k_2 + k_1)t}\right)$$

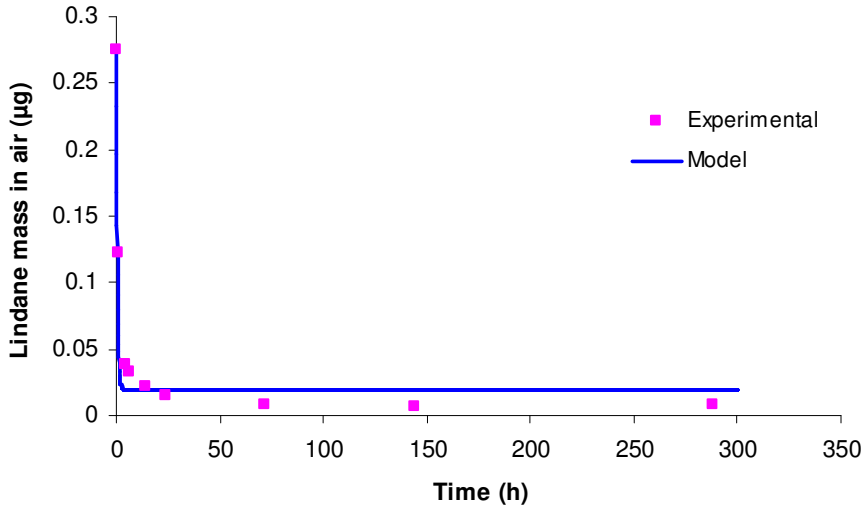


Figure 5.2 Fit of sorption data to the mass balance model (<20µm fraction).

Figure 5.2 illustrates the fit of the mass balance model $X(t) = \frac{X_o}{k_2 + k_1}\left(k_2 + k_1 e^{-(k_2 + k_1)t}\right)$ to the measured data. X_o is the mass of Lindane measured in air at time zero, whilst *X(t)* is the mass of Lindane at any given time. For the <20µm fraction, X_o is 0.2751µg, $k_1 = 1.686h^{-1}$ and $k_2 = 0.125h^{-1}$ with standard errors 1.888 and 0.324 respectively. This model appears to over predict the equilibrium mass of Lindane in air for the <20µm fraction as well as the other size fractions as is illustrated in Figures 5.3 and 5.4.

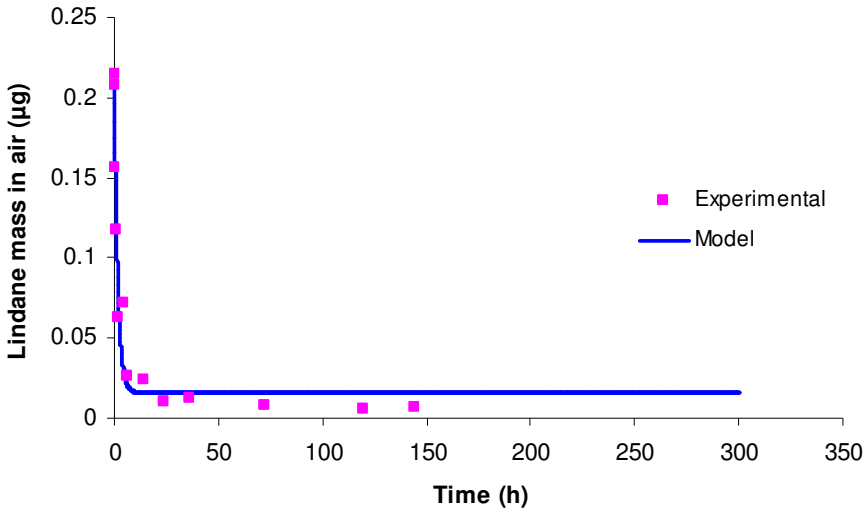


Figure 5.3 Fit of sorption data to mass balance model (>45µm<63µm dust fraction).

Figure 5.3 illustrates the fit using >45µm<63µm dust fraction. For the >45µm<63µm fraction, X_o is 0.2074µg, the rate constants $k_1 = 0.568h^{-1}$ and $k_2 = 0.047h^{-1}$, with standard errors 0.119 and 0.030 respectively. When compared to the k_1 and k_2 values of the 20µm fraction ($k_1 = 1.686h^{-1}$ and $k_2 = 0.125h^{-1}$), it can be seen that k_1 is higher for the 20µm fraction and thus indicates that adsorption of Lindane to the smaller size fraction is faster and stronger than larger size fractions. This finding agrees with trends in literature (Lewis et al 1999). Furthermore, the k_2 value is higher for the smaller 20µm fraction when compared to the higher >45µm<63µm fraction. As discussed earlier in chapter 2, $k_2 = k_d$, where k_d is the desorption rate constant. A higher desorption rate constant indicates a stronger sink hence the smaller 20µm fraction is a stronger sink when compared to the >45µm<63µm fraction.

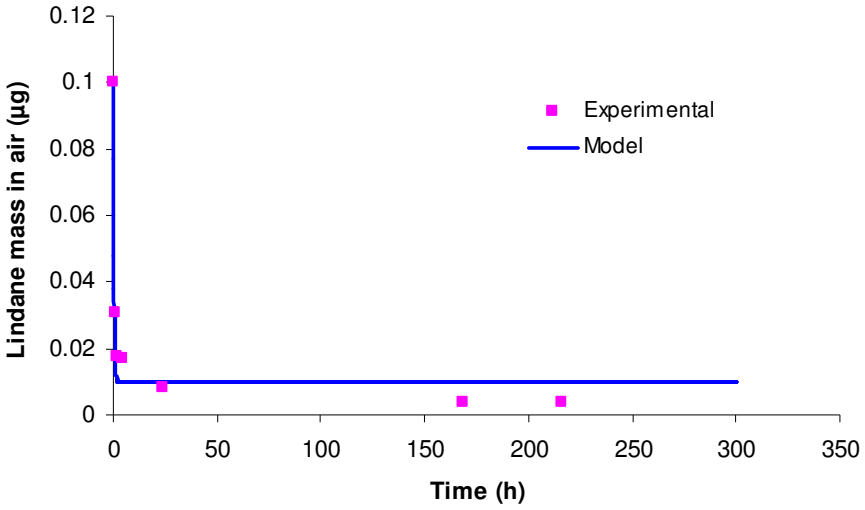


Figure 5.4 Fit of sorption data to the mass balance Model (Whole dust fraction).

Figure 5.4 illustrates the fit of the mass balance model to the measured data for the whole dust fraction. Mass measured at time zero X_o is 0.0993µg, the rate constants are k_1= 2.587 h^{-1}, k_2= 0.288 h^{-1} with the standard errors 0.514 and 0.113 respectively. The k_1 value is higher than both the 20µm and >45µm<63µm values. This finding is surprising as it would be expected that the value would not be less than the k_1 value of the <20µm fraction at the least. This is because even if the whole dust fraction contains a large portion of smaller particles <20µm, the overall effect on a 1g aliquot investigated should mean the k_1 value should be higher or at the very least equal to that for the <20µm.

5.3 Static Equilibrium Tests

The static equilibrium experiment was necessary in order to obtain an adsorption isotherm and derive a partition coefficient. The significance of this is to inform on the

preferred affinity of Lindane to dust or air and hence infer the strength of dust as a sink for Lindane.

5.3.1 Fit of simple Linear Model to the experimental data

This section presents results and analysis of the static tests and investigates the applicability of the simple Linear model to the experimental data.

Table 5.2

Values of C_e^* and M_{se}^* derived from static tests at equilibrium for 20µm fraction.

Total Lindane mass in vial[a] (µg)	Peak Area[b]	C*$_e$ [c] (µgm^{-3})	Lindane mass in air (µg)	Lindane mass in dust (µg)	M*$_{se}$ [d] (µgm^{-2})	C*$_e$/M*$_{se}$
10.0	228	259.90	0.01299	9.98700525	6878.1028	26.02
8.5	175	193.65	0.00968	8.49031775	5847.3263	22.81
7.0	147	158.65	0.00793	6.99206775	4815.4737	22.69
5.0	92	89.48	0.00447	4.995526083	3440.4450	17.91

[a] *Total mass of Lindane injected into vial*
[b] *GC-MS Peak area of Lindane in air.*
[c] *Concentration of Lindane in air at equilibrium.*
[d] *Mass of Lindane in dust at equilibrium derived from mass balance i.e. (mass injected – mass in air at equilibrium).*

Table 5.4 clearly indicates the measured concentration values of Lindane in air and dust at the point of equilibrium. At equilibrium, a small fraction of the total mass of Lindane injected into the vial is present the air with the remaining fraction present in the dust. This confirms the fact that dust acts as a sink for Lindane and indicates Lindane's preferred affinity to dust over air. A further indication of the affinity of Lindane to dust is shown by partition coefficient K_p obtained from an adsorption isotherm. The adsorption isotherm is generated from the plot of the mass of Lindane in dust at equilibrium, M_{se}^* against the equilibrium concentration in air C_e^*, and is shown in Figure 5.5.

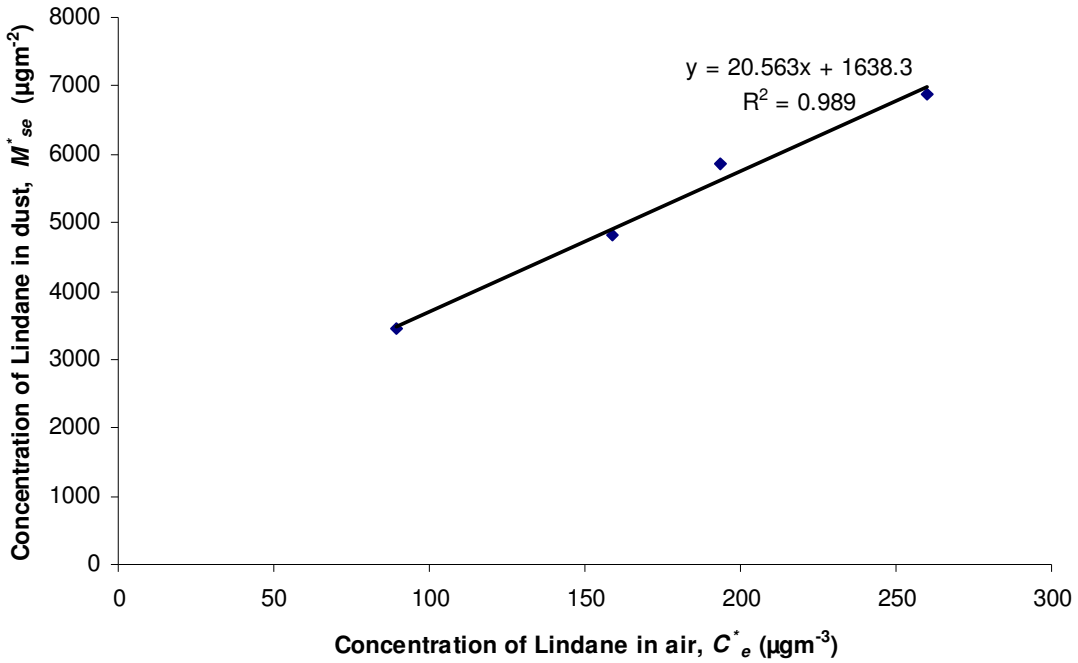


Figure 5.5 Adsorption isotherm (<20µm dust fraction).

A linear regression of the plot of the adsorption isotherm in Figure 5.5 gives an equation of $y = 20.563x + 1638.3$. A comparison to the Linear model, $M^*_{se} = K_p C^*_e$ implies that the plot would be expected to have a y intercept of zero. However this is not the case. This indicates that the linear model would not adequately describe the adsorption process for Lindane between air and dust. The slope of the graph however indicates the preferential affinity of Lindane to dust.

A further objective of this experiment was to assess the effect of size fraction on the partition coefficient. To this end adsorption isotherms were also generated for the >45µm<63µm fraction and whole dust samples. Table 5.5 shows the measured equilibrium concentration values of Lindane in air and dust for the >45µm<63µm fraction.

Table 5.3

Values of C_e^* and M_{se}^* derived from static tests at equilibrium for >45µm<63µm.

Total Lindane mass in vial[a] (µg)	Peak Area[b]	C*$_e$[c] (µgm^{-3})	Lindane mass in air (µg)	Lindane mass in dust (µg)	M*$_{se}$[d] (µgm^{-2})	C*$_e$/M*$_{se}$
10.0	208	234.895	0.0117	9.9883	6878.9637	23.52
8.5	177.5	196.77	0.0098	8.4902	5847.2187	23.18
7.0	147	158.645	0.0079	6.9921	4815.4737	22.69
5.0	97	96.145	0.0048	4.9952	3440.2154	19.25

[a]*Total mass of Lindane injected into vial*
[b] *GC-MS Peak area of Lindane in air.*
[c]*Concentration of Lindane in air at equilibrium.*
[d]*Mass of Lindane in dust at equilibrium derived from mass balance i.e. (mass injected – mass in air at equilibrium).*

Table 5.5 shows that the >45µm<63µm fraction also preferentially acts as a sink for Lindane over air as the equilibrium mass of Lindane in dust is substantially greater than in air. The adsorption isotherm is presented below in Figure 5.6.

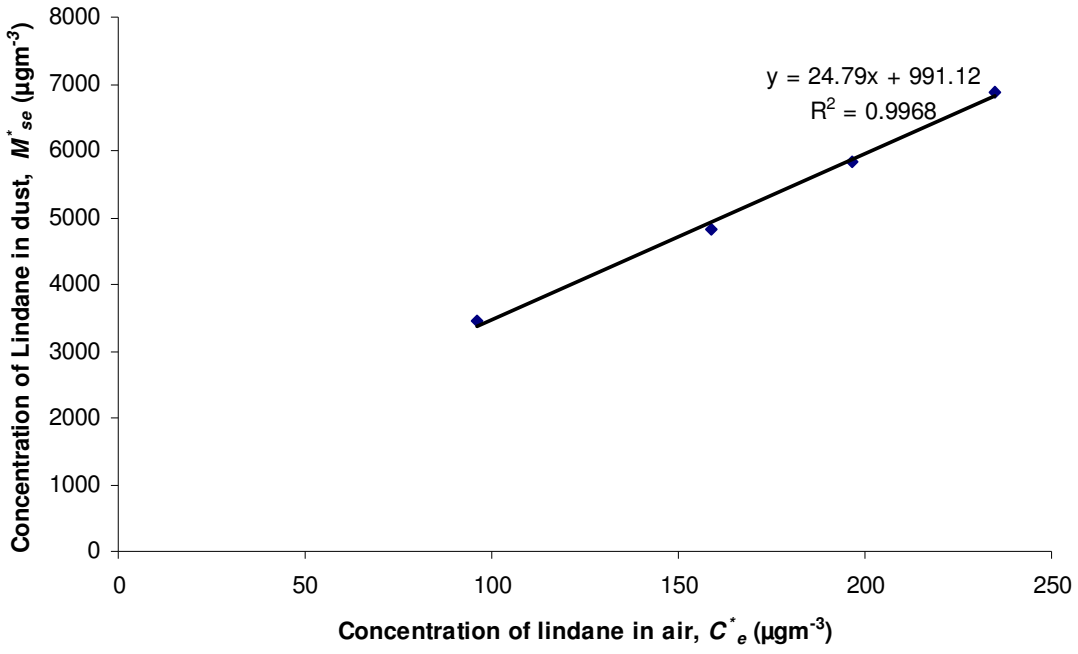


Figure 5.6 Adsorption isotherm (>45µm<63µm dust fraction).

As can be seen from the plot of the adsorption isotherm in Figure 5.6, the *y* intercept is not equal to zero; hence the simple linear model can not adequately describe the adsorption of Lindane between air and dust. A subsequent investigation into partition coefficient for whole dust samples generated the adsorption isotherm in Figure 5.7 values of which are presented in Table 5.6.

Table 5.4

Values of C_e^* and M_{se}^* derived from static tests at equilibrium for Whole dust.

Total Lindane mass in vial[a] (µg)	Peak Area[b]	C^*_e [c] (µgm^{-3})	Lindane mass in air (µg)	Lindane mass in dust (µg)	M^*_{se} [d] (µgm^{-2})	C^*_e/M^*_{se}
10.0	248	284.90	0.0142	9.99	6877.2419	28.53
8.5	146	157.40	0.0079	8.49	5848.5746	18.53
7.0	84	79.90	0.0040	7.00	4818.1854	11.42
5.0	70.5	63.02	0.0032	5.00	3441.3561	12.61

[a] *Total mass of Lindane injected into vial*
[b] *GC-MS Peak area of Lindane in air.*
[c] *Concentration of Lindane in air at equilibrium.*
[d] *Mass of Lindane in dust at equilibrium derived from mass balance i.e. (mass injected – mass in air at equilibrium).*

Again the whole dust samples indicate an affinity for Lindane as equilibrium mass in dust is consistently greater than in air. The adsorption isotherm is presented below in Figure 5.7.

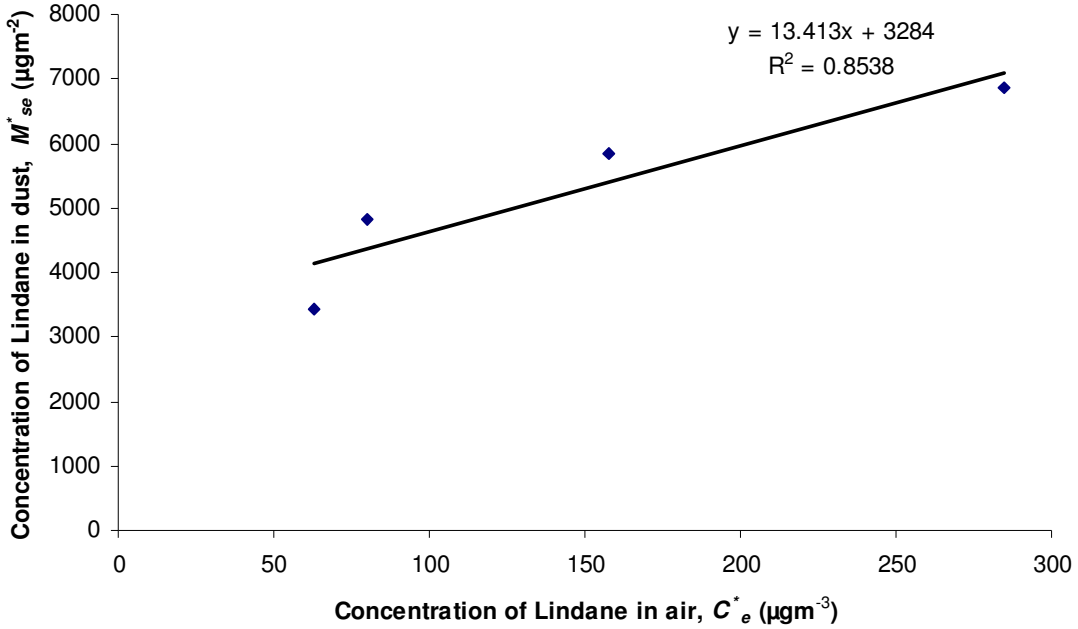


Figure 5.7 Adsorption Isotherm (Whole dust).

Again the *y* intercept shown forms the adsorption isotherm plot in Figure 5.7 and it shows that the simple linear model is not applicable for the Lindane-air-dust adsorption process. The simple linear model was not applicable for all three samples.

5.3.2 Fit of Linearised Langmuir model to experimental data

In order to assess the suitability of the linearised Langmuir Model describe in the literature review, to describe Lindane adsorption in air and dust, the adsorption isotherm was plotted in the form $\frac{C_e^*}{M_{se}^*}$ against C_e^*. Figure 5.8 illustrates the adsorption isotherm for the <20µm fraction.

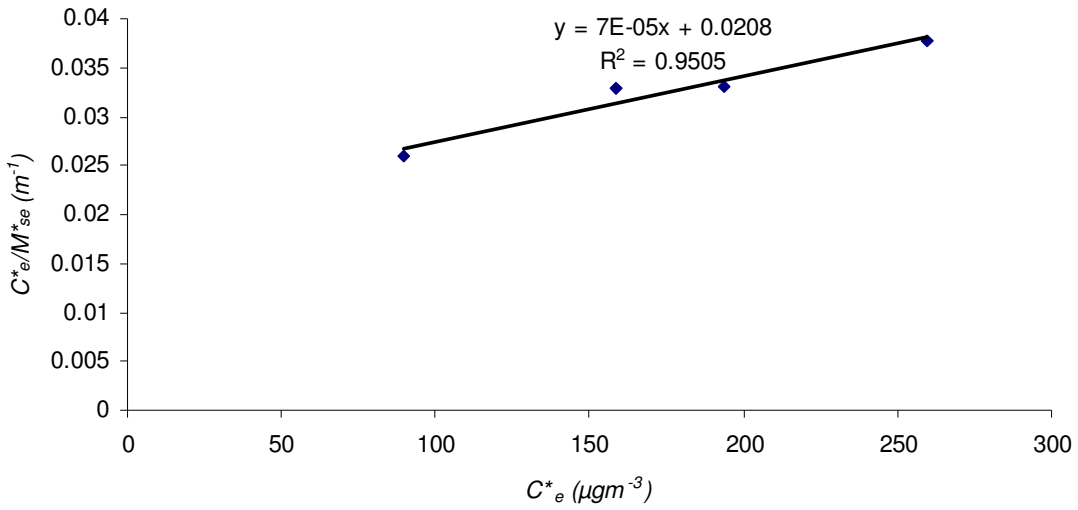


Figure 5.8 Linearised Langmuir (<20µm dust fraction).

Comparing the Linearised Langmuir equation,

$$\frac{C_e^*}{M_{se}^*} = \frac{C_e^*}{M_{so}} + \frac{1}{M_{so}K_L}$$

to the equation

$$y = mx + c$$

$$\Rightarrow y = \frac{C_e^*}{M_{se}^*}, m = \frac{1}{M_{so}}, c = \frac{1}{K_L M_{so}}$$

In the <20µm fraction,

y = 7 x 10^{-5} x + 0.0208

$$M_{so} = \frac{1}{7\times10^{-5}\,\mathrm{m^2 ug^{-1}}}$$

M_{so} = 14285.7µgm^{-2}

Also Langmuir constant $K_L = \frac{1}{0.0208\times14285.7}$ = 3.365 x 10^{-3}µg^{-1}m^3

Also,

$K_p = M_{so} K_L$

K_p=14285.7 x 3.365 x 10^{-3}

= 48.08m

As previously mentioned,

$$K_L = \frac{K_a}{K_d}$$

Also, the desorption rate constant,

$K_d = k_2 = 0.125 h^{-1}$

Therefore, the adsorption rate constant

$K_a = 4.21 \times 10^{-4} mh^{-1}$

The Linearised Langmuir fit to the adsorption isotherm for the >45µm<63µm is presented in Figure 5.9.

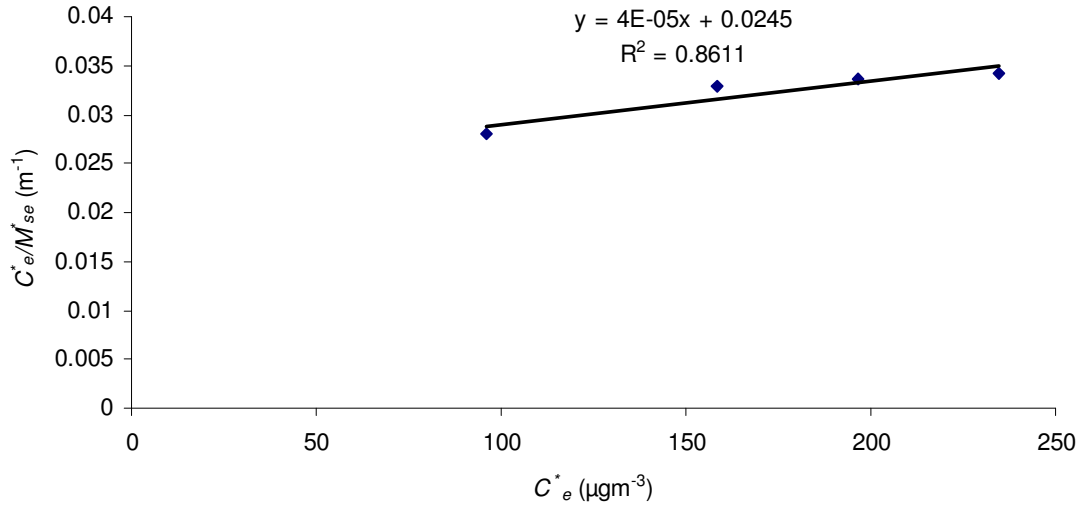


Figure 5.9 Linearised Langmuir (>45µm<63µm fraction).

As shown in Figure 5.9, slope is 4 x 10^{-5}. Therefore,

M_{so} = 25000µgm^{-2}

K_L = 1.633 x 10^{-3}µg^{-1}m^3

K_p = 40.81m

K_a = 7.67 x 10^{-5}mh^{-1}

K_d = 0.047h^{-1}

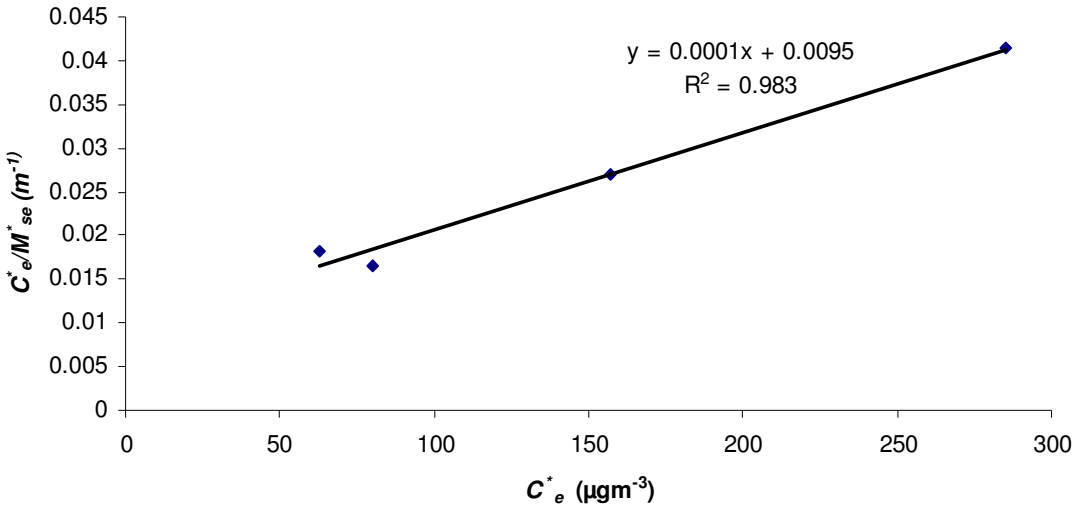


Figure 5.10 Linearised Langmuir (Whole dust).

For the whole dust sample, the constants derived from the adsorption isotherm above are as follows:

M_{so} = 25000

K_L = 1.05 x 10^{-2}µg^{-1}m^3

K_p = 105.26m

K_a = 3.03 x 10^{-3}mh^{-1}

$K_d = 0.288h^{-1}$

A summary of the constants are presented in Table 5.7 below.

Table 5.5

Summary of constants derived from adsorption/desorption experimental data.

Dust size	$k_1 (h^{-1})$	$k_2 (h^{-1})$	$K_a (mh^{-1})$	$K_d (h^{-1})$	$K_L (\mu g^{-1} m^3)$	$K_p (m)$
<20µm	1.686	1.25×10^{-1}	4.21×10^{-4}	1.25×10^{-1}	3.36×10^{-3}	4.8×10^{1}
>45µm<63µm	5.68×10^{-1}	4.7×10^{-2}	7.67×10^{-5}	4.7×10^{-2}	1.63×10^{-3}	4.08×10^{1}
Whole	2.587	2.88×10^{-1}	3.03×10^{-3}	2.88×10^{-1}	1.05×10^{-2}	1.05×10^{2}

As shown in Table 5.7, the higher partition coefficient K_p in the <20µm fraction compared to the >45µm<63µm fraction indicates that the smaller size fraction acts as a stronger sink. This trend is in agreement with the literature (Lewis et al. 1999). The higher K_p for the whole dust fraction might be as a result of the more fibrous nature of its constituents. The higher adsorption rate constant value K_a for the <20µm fraction indicates that adsorption occurs more quickly than in the larger size fraction. The desorption rate constants are also higher in the <20µm fraction, also indicating a faster rate of desorption, implying a shorter equilibrium time than >45µm<63µm fraction. For the whole dust sample, the K_a and K_d values were both higher than the two other fractions and thus desorption and adsorption rates are faster and equilibrium is reached faster.

5.4 Conclusion

The <20µm fraction had a higher partition coefficient than the >45µm<63µm fraction indicating that smaller size fractions act as a stronger sink which is consistent with

literature (Lewis et al. 1999). Therefore further study of the inhalable fraction of contaminated dust is of great importance.

The higher partition coefficient for the whole dust sample suggests that whole dust is a stronger sink than the individual smaller dust size fractions. This may be because whole dust contains more fibrous substances that may have stronger affinities for lindane than dust e.g. carpet fibres.

Chapter Six

6 Concluding remarks and recommendations for future work

It is important to investigate the presence of semi volatile organic compounds in the indoor environment as human beings spend over 90% of their time indoors. Therefore the indoor air is a critical determinant of their health. This research is concerned particularly with the suspected human carcinogen, Lindane, an insecticide with many known adverse health effects, which had been widely used in the UK prior to its ban in 2004. Lindane adsorbs to dust in the household which therefore acts as a reservoir or sink and subsequently remits this harmful pesticide back into the indoor air over time.

Humans can be exposed to Lindane through many routes including inhalation, ingestion, respiration and dermal contact. Smaller dust size fractions are available for inhalation and respiration. It was therefore important to investigate the effects of dust size fraction on partition coefficient of Lindane between air and household dust, dynamic and static tests of lindane in air and dust were conducted. For the <20µm fraction, $k_1 = 1.686h^{-1}$, $k_2 = 0.125h^{-1}$ (standard error 1.888 and 0.324 respectively), the >45µm<63µm, $k_1 = 0.568h^{-1}$ and $k2 = 0.047h^{-1}$, (standard error 0.119 and 0.030 respectively), and the whole dust $k_1 = 2.587\ h^{-1}$, $k_2 = 0.288\ h^{-1}$ (standard error 0.514 and 0.113 respectively). Static tests were carried out at equilibrium to establish an adsorption isotherm and obtain partition coefficients for different size fractions.

The Linearised Langmuir model adjusted well to the experimental data with r^2 values greater than 0.9 in the 20µm and >45<63µm. The adsorption constants K_a were 4.21 x

$10^{-4}mh^{-1}$, 7.67 x $10^{-5}mh^{-1}$, and 3.03 x $10^{-3}mh^{-1}$ respectively. The desorption constants K_d were $1.686h^{-1}$, $0.568h^{-1}$, $2.587\ h^{-1}$. The partition coefficients were 3.365 x 10^{-3}m, 1.633 x 10^{-3}m, 1.05 x 10^{-2}m respectively. The larger partition coefficients values of <20µm fraction compared to the >45µm<63µm fraction, suggests that lindane adsorbs more strongly to smaller size fractions. The findings suggest that smaller dust particles act as a stronger sink than larger fractions which is in agreement with literature (Lewis et al. 1999). However whole dust samples appear to have a stronger affinity for Lindane than the two other fractions. A possible explanation for this could be because whole dust contains more fibrous substances that may have stronger affinities for lindane than dust e.g. carpet fibres.

It is important to note that the limited previous attempts to measure Lindane in household indoor environment concentrated mainly on using test chambers and relatively expensive site visits and were focused on dust measurements. Therefore, a way had to be found to measure Lindane in air and dust using simple laboratory tests whilst maintaining data quality. To this end a vial method for measurement of the concentration of the SVOC Lindane in headspace above dust in a small vial at room temperature, using SPME, without the addition of water or any solvent was developed and used in this research. As a result of this study, it is now possible to execute such tests in the laboratory to predict Lindane concentration using dust samples collected from households. Another novelty of this research is that is now possible with the method developed as part of this study to measure the partition of Lindane between air and different dust size fractions in relatively simple tests. This is particularly important because the smaller fractions when unsettled from floors can get into the lungs and

cause harm. Also the partitioning of lindane which will occur between air and smaller dust particles suspended in air will have an effect on the amount of Lindane present in air for inhalation and respiration. It was found that the possibly carcinogenic and harmful Lindane adsorbs more strongly to the smaller dust fraction <20µm which is significant because inhalable and respirable fractions fall under this fraction. This information will be useful for researchers in the public health sector and indoor contamination exposure assessments.

The outcome of this study is expected to be of significant benefits to policy makers both in government and in the private sector who have to contend with SVOCs contamination in indoor environment. In particular, the ease with which Lindane in air and dusts can be measured as a result of this study could pave the way for such tests to be executed as part of home information packs before property completions.

6.1 Recommendations for future work

One area where future work is recommended is in determining the reason for the apparent stronger affinity of Lindane to whole dust fractions. Similarly, future work could also focus on validating the results from this study with improved data and equipment, which could possibly concentrate on larger concentration range over orders of magnitude to understand the effects of lindane concentration on the adsorption and partition coefficients.

The findings in this research suggest that Lindane may still be present indoors even years after its application and subsequent ban. It is therefore a recommended that

research into other harmful contaminants which have been banned is imperative and should not cease on the assumption that they will no longer be present in households. In instances where such investigations may have ceased, they should be revisited.

Following from the unaccounted loss of Lindane in attempted extractions from dust using the Soxhlet extraction, another area where this work could be further developed is in revisiting the extraction method to investigate how it can be improved. Another approach may be to adopt a different methodology altogether for the extraction of Lindane from dust. This could involve ultrasonic extraction of Lindane from dust followed by Solid Phase Micro Extraction (SPME) of Lindane from the resulting extract. This would negate the need to transfer the sample from the vial thus reducing possibility of loss of analyte in such steps.

Regarding equipment, the GC is a very delicate and is expensive equipment that requires a specialist engineer to keep going and be able to yield reliable data. Future researchers could certainly learn from my experience, which is crucially important to setting a realistic completion date. First, frequent and prolonged breakdown of equipments is a major problem that when it occurs causes major setbacks. It is therefore advisable that a service contract is always in place. Also it is important that where possible, the analyst should be trained and equipped to carry out basic repairs in order to minimise downtime whilst awaiting a specialist engineer. With regards to seals for vials, it is advisable to always use a crimp seal rather than screw caps because the crimp seal is more consistent. Also, once the septa of the seal is punctured with a syringe, it is important to leave in the syringe if possible as it provides a seal around the

puncture which is not necessarily as self re-sealable as might be expected. Similarly, the researcher should always be as close to the GC when taking a sample for subsequent injection into the GC, to prevent loss of analyte from the SPME fibre and syringe.

Finally, an area where this research could be further developed would be in the development of a simple and safe test where householders could use a simple kit to detect the presence of contaminants such as lindane on dust, in air or surfaces indoors. This could be in form of a wipe test or another means. Potential benefits of this would be a further reduction in the costs of contamination assessments and promotion of greater awareness and sense of responsibility for occupants of indoor environments.

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Appendix

Table A1 Pesticide Concentration range in past studies

Pesticide	**Author**				
	Fortune et al. 2000	**Lewis et al. 1999**	**Ruthan et al. 2003**	**Simcox et al. 1995**	**Camann et al. 1994**
	μgm^{-2}	**μgg^{-1}**	**μgg^{-1}**	**μgg^{-1}**	**μgg^{-1} median (max)**
Aldrin	0.056 - 477	Not detected	Not detected	n/a	n/a
Bendiocarb	0.06 - 56.5	0.11 - 1.43	<0.2 - 40.7	n/a	0.36(318)
Carbaryl	0.05 - 868	0.19 - 4.61	<0.4 - 34.4	n/a	0.4(1160)
alpha-Chlordane	0.0476-12.06	0.04 - 0.49	<0.3 - 9.97	n/a	0.4(15)
gamma-chlordane	0.05 - 70.4	<0.05 - 0.65	<0.3 - 10.6	n/a	0.46(17)
Chloropyrifos	0.13 - 2479	0.16 - 4.52	<0.2 - 228	<0.017- 3.585	0.56(324)
Coronene	0.04 - 4.6	0.07 - 0.46	N/a	n/a	n/a
Chyrsene	0.04 - 29.3	0.14 - 1.67	N/a	n/a	n/a
Dacthal	0.18 - 86.9	Not detected	N/a	n/a	n/a
Diazinon	0.02 - 14751	Not detected	<0.2 - 51	n/a	n/a
Lindane	0.027	Not found	<0.4 - 1.04	n/a	n/a
Malathion	0.06 - 2.97	Not detected	<0.2 - 1.48	n/a	n/a
Methoxychlor	0.13 - 5.0	0.12 – 1.0	<0.5 - 12.9	n/a	0.59(28)
cis-Permethrin	0.18 - 60440	1.34-15.17	< 0.3 - 61.9	n/a	1.75(588)
	0.11 -	1.50 -	<0.4 - 98	n/a	0.8(299)

Pesticide	**Author**				
	Fortune et al. 2000	**Lewis et al. 1999**	**Ruthan et al. 2003**	**Simcox et al. 1995**	**Camann et al. 1994**
	µgm^{-2}	**µgg^{-1}**	**µgg^{-1}**	**µgg^{-1}**	**µgg^{-1} median (max)**
trans-Permethrin	112012	21.87			
o-Phenylphenol	0.05 - 117	0.04 - 1.20	<0.3 - 2.4	n/a	n/a

Table A2 Comparison of methods used in previous works

Author	Area of Research	Type of surface	Collection methods and standards where followed	Fractionating method and Standards where followed	Extraction and standards where followed	Analysis and standards where followed
Pedersen et al. 2002	Emissions from heated indoor dust	Textile surfaces of chairs	Vacuum	Fluidised best dust tube but later sieving was adopted due to its simplicity	Thermal desorption unit	GC-MS
Fortune et al. 2000	Distribution of pesticide residues between dust, carpet, and pad compartments	Carpets (various sections from surface to sub floor dust)	PUF roller (ASTM D6333), HSV3 vacuum (ASTM D5438-93), Hoover Dirt finder vacuum, steel cutting tool	Sieving	Soxhlet extraction	GC-MS
Lewis et al. 1999	Distribution of pesticides and polycyclic aromatic hydrocarbons in house dust as a function of particle size	Carpets	Upright vacuum cleaner	Tyler Ro Tap Sieve shaker followed by Air classifier	Soxhlet extraction with 6% diethyl ether in n-hexane	GC-MS

Author	Area of Research	Type of surface	Collection methods and standards where followed	Fractionating method and Standards where followed	Extraction and standards where followed	Analysis and standards where followed
Gebefuegi and Kettrup 1995	Adsorption of volatile and semi volatile organic compounds on particle surface as indoor contaminants	Not stated	Commercial vacuum cleaner	Grinding and mixing till homogenous state	Liquid extraction with hexane/acetone	GC-ECD-MS
U.S. EPA 1999	Determination of pesticides and polychlorinated biphenyls in ambient air	Air	High volume sampler consisting of PUF adsorbent cartridge (ASTM D4861-94)	N/A	Soxhlet extraction	GC-MultiDetector including ECD (ASTM E260)