CRANFIELD UNIVERSITY

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Indoor and Outdoor Dust in Damaturu Nigeria; Composition, Exposure and Risk to Human Health.

Cranfield Health

Supervisor: Dr. Derrick Crump

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ABSTRACT

Harmattan and Dust (sand) storms together with anthropogenic activities including the use of firewood and kerosene as fuel for cooking, and diesel/petrol generators for electricity generation are potential sources of particulate and gaseous pollutants in homes in Damaturu town, Nigeria. Other activities like the burning of locally produced incense and mosquito coils as well as the use of aerosol sprays are further possible sources of indoor pollution, which may result in exposure of people to a range of pollutants through inhalation, by ingestion of settled dusts as well as dermal contact. Local people associate occurrence of dust events with adverse health effects and hence there is a need for an understanding of the composition of the settled and airborne dusts in order to assess the possible associated health risks.

The first phase of the study involved selection and development of methods of dust sampling and analysis. For validation of the methods employed and to establish a broad understanding of the characteristics of the settled dusts, an initial survey study was conducted involving the application of thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) analysis for organic compound analysis, scanning electron microscopy (SEM), inductively coupled plasma-mass spectrometry (ICP-MS) for analysis of metals, and microbiological analysis. Airborne samples were also collected using sorbent tubes to determine organic compounds in air during activities such as cooking with kerosene, gas, and firewood as well as during electricity generation with fossil fuels. Carbon monoxide (CO) and ultrafine particles (UFPs) monitored simultaneously during some of the household activities.

The study involved a novel method of extracting organic chemical emissions from dust by heating of the dusts directly in a micro chamber (μ-CTE^{TM}) and collection of emissions on sampling tubes. The method provided a relatively quick way of collecting chemical emissions from dusts that are readily available for release. The sampled tubes were analysed by TD/GC/MS. The conventional solvent extraction of the dusts was also carried out and the extracts were analysed by liquid injection-GC/MS and results of the two methods compared.

The study determined a number of constituents (metals, SVOCs, phthalates and physical properties) of dusts collected from households in Damaturu during different weather events and from different indoor/outdoor locations; and compared with some UK samples. The samples investigated include dusts deposited; during two notable dusty-weather events (Harmattan and Storm) as well as when there was no notable dust event; during human activities; and dusts from different types of buildings (modern and traditional homes) as well as inside and outside homes. A standard reference material for organic chemicals (SRM 2585) was also analysed.

The physical characterization of the settled house dust samples analysed revealed the various shapes and sizes, and elemental composition of the constituents, which included respirable particles. The microbial analysis also indicated the presence of the spores of a host of fungi and bacterial species; and the possible contributions of

household activities to the increased production of pollutants (UFP and CO) ascertained.

The µ-CTE extraction of the house dusts by heating with TD/GC/MS analysis of the emissions as well as the solvent extraction-GC/MS revealed the presence of many organic chemical compounds with different analytical retention times and varying concentrations in the dust samples. Chemicals of interest quantified: benzene, hexanal, nonanal, diethyl phthalate (DEP), diisobutylphthalate (DIBP), dibutylphthalate (DBP), and diethylhexylphthalate (DEHP). A host of other chemicals commonly present in the analysed samples identified using the NIST library associated with the MS system software. These chemicals included naphthalene and C_{10}-C_{16} aliphatic and aromatic hydrocarbons, which would need confirmation by running the pure compound samples.

There was an observed higher concentration of the chemicals in the solvent extracts than the µ-CTE extracted dust. The higher concentration of the chemicals in the solvent extracts expected due to the aggressive removal of the chemicals by the organic solvent whereas in the case of thermal extraction only the readily available chemicals (loosely bound to the matrix) released by increases in temperature were removed. Generally, the concentrations of the chemicals found were higher in the indoor than in the outdoor dust samples. In the analysis of the dusts collected during weather events; higher chemical concentrations observed in the samples collected during Harmattan period than the other periods. The Harmattan dust period may pose increased exposures to dust and possible health risks. More exposure is expected to occur in the traditional homes compared with the modern homes due to the higher concentrations of the chemicals in both the indoors and the outdoors and this may be especially important to women and children who spend most of their times at home.

Metal analysis involved microwave-assisted digestion of the dust samples followed by ICP-MS analysis. The total quant method of metal analysis for a general profiling indicated the presence of more than 50 elemental contaminants in house dust. The results of the quantitative analysis for six target metals: Cd, Cr, Cu, Ni, Pb, and Zn showed their presence in all indoor and the outdoor dust samples. The mean concentrations showed that the metals were in higher concentrations in the indoor dusts than in the outdoor dusts.

The quantitative analysis carried out indicated higher metal contents in the storm dusts than the dusts during the other periods. Results of the dusts collected from modern and traditional homes indicated the presence of the metals in higher concentrations in the dusts from traditional homes than the dusts from the modern homes.

The estimated mean concentrations of the metals and phthalates inadvertently ingested as a constituent of dust indicated that some of the pollutants could exceed the tolerable daily intake (TDI) due to high exposures to dust expected to be the case in Damaturu.

The results of the investigation of the dust composition, combined with information on exposure to dust and pollutants, show that dusts are a risk to the health of people in the Damataru community.

Recommendations are made for more studies to provide a better understanding of dust ingestion and exposure to some phthalates and heavy metals in particular and the possible health risks.

To the best of my knowledge, this is the first ever research study of airborne and settled dusts undertaken in North-Eastern Nigeria.

Keywords:

Dust Storm: A strong and turbulent wind, which carries a large cloud

Harmattan; A dry and dusty wind, which blows northeast and west off the Sahara and into the gulf of Guinea between November and March.

Harmattan Dust: A fine particulate dust known to rise in the Sahara desert and be carried southwards by strong Northeast trade winds called Harmattan.

Harmattan Haze: The effect caused by the dust and sand, stirred by the Harmattan wind.

Microbial Spores: A small, usually single-celled asexual or sexual reproductive body that is highly resistant to desiccation and heat, and is capable of growing into a new organism and is produced especially by certain bacteria, fungi, algae, and non-flowering plants.

Particulate Matter (PM): A complex of extremely small particles and liquid droplets, made up of a number of components, including acids, organic chemicals, and other organic matter, metals, and soil or dust particles.

Toxic Metals: Metals that form poisonous soluble compounds, these include heavy metals such as mercury, plutonium, and lead and lighter metals such as beryllium. Some are essential trace elements because they have biological roles such as iron, cobalt, copper, manganese, and zinc, but excessive levels can be damaging to organisms.

Volatile organic compounds (VOCs) are a group of chemicals that contain organic carbon and readily evaporate changing from liquids to gases when exposed to air. VOCs are usually present in a wide range of products such as paint and paint wastes, dry cleaning chemicals, furniture stripper, cleaners, cosmetics and liquid fuels. Many of chemicals have been considered as hazardous to the environment. In the indoor sciences, it is common to categorize this group of compounds into very volatile organic compounds

(VVOCs), volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs).

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DECLARATION

This is a declaration to certify that:

(a) The contents of this thesis represent solely my own work

(b) The thesis has not been submitted for any other academic or professional award

(c) The thesis is submitted on the conditions contained in the regulations

(d) The work was carried out during my period of study from October 2009 to September 2013.

Some results from the research study have in parts been published in the International Journal of Engineering and Technology (IACSIT) vol. 5, No.1, 2013 (IJET, ISSN: 1793-8244), and in the book of proceedings of the Annual UK Review Meetings on Outdoor and Indoor Air Pollution Research, 2010, 2011, 2012, and 2013.

Fatima Sule Mohammed

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Abbreviations/Nomenclature

AM	Arithmetic mean
ATSDR	Agency for Toxic Substance and Disease Registry
CFU	Colony forming units
CAFÉ	Clean Air for Europe programme
DEFRA	Department for Environment, Food, and Rural Affairs
ECA-IAQ	European Collaborative Action on Indoor Air Quality
e.g.	Example
EU	European Union
et al.	*et alteri*
GM	Geometric mean
GRSD	Geometric relative standard deviation
ICP/MS	Inductively coupled plasma - mass spectrometry
SE/GC/MS	Solvent extraction/gas chromatography/mass spectrometry
LOQ	Limit of quantification
m^{-3}	Per metre cube
ng	Nano gram
ng g^{-1}	Nano gram per gram
PEM	Personal environmental monitor
RSD	Relative standard deviation

SD	Standard deviation
SEM	Scanning electron microscopy
TDI	Tolerable daily intake
TD/GC/MS	Thermal desorption/gas chromatography/mass spectrometry
UNECE	United Nations Economic Commission for Europe
USEPA	United States Environmental Protection Agency
µm	Micrometre
WHO	World Health Organisation
<	Less than
>	Greater than
%	Per cent

Chemicals and Pollutants

CO	Carbon monoxide
CO_2	Carbon dioxide
H_2S	Hydrogen sulphide
HC	Hydrocarbons
HONO	Nitrous acid
NH_3	Ammonia
NO_2	Nitrogen dioxide
NOx	Nitrogen oxides
O_2	Oxygen
PAH	Polycyclic aromatic hydrocarbon

PM	Particulate matter
$PM_{2.5}$	Particulate matter with aerodynamic diameter less than 2.5µm
PM_{10}	Particulate matter with aerodynamic diameter less than 10µm
SO_2	Sulphur dioxide
SVOCs	Semi volatile organic compounds
VOCs	Volatile organic compounds
VVOCs	Very volatile organic compounds

1 INTRODUCTION

1.1 Air Quality

Good air quality is essential for our health, quality of life and the environment. Air is considered polluted when it contains substances which can have a harmful effect on the health of humans, animals, and vegetation. Air pollutants both indoors and outdoors, are regarded as a significant cause of health problems worldwide in both urban and rural environments (World Health Organization, 2005). Air pollution was first noticed as a problem of city dwellers, but now it is acknowledged as a problem of global significance (Zhang and Smith, 2003). While ambient air pollution is a major concern, indoor air can be more polluted than outdoor air (Wilson *et al.*, 2001) because the indoor environmental quality may be affected by numerous factors, including biological, chemical, and particulate pollutants (Mitchell *et al.*, 2007). The indoor and outdoor air may contain infectious microbial spores, allergens, irritants, and chemical toxins that can reduce the quality of life and cause diseases (Mølhave *et al.*, 1997; Mølhave, 2004). As well as inhalation of these airborne pollutants, there is increasing recognition of the risks to health from settled dust in indoor environments acting as a source of chemicals and re-suspended particles and thereby leading to occupant's exposure through both inhalation and inadvertent ingestion. The increased exposure to indoor pollutants in dust may result in health effects especially in children; these include retarded growth, learning disabilities, allergies, cancer, nervous system damage, and other illnesses (Roberts and Dickey, 1995; Roberts *et al.*, 2009).

People in the Damaturu community of north-eastern Nigeria spend most of their time indoors because of the harsh weather conditions: cold, dry, strong, and dusty wind during Harmattan, thick dust during storm, and heavy downpours during the rainy season. The habit of using fire wood and kerosene in cooking, and diesel/petrol powered generators for electricity are potential factors of increased indoor pollution including dust particulate deposition. Other activities like the burning of local and assorted incense, burning of mosquito coils and application of aerosols as insect repellents indoors and outdoors could also generate particulate, organic, and elemental pollutants, which may linger in the air or cling to dust particles and settle on raised surfaces and floors (Mohammed and Crump, 2013). The pollutants present in air and dust may potentially cause exposure via inhalation and ingestion of house dust particles adhering to food and objects, or via direct absorption through the skin (Lewis *et al.*, 1995). These natural and anthropogenic sources of airborne and deposited dust are a risk to the health of the local population amongst which there is a general acceptance of the adverse outcomes considered as arising from natural phenomena and thus a situation that cannot be changed.

The months of June to October are the rainy season in the north-eastern region of Nigeria, which is characterised by hot and humid weather conditions with occasional thick reddish dark plumes of dust storm. From the month of November through to March, the weather conditions tend to be cold and dry with a prevailing northeast trade wind, which is associated with a grey dusty atmosphere, called the Harmattan haze. These conditions lead to high levels of settled, and or suspended dust in the indoor environment for a long period. The months of October, April and May are hot and dry without notable dust or weather events. However, for most of the year the weather events lead to heavy dusts that remain in the atmosphere for a long time. In addition, the types of buildings in the region allow easy penetration of outdoor air, which results in the deposition of large amounts of dust indoors within the communities in Damaturu.

1.2 Indoor Air Pollution and Health

Indoor pollutants can be classified either as biogenic or anthropogenic pollutants. Biogenic pollutants include aerosols of viruses, bacteria, fungal spores and mycelial fragments which may contain toxic metabolites (e.g. Stachybotrys containing Stachybotrylactam and Satra toxins), pollen, animal dander, dust mite residues and other particles of biological origin (Lemley *et al.*, 2002). A variety of adverse health effects following human exposure to bioaerosols have been well documented (Obendorf *et al.*, 2006). Some of them are allergy, hypersensitivity, respiratory and toxicological problems, and infectious diseases (Axel Clausen *et al.*, 2003). Anthropogenic pollutants emanate from a range of sources; these include those emitted by the fabric of buildings or as a by-product of the activities undertaken within them, such as combustion of substances for heating or cooking. For some contaminants infiltration from outside, either through water, air, or soil, can also be a significant source. Table 1.1 shows some indoor pollutants and their sources of emission (Jones, 1999; Jones *et al.*, 2000). A USEPA study by Wallace et al. (1985) found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside, regardless of whether the homes were located in rural or highly industrial areas.

Table 1-1 Pollutants, their sources and health impacts

Pollutants	**Sources**	**Health effects**
Allergens (microbial)	Moulds and house dust mites.	Worsening of symptoms of asthma and causation of wheezi
Carbon monoxide (CO): odourless, colourless gas that is produced from incomplete fossil fuel comb	Produced by emissions from vehicles, engines, boilers, and incinerators. Parking garages, poorly ventilated areas.	Dizziness, headaches, nausea, fatigue, memory, visual, cardiovascular, pulmonary, and nervous systems impairment, decreased muscular control.
Elemental contaminants e.g. cadmium (Cd), lead (Pb); occur in foodstuff, air, water, and soil.	Found in soils, used in jewellery, plating agents, welding rods, coinage, batteries, and chemical catalysts.	Irritates and may cause damage to the upper and lower respiratory tracts. Oxide fumes cause acute pneumonitis with pulmonary oedema, which may be lethal.
Nitrogen dioxide (NO_2): brownish gas that forms quickly when fuel is burned at high temperatures.	Motor vehicle emissions, electric utilities, industrial boilers, and off-road equipment.	Irritates the lungs, may cause lung damage and lower resistance to respiratory infections such as influenza.
Organic chemicals (SVOCs/VOCs e.g. phthalates).	Paints, paint and other solvents, preservatives, aerosol sprays, insect repellents and air fresheners, automotive products and cosmetics.	Cause sensory irritations, dryness, and weak inflammatory irritation of eyes, nose, airways, and skin. Systemic effects may include risk of cancer and endocrine disruption.
Ozone (O_3): At ground level, colourless gas that forms because of chemical reactions between volatile organic compounds (VOCs), nitrogen oxides (NOx), and oxygen in the presence of heat and sunlight.	Motor vehicles, electric utilities, factories, landfills, industrial solvents, lawn equipment, etc.	Respiratory system irritation aggravates chronic lung diseases leading to permanent lung damage, reduced yield of agricultural crops and damage to forests and other vegetation.
Particulate matter (PM): $PM_{2.5}$–PM_{10}, ultrafine particles	Cooking and aerosols, mechanical abrasions, skin flakes, spores, pollen etc.	Reduced lung function and increased risk of heart and respiratory diseases.

(From various sources including Morawska and Salthammer, 2006a, b)

1.3 Air Quality Guidelines and Regulations

The growing concern over health effects that occur due to exposure to pollutants attributed to indoor as well as outdoor environments has led to the establishment by international health organisations, as well as national authorities, of recommended air quality guidelines for the protection of people against health effects. However, there are currently no agreed guidelines for settled dust pollutants. The W.H.O air quality guidelines (AQGs) first produced in 1987 and updated in 1997 and had only a European scope. The 2005 updates sought to make the guidelines relevant and applicable worldwide and take into consideration the large regional inequalities in exposures to air pollution (Krzyzanowski and Cohen, 2008). The guidelines entailed recommended revised limits for the concentration of selected air pollutants: particulate matter (PM), ozone, nitrogen dioxide, and sulphur dioxide, applicable across all W.H.O regions (World Health Organization, 2010; 2011) and a decision taken by W.H.O to apply some of the ambient guidelines to indoor air. Table 1.2 shows the WHO ambient air quality guidelines as well as US EPA standard values for some air pollutants (U.S.E.P.A, 2011).

The guidelines are defined as annual, monthly, daily or hourly averages signifying the acceptable/duration of exposure to a certain concentration of a particular airborne pollutant.

Table 1.2 Example ambient air quality guidelines and standards for some pollutants

Pollutant	**Guideline Values**			
	Annual mean		**Hourly mean**	
	WHO	**US EPA**	**WHO**	**US EPA**
Benzene	5 µg m^{-3}	3.6 µg m^{-3}	n/a	n/a
O_3	10 µg m^{-3}		100 µg m^{-3} 8 hrs	0.075 ppm 8 hrs
$PM_{2.5}$	10 µg m^{-3}	15 µg m^{-3}	25 µg m^{-3} 24 hrs	35 µgm^{-3} 24 hrs
PM_{10}	20 µg m^{-3}		50 µg m^{-3} 2 hrs	150 µgm^{-3} 24 hrs
NO_2	40 µg m^{-3}	53 ppb	200 µg m^{-3} 1 hr	100 ppb 1hr
SO_2	n/a	n/a	20 µg m^{-3} 24 hrs 500 µg m^{-3} 10 min	0.5 ppm 3 hrs
CO	n/a	n/a	30 µg m^{-3} 1 hour 10 µg m^{-3} 8 hrs	35 ppm 1 hr
Pb	0.5 µg m^{-3}	0.15 µg m^{-3} 3 month	n/a	50 µg m^{-3} 8 hrs
Zn	500 ng m^{-3}	n/a	2000 ng m^{-3} 24 hrs	n/a
Cu	n/a	0.54 µg m^{-3}	n/a	n/a
Ni	n/a	0.020 µg m^{-3}	n/a	n/a
Cr	0.04 µg m^{-3}	0.11 µg m^{-3}	n/a	n/a
Cd	5 ng m^{-3}	n/a	100 µg m^{-3} 8hrs	n/a

(Source: WHO 2005, 2011; USEPA, 2011) n/a= not available

The W.H.O guidelines are widely agreed and up-to-date assessments of health effects of air pollution, recommending targets for air quality with significantly reduced health risks. For instance the World Health Organization indicated that by reducing particulate matter (PM_{10}) pollution from 70 to 20 µg m^{-3}, air quality related deaths can be cut by around 15% (World Health Organization, 2010). In most United Nations Economic Commission for Europe (UNECE) countries, ambient air quality has improved considerably in the last few decades. The improvement has been achieved by a range of measures to reduce harmful air emissions, including those stipulated by the various protocols under the Convention on Long-range Trans-boundary Air Pollution (Brunekreef and Holgate, 2002). The European Union has established a comprehensive legal framework to protect Europe’s air quality under the Clean Air for Europe (CAFE), which is a programme with the involvement of all major European stakeholders, as a basis for future policy initiatives (Amann *et al.*, 2005). The regulatory guidelines however, are concerned with concentrations of pollutants in the air and there are no corresponding guidelines for pollutants in settled house dust.

For some contaminants national and local authorities have guideline concentrations regarding some metals and organic chemicals in soil that are applied for risk assessment purposes such as determining when land is contaminated and requiring remedial treatment. For example the UK Environment Agency recommended health criteria values (HCV) for use in assessing the health risk to humans from chemical contaminants in the soil which represent levels of minimal or tolerable risk from long term exposure to various chemical contaminants such as the inorganic chemicals; arsenic, cadmium, mercury, nickel and selenium (Cole and Jeffries, 2009).

In the Nigerian context, the Federal government has established the Federal Environmental Protection Agency (FEPA) under the decree 58 of 30th December 1988, with the statutory responsibility for overall protection of the environment. FEPA was tasked to establish environmental guidelines and standards for the abatement and control of all forms of pollution, which resulted in the production of interim guidelines and standards for environmental pollution control in Nigeria in 1991. The objective was to achieve a desired environmental quality such as safe levels of air, water, and soil pollutants, which are tolerable to humans, aquatic organisms, and vegetation (FEPA, 1991).

1.4 Background of Study Area

Damaturu town is the capital of Yobe state, Nigeria. It is located on coordinates of 11^{o} 44’40”N and 11^{o} 57’40”E in the north-eastern part of Nigeria with an area of 2,366km^2 and a population of 88,014 based on the 2006 census. Yobe borders the Nigerian states of Bauchi, Borno, Gombe, and Jigawa. It also borders the Diffa and Zinder regions in the Republic of Niger to the north. The state lies mainly in the dry semi- arid region, thus it is dry and hot for most of the year except in the southern part, which has a milder climate. Most of the settlements across the state are rural, with a number of semi-urban areas that include Damaturu, Potiskum, Nguru, and Gashua. Damaturu being the state capital is a semi-urban settlement where most of the government offices and estates are located. However, the majority of the communities are rural, with mud houses, some with corrugated iron sheet roofing, and others with thatched roofs. These house types are often preferred due to the high temperatures observed during long summer months (Yobe State, 2007). The location of Damaturu is shown on the political map of Nigeria in Figure 1.1.

(Source- online@:Nigeria maps)

Figure 1.1 Map of Nigeria showing location of Damaturu town (NE Nigeria)

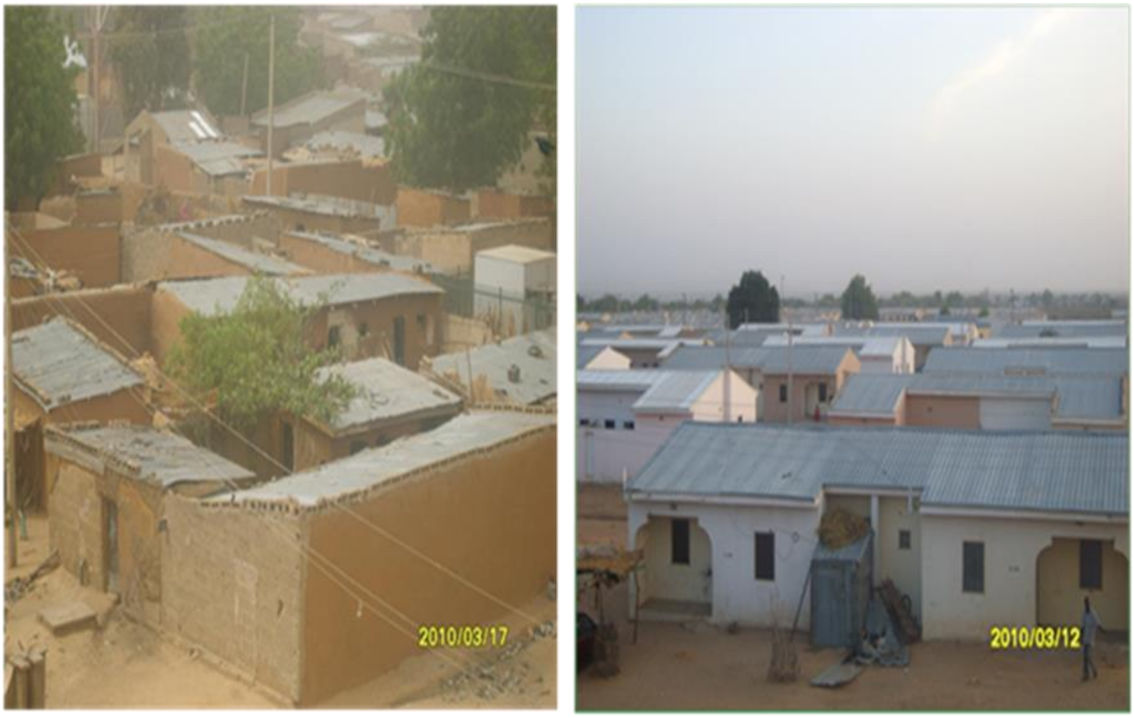
The houses in Damaturu township wards comprise of two main types of buildings:

Traditional buildings: These are buildings located within the old sector of the town, which include different household settings ranging from flats to open compounds with single rooms for extended family members. The houses are mostly built of mud bricks, corrugated iron roofs and with wood pillars that are replaced only when necessary (when blown off by storm or rusted). They are not cross-ventilated, often having only one window opening that faces the compound, with other houses attached to the back and sides in rows. The majority of the buildings were built in the 1950s and 1970s with a few built in the 1990s. The households have an average of 7 to 8 members (4 or more children). The occupants are mostly local settlers who are traders and farmers and have received little or no formal education.

Modern Government built estates: *These* comprise of mostly new government built estates with modern, detached, or semi-detached flats built of cement or burnt clay bricks and aluminium sheet roofs. The houses have wide windows but mostly on only one side of the building resulting in low levels of cross ventilation. They were built on new sites (built from the 1990s) after the creation of Yobe state from the former Borno state in 1991. The areas are more sparsely populated area with more open space (comprising both large and small households). Each household may have an average of five members (3 children). The occupants are mainly civil servants and high-ranking business personnel.

The type of buildings, together with the level of education and lifestyle of the building occupants, could contribute to differences in the amounts and types of indoor air pollutants. For instance in some of the traditional homes domestic animals (sheep, goats, poultry and pets) roam about in the open compounds and even inside the living rooms together with the home occupants including children. Soils and dust deposit on all surfaces and thereby may readily be ingested and inhaled. In the modern homes on the other hand, the buildings are mostly closed and livestock do not go indoors and therefore it is expected that there will be less transfer of soil and dust from the outdoors to the indoors.

The most common types of buildings in Damaturu Township are shown in Plate 1.1.



Pampomari ward Damaturu

Ali Marami ward Damaturu

Plate 1-1 Types of buildings in Damaturu town; traditional (left) and government built estates (right)

1.5 Statement of the Problem

In recent years, the onset of the rainy season (June to October) in most parts of the north-eastern semi-arid region of Nigeria is characterized by heavy dust storms (smog-like), accompanied by reduced visibility for 3 – 5 minutes. The storms last between 3 to 15 minutes mostly followed by torrential rains with thunderstorms, leaving behind heavy dust deposits, which settle down on every available surface. They occur most often in areas with less vegetation cover and relatively dry zones, and high temperatures within the sub-Saharan region. During winter (November to March), Harmattan (characteristic northeast wind, which blows southwards) with thick haze containing heavy particulate materials may persist in the atmosphere continuously for days to weeks. These events are thought to bring about high exposure of people to dust particles (as well as gases and vapours) in the local communities.

In Damaturu and the surrounding communities local people attribute various types of ailments ranging from eye inflammatory diseases, gastro-intestinal disorders and respiratory tract infections to the dusty weather conditions (Harmattan and Dust storm) observed in the area. During the dust events people spend much of their time indoors. Therefore the exposure to dust indoors along with particulates and gases generated by other indoor sources will determine their exposure to air pollutants. In addition, the dust that settles indoors lingers within the home and therefore exposure continues even after a dust event.

The nature, transport and possible health impacts of dust storm have been outlined (Goudie and Middleton, 2001; Griffin and Kellogg, 2004) and (Molesworth *et al.*, 2002). The World Health Organization study group in the West African sub-Saharan regions have reported storm as the cause of the regional outbreaks of bacterial cerebrospinal meningitis in Benin Republic, Niger, Ghana, and Nigeria (Besancenot *et al.*, 1997; Campagne *et al.*, 1999; Hodgson *et al.*, 2001; Mohammed *et al.*, 2000). Storm dust exposure has also been associated with asthma in Barbados (Blades *et al.*, 1998). Plates 1.2a and 1.2b show the airborne dust during an approaching sand storm episode and the associated clouding of the atmosphere in Damaturu, and Plate 1.3 shows how Harmattan haze envelops Damaturu during the Harmattan period.

Some studies have been carried out by researchers about the nature, composition, and mineralogy of Harmattan dust and dust storm in Ghana and north-west Nigeria, these studies focused on particulate composition of the dusts (Breuning-Madsen and Awadzi, 2005; Achudume and Oladipo, 2009). Even though there was mention of the possible health effects elsewhere (Adepetu *et al.*, 1988), no study has been carried out on possible pollutant constituents of Harmattan and storm dusts. There is a need therefore to conduct research on the composition of the dust particles as well as other sources of indoor pollution to improve understanding of the possible risk to health of the Damaturu community.

Plate 1-2a and 1.2b Storm Dust approaching Damaturu, Nigeria

Plate 1.3 Harmattan haze over Damaturu, Nigeria

1.6 Research Hypothesis

The people in Damaturu communities in Yobe State, Nigeria, are exposed to amounts of dusts that have the potential to cause adverse health effects because of its physical, biological and/or chemical characteristics.

1.7 Aim and Objectives of the Study

The main aim of this research is to investigate the various constituents of dust, which may result in exposure of people to harmful substances by inhalation, ingestion, and dermal contact that could be responsible for causing health effects within communities in north-eastern Nigeria.

1.7.1 Study Objectives

The objectives established to achieve the overall aim of the research are:

- Exploration of various sample collection methods for settled dust and airborne particles in indoor and outdoor environments, and the selection and possible development of appropriate methods,

- Collection of airborne and settled dust samples during weather events: Harmattan, Dust storm, No–dust event and during some anthropogenic activities,

- Collection of settled dusts from homes with different characteristics that could influence the dust composition and people’s exposure,

- Compositional analysis including physical analysis (SEM), microbiological analysis (fungal and bacterial culture/microscopy), organic chemical compounds analysis (TD/GC/MS and solvent extraction-GC/MS), and elemental analysis (ICP-MS),

- Exposure and health risk assessment; comparison of pollutant concentrations with results of other studies and available health based guidelines.

1.7.2 Significance of the Study

The study provides data on the composition of the dust samples in the indoor and nearby outdoor environment of homes and an assessment of the level of the pollutant concentrations as well as the possibility of exposure and the potential for associated risks to human health.

Members of the Damaturu community will be informed about the health risks associated with exposure to the pollutants in the indoor and outdoor environments. Leaflets targeting women will be used to inform people about exposures associated with activities such as cooking, cleaning, and playing with soil. The use of local media broadcasts will be used to inform groups with low literacy levels (when practical given the political situation). The intention is to advise on possible ways of reducing human exposures and health risks. The research findings would inform the relevant Government agencies for necessary action.

1.8 Study Design

The research study has been undertaken in 4 phases;-

Phase I. Exploration and development of methods for the collection of indoor/outdoor settled dust and airborne particles/vapour samples carried out by employing various existing methods as well as improvisation. This was to ascertain which method is optimum for a particular pollutant analysis and the circumstances in the field. The dust samples were obtained from bedrooms, living rooms, kitchens, and the frontage of households with different types of building and occupant living standards in Nigeria and in the UK. Methods were adopted and modified/improvised based on their suitability; practicality, affordability, and durability of equipment and samples for transport between Damaturu, Nigeria (sampling site), and the laboratory at Cranfield University, UK. Some of the sampling techniques investigated and the type of techniques investigated are shown (Table 3.1).

Phase II. Initial survey studies carried out involved analyses of some of the samples collected via the various trial methods in phase I using the existing methods with modifications as appropriate. This informed the selection of the sampling and analytical methods applied in phase III. Work was undertaken to develop a method of measuring organic compounds in dust by micro chamber thermal extraction (µ-CTE) combined with thermal desorption-gas chromatography- mass spectrometry (TD/GC/MS) and then compared with the conventional solvent extraction procedure.

Phase III. The most suitable method for dust sampling was applied to the collection of more dust samples from Nigeria and further analyses were conducted using the established methods:

a). Dust samples were obtained from five homes during notable (seasonal) dusty events: Harmattan period and Dust storm period and when there was no dust event (No-event period). The samples were analysed for the presence of selected chemical and metal pollutants and their concentrations in the different periods compared.

b). A further 52 settled dust samples were collected from the indoors and outdoors of 26 different homes based on two main categories; - modern and traditional. Soil (sand) samples were also collected from a location distant from the community. Metal and organic chemical analyses of the sampled dusts included a standard reference material for organic chemical analysis in dust obtained from the National Institute of Standards and Technology (NIST) USA (SRM 2585), analysed alongside the collected house dust samples for comparison. The sampling period and the samples collected are shown in Table 3.2.

Phase IV. Involved data analyses of the analytical studies/experiments carried out and exposure/health risk assessment:

Statistical analyses of the analytical results obtained: To understand any significant differences in the concentrations of the individual chemicals and the relationships between emissions of chemicals and type of homes/weather events. These statistical analyses were performed using the statistics software (IBM SPSS 21), USA.

Exposure and health risk assessment: Comparison of the results obtained from this study and those from other countries/regions in previous studies and comparison with the exposure limits set by regulatory/health agencies to assess the possible risks to health.

Conclusions/Recommendations: Conclusions drawn about the significance of the levels of pollutants in the dusts; recommendations for remedial actions and further studies formulated based on the findings and limitations of the study. The sequential work plan designed for the execution of the research over the study period is shown in a flow chart (Figure 1.2).

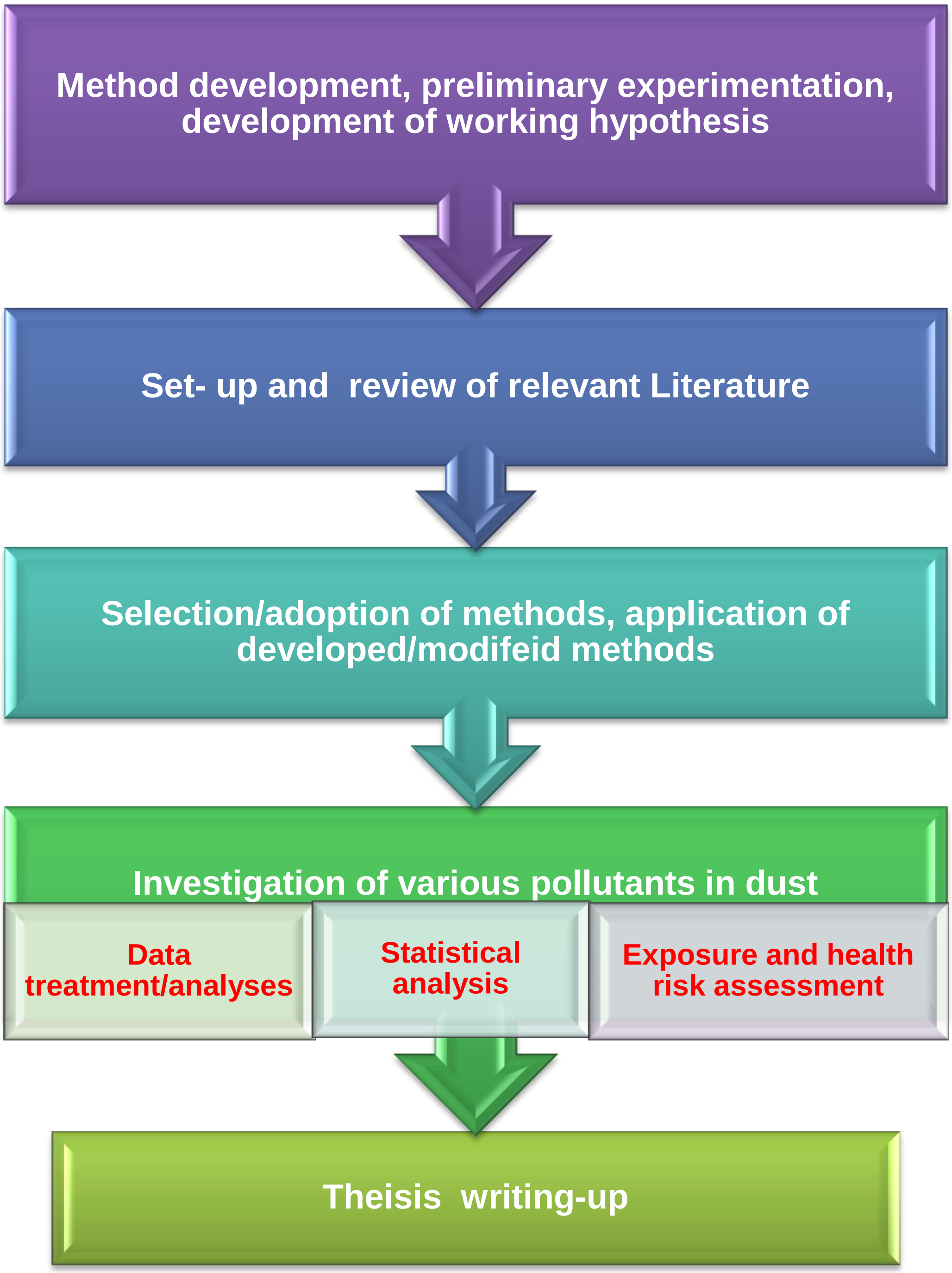


Figure 1.2 Study design flow chart

2 LITERATURE REVIEW

2.1 Introduction

A platform for the research study was prepared by undertaking an extensive review of published studies, reports by regulatory agencies and relevant books on indoor environments and pollutants including their impacts on health. Electronic resources were used as initial sources of information. Scopus, being the world's largest abstract and citation dataset, has been the main electronic data mining tool used due to its usefulness, and through which other links to journal article databases such as Medline, Elsevier, Science direct and Springer were accessed.

2.2 Dust in the Indoor/Outdoor Environment

Dust is generally considered to be particulate matter that is found either suspended in the air or settled onto a surface, and originates from a number of sources including soil, abrasion of materials, pesticides, asbestos, pollen, bacteria, shed skin, cigarette smoke and dust mites (Morawska and Salthammer, 2006a; Leese *et al.*, 1997). Airborne dust is the distribution of solid material of less than 100 µm in air formed through mechanical processes and subject to dispersion and suspension in the atmosphere (Butte and Heinzow, 2001). Numerous factors affect the indoor environmental quality including biological, chemical, and particulate pollutants (Mitchell et al., 2007). A World Health Organization report stated air pollution was a major environmental risk to health estimated to cause approximately 2 million premature deaths worldwide per year. The report further explained that exposure to air pollutants is largely beyond the control of individuals and requires action by public authorities at the national, regional and international levels (World Health Organization, 2005).

Mitchell et al., (2007) reported that settled dust was a good surrogate for indoor air pollution and for health monitoring purposes due to its being relatively easy to sample and because it can be collected directly from vacuum cleaner bags or by use of specific collecting devices. In addition, many compounds including biocides remain stable when attached to dust and analysing compounds in dust tends to be easier than other media such as air because they have a propensity to accumulate in higher concentrations. It also represents a direct pathway of human exposure to air pollution through inhalation of re-suspended airborne particulates and ingestion of settled dust that has contaminated food or by hand to mouth contact (Morawska, 2004; Morawska and Salthammer, 2006b).

2.3 Exposure to Indoors/Outdoors Pollutants

The contact of a toxic substance with the human body over time and space is described as exposure (WHO, 2000). Biological, chemical, and particulate pollutants affect the environmental quality leading to possible exposure via ingestion, inhalation, or dermal contact (Weschler, 2006). The Human Health Working Group in New York (2001) considered that typical exposures to pollutants occur from ingestion of contaminated food or drinking water, inhalation of contaminated air or from ingestion of contaminated soil. Zhang and Smith (2003) reported that while workplace exposure may involve one or more known chemicals, residential/office exposure usually involves complex mixtures of pollutants (Zhang and Smith, 2003).

Many research studies have reported that pollutants (biological, chemical and metals) can cause short term respiratory and inflammatory health effects which may potentially lead to chronic, long term health impacts and health effects that may be experienced soon after exposure or, possibly, years later (Hoskins, 2011; Perez-Padilla et al., 2010). Exposure to phthalates in house dust plus other indoor particulates and dust pollutants have been associated with childhood asthma and other allergy as reported in Taiwan (Hsu et al., 2012). Dust can be ingested through hand to mouth activities and by its presence in food and thereby enters the body causing systemic health effects. The ingestion of house dust by children is particularly high relative to their lower body weight; especially young children ingest considerable amounts of house dust via hand-to-mouth and object-to-mouth behaviour (Lijzen et al., 2001). Lijzen et al., (2001) gave conservative but realistic estimates of mean ingestion rates of house dust of 50 and 100 mg for adults and children in the Netherlands. A child is assumed to inhale 7.6 m^{-3} of air daily and an adult 19.9 m^{-3} (with default values for body weight). Table 2.1 shows estimated intake values for house dust via the two main routes of ingestion and inhalation indicating that 0.8 mg is inhaled daily by an adult and 0.2 mg by a child in the Netherlands, assuming a constant concentration of suspended particles in air of 100 µg m^{-3} (Oomen et al., 2008).

Table 2-1 Estimated values for house dust ingestion and inhalation

	Ingestion of house dust (mg day^{-1})	**Inhalation of house dust (mg day^{-1})**	**Total intake of house dust (mg day^{-1})**
Adult	50	0.8	50
Child	100	0.2	100

(Source: Litzen et al., 2001; Oomen *et al.*, 2008)

The Dutch National Institute for Public Health and the Environment (RIVM) in its screening of the potential risks posed by various chemical substances in house dust indicated that exposure to substances via house dust can be calculated based on the mean ingestion rates and typical concentrations of substances present in the dust. The RIVM compared the exposure of adults and children to substances via house dust to the tolerable daily intake (TDI). The TDI was used as a criterion for a potential health risk, plus the background exposure (via food and water consumption), where mean ingestion rates of house dust of 50 and 100 mg were estimated for adults and children, respectively (Oomen et al., 2008).

The majority of substances present in house dusts have not been identified as presenting a potential human health risk. However, some substances in house dust are frequently found to exceed the tolerable daily intake (TDI) limit; these include lead, DEHP, arsenic, cadmium, and sum PAHs, indicating that they may cause a potential risk (Lijzen *et al.*, 2001).

Particles with aerodynamic diameter of 10 µm or smaller (PM_{10}, $PM_{2.5}$) and the ultrafine particles (UFPs) can be inhaled by humans and are deposited deep in the lungs, while the larger particles mainly deposit in the upper bronchial tubes and in most cases are transferred upwards by mucous and subsequently ingested (Carrizales *et al.*, 2006).

The International Standards Organisation has defined three fractions of inhaled dust these are -

The inhalable fraction, which is the total mass inhaled,

The thoracic fraction, which is the mass that reaches and penetrates the larynx, and

The respirable fraction, which is the mass, that penetrates through the airways.

Typically observed concentrations of suspended dust particles range between 10 and 35 µg m^{-3} inside EU homes, with higher concentrations are usually found directly around persons (personal cloud) than in other places in a room (Carrizales et al., 2006a).

2.4 Sources and Composition of Indoor Particles and Dust

Outdoor particles penetrate indoors and the measure of the ability of particles to penetrate a building envelope is defined as the penetration factor Particles from outdoor air penetrate indoors because of ventilation or through cracks, gaps, or holes in the building envelope (Morawska and Salthammer, 2006). An US EPA study in 1985 found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside regardless of whether the homes were located in rural or highly industrial areas, thus making household dust and indoor air contaminants a good measure of the air pollution to which people are exposed (U.S.E.P.A, 2011). As well as windblown penetration, dust enters into the home by a number of other methods including on the shoes of residents, picked up by pets, or generated in the home such as with household products used for washing and cleaning (Morawska *et al.*, 2001). Dust particles are also generated by use of beauty care products, paints, varnishes, clothes and furniture. Indoor activities such as cooking, smoking, and burning of incense and candles are other known sources of chemical contaminants (Ali *et al.*, 2012). The release of organic chemicals from consumer products such as carpets, mattresses, pesticides, flame-retardants, children’s toys, and their presence in indoor dust have also been established (Mercier *et al.*, 2011). According to Dionisio *et al.*, 2008, indoor air pollution from biomass fuels, especially when burned in open or poorly ventilated stoves, contains high concentrations of many health damaging pollutants and can be associated with an increased risk of childhood pneumonia. This has been identified as being among the leading causes of death in children less than 5 years of age. Exposure to unprocessed solid fuels occurs in developing countries with over 2 billion people relying on biomass fuel as their main source of domestic energy (Fullerton *et al.*, 2009).

2.4.1 Dust Storm and its effects on Health

The term Sandstorm is often used in the context of desert sandstorms, especially in the Sahara, when, in addition to fine particles obscuring visibility, a considerable amount of larger sand particles are blown closer to the surface (Griffin et al., 2002). Dust Storm is a meteorological phenomenon common in arid and semi-arid regions characterized by a strong, turbulent wind carrying large clouds of dust. In a large storm, clouds of fine dust are raised to heights of well over 10,000 feet (3 km) and carried for hundreds or thousands of miles (Goudie and Middleton, 2001). The Sahara desert is a key source of dust storms, particularly the Bode’le Depression, and an area covering the confluence of Mauritania, Mali, and Algeria. The Bodélé Depression is the lowest point in Lake Chad located at the southern edge of the Sahara Desert in north central Africa. The persistent drought conditions associated with the great Sahel drought coupled with increased demand for fresh water for irrigation have reduced Lake Chad to about 5 per cent of its former size. As the waters receded, the silts and sediments resting on the lakebed dried and could potentially become wind-blown.

Dust storms occur with an average frequency of about 100 days per year and they move across the Bodélé Depression at about 47 kilometres per hour (29 miles per hour). Small grains of diatomite are swept up by the strong gusts of wind that blow over the region (Washington *et al.*, 2006). A satellite picture (Plate 2.1) shows the Dust storm activities around Lake Chad with the surrounding countries Niger and Chad to the northwest and northeast, and Nigeria and Cameroon to the southwest and southeast.

(Source: earthobservatory.NASA2007)

Plate 2-1 Dust Storm around the Bodélé Depression

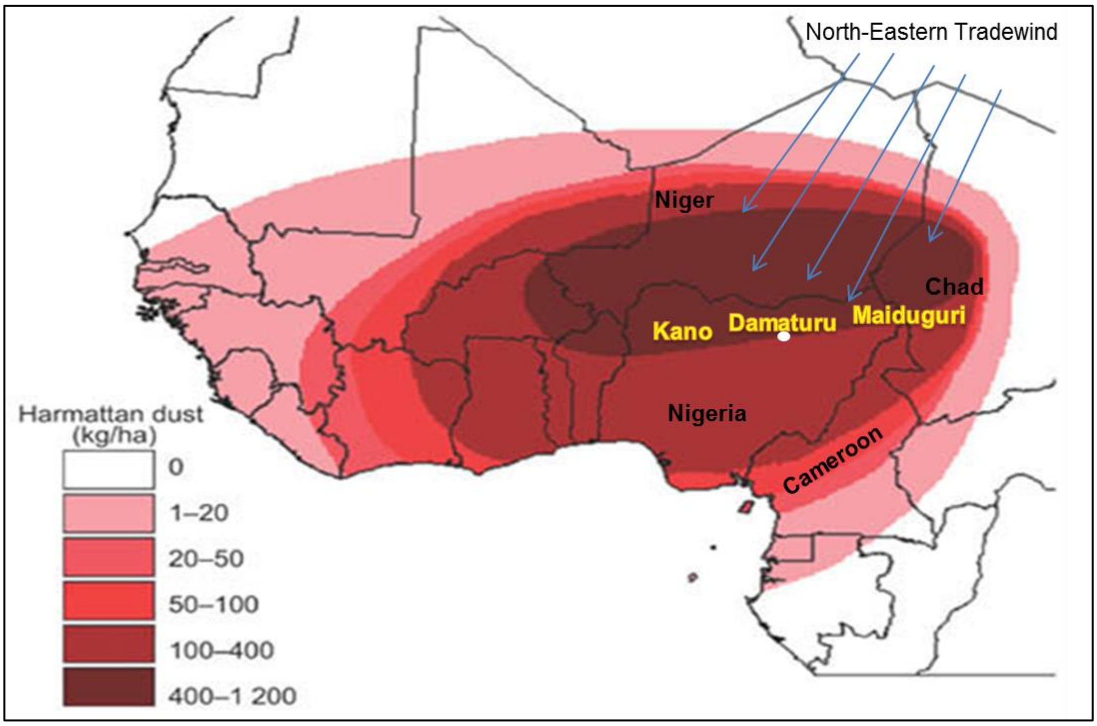
A research study carried out by Griffin, et al., (2002) reported that the Sahara is the major source on Earth of mineral dust (60-200 millions of tons per year) in the atmosphere. The dust is lifted by convection over hot desert areas to a very high altitude and then transported over distances of thousands of kilometres across the tropical Atlantic to the Caribbean and Florida. The frequency of Saharan dust storms has increased approximately 10-fold during the half-century since the 1950s, causing topsoil loss in Niger, Chad, northern Nigeria, and Burkina Faso and making Dust storm events responsible for injecting huge amounts of mineral dusts into the atmosphere, estimated as two billion metric tonnes annually (Griffin *et al.*, 2002). The deposition of Saharan dust has been observed over southern Europe, and less frequently, deposition occurs further north over the British Isles (Wheeler, 1986), the Netherlands, (Reiff *et al.*, 1986), Germany as well as Northern Scandinavia (Franzen *et al.*, 1994).

The Saharan Dust Storms envelop communities in the areas experiencing the event in a thick reddish dust. The event typically last for three to five minutes usually followed by rain and/or thunderstorm leaving behind heavy dust deposits (Matsumoto *et al.*, 2003). That Desert-dust storms disperse tons of soil and dried sediment of dust with the potential to induce regional health impacts such as asthma outbreaks, particularly in sensitive sub-populations like the elderly, infants, and adolescents, and ecosystem responses such as red tides or degradation of coral reefs due to infestation of foreign fungal or microbial populations. A gram of desert soil may contain as many as 1 billion bacterial cells; thus, the presence of airborne dust may be expected to correspond with increased concentrations of airborne microorganisms (Kanatani *et al.*, 2010). The Saharan dust transport is also said to be responsible for heavy metal mineral deposition in the tropical Atlantic and may have impacts on regional atmospheric chemistry via dust induced smog and heterogeneous reactions (Goudie and Middleton, 2001). The storm (desert) dust particulates may carry some toxic substances and pathogens into the atmosphere in addition to the native dust constituents that may create conditions conducive for novel outbreaks of disease (Griffin et al., 2004).

2.4.2 Harmattan Dust and its effects on Health

Harmattan dust, (fine particle dust, typically 0.5 µm–10 µm) is known to rise in the Sahara desert and is carried south by winds from that area. It is a common and widespread meteorological phenomenon in the savannah region of Africa and even reaches the coast for a brief period. The Harmattan is a dry and dusty wind resulting from storm activities in the Bilma and Faya Largeru area in the Chad Basin. This raises large amounts of dust into the atmosphere, which is then carried southwest by the predominant north-east trade winds, from the Sahara into the Gulf of Guinea, including Nigeria and other west African countries, between November and March (winter) every year (Achudume and Oladipo, 2009). In winter, an average of 700,000 tons of dust is produced in the Bodélé Depression each day. Diatoms from the dried banks of the receded fresh water lakes, once part of Mega-Lake Chad that make up the surface of the depression, are the source material for the Harmattan dust (Todd *et al.*, 2007). The composition of the Harmattan dust is complex, consisting of both inorganic and organic compounds, as well as microbial entities. For a greater part of the Harmattan period in Nigeria, the atmosphere often becomes heavily clouded with the Harmattan dust, causing a variety of domestic inconveniences as a result of the layers of dust that envelopes everything both indoors and outdoors (Adedokun *et al.*, 1989). During the weather event, the high amount of dust in the air can severely limit visibility and block the sun for several days, comparable to a heavy fog known as the Harmattan haze. This causes the cancellation and diversion of aircraft each year in most of West African countries like Niger, Nigeria, Chad, Benin, Togo, Ghana, Cote Devoir, and Sierra Leon (Dajab, 2006). Several studies on Harmattan dust in the West African sub-region have investigated the nature and distribution of Harmattan dust including Harmattan dust deposition in Ghana, and dust particle size in Mali (Breuning-Madsen and Awadzi, 2005; McTainsh *et al.*, 1997).

Figure 2.1 shows the intensity of the Harmattan dust as it is blown by the north-east trade winds across the sub-sahelian region of West Africa with north-eastern Nigeria having the highest Harmattan dust deposit.



(Adopted online@: blocs.extec.cat)

Figure 2.1 Distribution of Harmattan in the Sub-Sahelian Region

The Harmattan haze is composed of dust/fine-particulate matter that is associated with dry cold weather especially in northern Nigeria, which could trigger health problems associated with nasal congestion, cough, muscular aches, and pains (Dajab, 2006). Other reported symptoms are painful watery eyes known as ‘apollo’, and unusually high body temperature during the dustier Harmattan periods possibly due to the effects of the pollutants in the dust. Exposure to the dust particulates can also worsen existing conditions such as acute respiratory infections, pneumonia, and bronchitis (Adepetu *et al.*, 1988). Increases in levels of ambient particulate matter deposition rates and associated heavy metal (As, Cd, Cr, Cu, Fe, Ni and Pb) concentrations in northern Nigeria have been reported during the Harmattan season, with potential health and environmental effects (Dimari *et al.*, 2008).

2.4.3 Particulates in Air and Dust

Particulate matter (PM), also known as particle pollution, is a complex mixture of extremely small fractions of solid and liquid particles of organic and inorganic substances suspended in the air or in dust. Airborne particulates of significance to health have been classified (Morawska and Salthammer, 2006a) as follows;

PM_{10}, that is less than 10 µm in diameter (which is equivalent to about one-seventh of the width of a strand of human hair),

$PM_{2.5}$, which is smaller, measuring 2.5 µm or less and,

Ultrafine particles (UFPs) with less than 0.1 µm aerodynamic diameter.

PMs may contain primary particles derived from geological, biological, and combustion sources and secondary aerosols, formed by gas-to-liquid conversion (Veranth *et al.*, 2006). The particles are generated through various activities both outdoors and indoors and travel along often-unexpected pathways to areas that may be far from their sources. The ways of generating particulates and their subsequent release to the environment include natural sources, anthropogenic outdoor sources, and indoor sources (Morawska and Salthammer, 2006a) as shown in Table 2.2.

Table 2-2 Sources of particles (Morawska and Salthammer, 2006a)

Natural outdoor sources	**Anthropogenic outdoor sources**	**Indoor sources**
Forest fires (combination of smoke, dust and gas), sea salt, volcanic debris, particles formed from gaseous emissions of H_2S, NH_3, NO_x and HC, Dust storms.	Fuel combustion and industrial processes emissions, non-industrial fugitive emissions, transportation.	Human occupants; skin, hair, nail cuttings, plants, pets, cooking, building materials, mineral fibres-asbestos etc. Combustion appliances, tobacco combustion, air fresh aerosol, perfume, etc. Maintenance products such as paints, wood polish etc.

A study that involved the characterization of fine and ultrafine particles released from 13 different internal particle sources in a full-scale test chamber reported that humans and their activities do generate substantial amounts of particulate matter indoors, which potentially have a strong influence on short-term exposure (Afshari *et al.*, 2005). One of the significant factors that can contribute to increased indoor air pollutants is the use of biomass fuels such as wood, charcoal, crop residues, dung, coal, and kerosene. These are the primary source of energy for approximately half of the world's population and 80 per cent of the population of sub- Saharan Africa (Fullerton *et al.*, 2009; Fullerton *et al.*, 2008).

2.4.3.1 **Human Exposure to Particulates**

The WHO guidelines for air quality for 24-hour mean particulate matter levels are 50 µg m^{-3} for $PM_{10;}$ and 25 µg m^{-3} for $PM_{2.5}$ (World Health Organization, 2006). In many parts of the developing world, the peak indoor concentration of PM_{10} often exceeds 2,000 µg m^{-3}. PM concentrations of >30 000 µg m^{-3} were reported in Malawi homes by Fullerton et al.,(2009), where age, gender and socioeconomic differences critically, were said to affect the levels of exposure and the consequent health effects (Fullerton *et al.*, 2009; Ezzati, 2005).

Personal exposure to UFP can occur during cooking with firewood, kerosene stoves and gas cookers, burning of incense, use of insecticide sprays and during driving, smoking, and operating small appliances such as hair dryers and printers.

2.4.3.2 Health Effects of Particulates

The WHO (2005) report indicated that PM affects more people than any other pollutant and that the effects of PM on health occur at levels of exposure currently being experienced by most urban and rural populations in both developed and developing countries. Most epidemiological studies on large populations have been unable to identify a threshold concentration below which ambient PM has no effect on mortality and morbidity (World Health Organization, 2005; (Dockery, 2009). The PM number concentration levels in clean environments are usually in the order of a few hundred particles cm^{-3}. Ultrafine particles are widely believed to be responsible for the adverse effects of airborne particles upon health (Schwartz and Neas, 2000). The number of particles to which the individual is exposed is more important than their mass with the $PM_{2.5}$ and UFP fractions regarded as more dangerous since, when inhaled, they may reach the peripheral regions of the bronchioles, and interfere with gas exchange inside the lungs (Abbey et al., 1999). Exposure to PM in ambient air has been linked to a number of different health outcomes, starting from modest transient changes in the respiratory tract and impaired pulmonary function, and continuing to restricted activity/reduced performance, visits to the hospital emergency department, time lost from work and school, admission to hospital and death (Oberdörster, 2000; Schwartz and Neas, 2000).

Chronic exposure to particles contributes to the risk of developing cardiovascular and respiratory diseases, as well as of lung cancer. In developing countries, exposure to pollutants from indoor combustion of solid fuels on open fires or traditional stoves increases the risk of acute lower respiratory infections and associated mortality among young children; indoor air pollution from solid fuel use is also a major risk factor for chronic obstructive pulmonary disease and lung cancer among adults (Pope *et al.*, 1995). The mortality in cities with high levels of pollution exceeds that observed in relatively cleaner cities by 15–20 per cent. The collective evidence across disciplines indicates that some characteristics, including life stage genetic polymorphisms, pre-existing cardiovascular and respiratory diseases may increase the susceptibility of populations to PM-related health effects as shown in Table 2.3. Additional relevant characteristics (e.g. obesity and diabetes) have also been identified (Sacks *et al.*, 2011). According to Dionisio *et al.*, (2008), indoor air pollution from biomass fuels, especially when burned in open or poorly ventilated stoves contains high concentrations of many health-damaging pollutants and can be associated with an increased risk of childhood pneumonia. The burden of disease due to air pollution is predominantly in developing countries; with Asia estimated to contribute approximately two-thirds of the global burden expressed as the disability-adjusted life year (DALY - the number of years lost due to ill health, disability or early death). The overall burden of air pollution from all sources considered in the indoor, outdoor, and occupational environments account for about 1.9 million premature deaths annually (Cohen *et al.,* 2005).

Table 2-3 Susceptibility to PM-related health effects (Sacks et al., 2011)

Characteristic	**Susceptible population**
Life stage	Children (< 18 years of age) Older adults (≥ 65 years of age)
Sex	No evidence
Genetic factors	Genetic polymorphisms
Pre-existing diseases	Respiratory diseases: asthma, diabetes (Little evidence), COPD(little evidence)
Obesity	Increased BMI - Little evidence
Socioeconomic status	Low educational attainment, Low income

BMI-Body mass index COPD-chronic obstructive pulmonary disease

2.4.4 Microbial Flora in Air and Dust

In addition to gases, dust particles and water vapour, air also contains microorganisms as vegetative cells and spores of bacteria, fungi, algae, viruses and protozoan cysts. Though they occur in relatively small numbers in air when compared with soil or water, air is mainly a transport or dispersal medium for microorganisms with the main source of airborne microorganisms indoors being human beings. Humans and animals shed their surface flora and these are disseminated into the air. Similarly, the commensal as well as pathogenic flora of the upper respiratory tract and the mouth constantly discharged into the air by activities like coughing, sneezing, talking, and laughing (Horak, 1987).

Fungal spores are ubiquitous in outdoor air and often constitute the dominant biological components of air. The diameter of most fungal spores is in the range of 2–10 µm, allowing easy penetration of the lower airways of the human respiratory tract, from where infection by pathogens and their subsequent dissemination is possible (O'Gorman and Fuller, 2008). Dispersion and dilution by a large volume of air is an inherent mechanism of air sanitation in outside air. The chance for the spread of infectious disease is higher in indoor air, especially in areas where people gather in large numbers, for example, in theatres, schools etc., resulting in higher concentrations of disease causing pathogens in indoor air (Jo and Seo, 2005).

The numbers and types of fungal spores in air vary greatly in response to different factors (Jones *et al.*, 2000). Experimental studies have also demonstrated that spores as well as fragments that are smaller than spores can be released from fungal cultures by an air stream. This has been shown for several species, e.g. *Aspergillus versicolor, Cladosporium cladosporoides, Penicillium melinii, Streptomyces albus, Trichoderma harzianum*, and *Ulocladium species* (Górny *et al.*, 2002; Meyer *et al.*, 2005).

2.4.4.1 Effect of Micro Flora on Health

Microflora in air are responsible for several allergic disorders with a range of airborne bioparticles, such as pollen, fungal spores, insect debris, animal dander, mites etc. being recognised allergens. A study has reported that 469 (50%) out of 936 children who underwent allergy skin testing, had a positive allergy skin test to at least one positive-reaction to *Alternaria*, *Aspergillus*, *Cladosporium*, or *Penicillium* species of fungi (O'Connor *et al.*, 2004). The indoor environments of different buildings have their own pattern of bacteria in indoor dust, which includes species normally found in the human gut. A Finnish-based research team investigated the species level diversity and seasonal dynamics of bacterial flora in indoor dust by sequencing DNA from the dust samples collected. They reported that the microbial flora from indoor dust samples from two buildings they investigated was complex and dominated by bacterial groups originating from users of the buildings. As people spend most of their lives in different indoor environments: homes, schools, workplaces; they are constantly challenged by airborne microbes (Rintala *et al.*, 2008). There are droplets, and infectious dust and these are categorized according to whether they are allergenic, infectious, or capable of inducing toxic or inflammatory reactions when inhaled (Jo and Seo, 2005).

The indoor fungal exposure can be reduced by removing moisture from the indoors and proper maintenance of air filters, A noticed presence of fungal contamination can be cleaned with a dilute bleach solution which kills viable colonies and removes their mycelia (Portnoy *et al.*, 2005).

2.4.4.2 Characterization of Microbial Pollutants in Air and Dust

The microbial components of airborne particles may vary in quantity and quality depending on the situation of the building, activities, and on seasonal changes. Microorganisms can be carried within airborne particles and eventually settle in dust as shown in a study where dust samples were collected from the cuttings of archival bindings and from shelves in libraries in state archives in Rome, Italy, on sterile Millipore samplers during summer and winter periods (Maggi *et* *al.*, 2000). They also found that *Cladosporium* species dominated in the winter dust samples and *Penicillium* species were dominant in summer dust samples. In another study, eighty volatile organic compounds were identified in dust collected from mouldy buildings in the USA of which forty were identified as possible microbial metabolites. The report indicated the presence of metabolites of microbial-volatile organic compounds of fungal species (*Penicillium commune*, *Chrysogenum*, and *Aspergillus versicolor*) and bacterial species such as actinomycetes (Wilkins *et al.*, 2004).

2.4.5 Metal Contaminants in Air and Dust

Heavy metals occur in both natural and contaminated environments and at high concentrations are of concern because of the risk to public health (Fergusson and Kim, 1991). In natural environments, they generally occur at low concentrations. However, at high concentrations, as is the case in contaminated environments, they result in public health impacts. The elements that are of particular concern include lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), zinc (Zn), nickel (Ni), and copper (Cu). Heavy metals released into the environment come from metal smelting and refining industries, scrap metal, plastic and rubber industries, and are released from consumer products and from burning of waste containing these elements. The metals found in street dust such as Cd, Cu, Ni, Pb, and Zn, are mostly generated from road traffic, worn out vehicle parts, tyres and from burning fossil fuels causing pollution in different environmental media (Rashed, 2008). On release to the air, the elements travel for large distances and are deposited onto the soil, vegetation, and water. Once deposited, these metals are not degraded and persist in the environment for many years with potential for human exposure through inhalation, ingestion, and skin absorption (Fergusson and Kim, 1991).

Charlesworth et al., (2011) reviewed the evolution, state of the art and future lines of research on the sources, transport pathways, and sinks of particulate trace elements in urban terrestrial environments including the atmosphere, soils, and street and indoor dusts. Their study (in Milton Keynes, UK) highlighted the reductions in the emissions of some elements of historical concern such as Pb, with interest consequently focusing on other toxic trace elements such as As, Cd, Hg, Zn, and Cu.

2.4.5.1 Effects of Metal Pollutants on Health

Metals are emerging as an important class of human carcinogens, for instance As, Cd, chromium VI, beryllium (Be), and Ni have been recognised as human carcinogens though the mechanism(s) responsible for metal carcinogenesis is elusive, partly because of the complex nature of metals' interactions in biological systems, with many following similar metabolic pathways as essential metals. This is probably the result of similar binding preferences between carcinogenic metals and nutritionally essential metals (Florea and Büsselberg, 2006).

Studies have indicated the possibility that metals in the indoor dust can accumulate in humans, either directly or indirectly by inhalation, ingestion because of hand-to mouth activity or via dermal contact absorption (Al-Rajhi *et al.*, 1996; Mølhave *et al.*, 2000). The extent to which atmospheric metals can be a health hazard depends on their ability to penetrate the respiratory system (Lemus *et al.*, 2011), and acute exposure may lead to nausea, anorexia, vomiting, gastrointestinal abnormalities, and dermatitis. An outbreak of fatal childhood lead poisoning because of gold mining activities in family compounds was reported to have occurred in two villages of north-western Nigeria between 2009 and 2010. This resulted in high exposures and the death of 581 children <5 years of age with 204 out of 345 children of <5 years old suffering from lead poisoning within the two villages (Dooyema *et al.*, 2012). The high exposures to metal pollutants which are consequently fatal among children is attributed to the fact that they spend most of their time indoors and mostly in contact with contaminated floors, engaging in mouthing of hands, toys and other objects or eating food using contaminated hands (Muhamad-Darus *et al.*, 2011). Some heavy metals with established health effects are listed in Table 2.4.

Table 2-4 Toxic metals with established health effects (Kimani, 2007)

Metal	**Sources of Environ mental exposure**	**Minimum Risk level**	**Chronic exposure toxicity effects**
Lead	Industrial, vehicular emissions, paints and burning of plastics, papers, etc.	Blood lead levels below 10 µg dl^{-1} of blood*	Impairment of neurological development, suppression of the haematological system and kidney failure
Mercury	Electronics, plastic waste, pesticides, pharmaceutical and dental waste	Below 10 µg dl^{-1} of blood* Oral exposure of 4 $mg^{-1}kg^{-1}$ day**	Gastro-intestinal disorders, respiratory tract irritation, renal failure and neurotoxicity
Cadmium	Electronics, plastics, batteries and contaminated water	Below 1 µg dl^{-1} of blood*	Irritation of the lungs and gastrointestinal tract, kidney damage, abnormalities of the skeletal system and cancer of the lungs and prostate

µg dl^{-1}* micrograms per deciliter of blood; mg kg^{-1}** milligrams per kilogram body weight

2.4.5.2 Characteristics of Metal Pollutants in Dust

A German study found a seasonal variation in dust precipitation and chemical dust composition with the highest concentrations of trace elements occurring during winter and the highest deposition of dust during summer (Nora and Stüben, 2009). Areas of different land use are distinguished by their specific patterns of atmospheric dust and trace element precipitation. For instance, dusts emitted from industrial areas with fossil fuel processing are enriched in vanadium (V), nickel (Ni) and cobalt (Co). Dusts of other urban sites are influenced by diffuse pollution caused by non-point and dispersed pollution sources, or by specific industrial emissions (Norra and Stüben, 2009). Joshi et al., (2009) collected samples of street dusts on a weekly basis for 6 months (from three different locations in Singapore, viz. residential, commercial and industrial areas). The concentration of 13 elements was determined; aluminium (Al), arsenic (As), cobalt (Co), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), titanium (Ti), vanadium (V), and zinc (Zn). They found the concentrations showed considerable variations between sites, and within the same site over a period of time. The mobility and potential bio-availability of the trace elements from dust was in the order; Cd greater than Zn, Pb greater than Mn, Cu greater than Fe. Dust samples collected from the industrial area were of serious concern, as they comprised elevated concentrations of most of the potentially toxic metals such as Cd, Cr, Cu, Pb, and Zn.

Chineke and Chiemeka (2010) carried out the determination of the elemental composition of air collected during the Harmattan season at Uturu, south-eastern Nigeria. The analysis was undertaken using atomic absorption spectroscopy following wet acid digestion and they reported the results obtained as; K 6.50 mg cm^{-3}, Mg 9.1 mg cm^{-3}, Ca 331.1 mg cm^{-3}, Fe 47.7 mg cm^{-3}, Zn 81.6, mg cm^{-3} Mn 12.8 mg cm^{-3}, and Pb 1.2 mg cm^{-3}. Gomez et al., (2003) determined platinum (Pt), palladium (Pd), and rhodium (Rh) in airborne dust (from Madrid) and road dust (from Graz, Austria) by ICP-MS analysis and suggested a possible increase in soil fertility because of heavy dust fall. In a study of metals in indoor and outdoor dust in Riyadh, Saudi Arabia, concentrations of Cd, Cr, Cu, Li, Ni, Pb, and Zn have been investigated in relation to particle sizes using atomic absorption spectroscopy indicating high metal concentrations in fine particles (Al-Rajhi *et al.*, 1996).

2.4.6 Volatile Organic compounds (VOCs) and semi-Volatile Organic compounds (SVOCs) Pollutants

These chemicals contain organic carbon, and are usually present as solvents such as in paint wastes, dry cleaning chemicals, furniture stripper, cleaners, cosmetics and waste sludges. Many are considered as hazardous to the environment and health. In the indoor sciences, it is common to categorize organic compounds into very volatile organic compounds (VVOCs), volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) (WHO, 1987). VOCs include a variety of chemicals such as benzene some of which may have both short- and long-term health effects.

Phthalates and phosphate esters, which are SVOCs, adsorb to solids such as airborne particles and settled dust and partition between gaseous and particulate phases (Weschler, 2004; Weschler *et al.*, 2008; Weschler *et al.*, 2006). Phthalates, saturated aldehydes, carboxylic acids, and hydrocarbons have been shown to be dominant in desorbed VOCs from household dust while indoor air is characterized by the presence of primary aromatic and aliphatic hydrocarbons and aldehydes (Wilkins *et al.*, 2004; Hirvonen *et al.*, 2004). The World Health Organization (WHO, 1989) gave the classification of the organic compounds as shown in Table 2.5.

Table 2-5 Classification of organic chemical pollutants (WHO, 1989)

Classification of organic chemical pollutants		
Abbreviation	**Boiling point range (˚C)**	**Example of compounds**
VVOCs	<0 to 50-100	Propane, butane, methyl chloride formaldehyde
VOCs	50-100 to 240-260	d-limonene, toluene, acetone, toluene, ethanol (ethyl alcohol) 2-propanol(isopropyl alcohol), hexanal
SVOCs	240-260 to 380-400	Pesticides (DDT, chlordane), plasticizers (phthalates), fire retardants (PCBs)

2.4.6.1 Effects of Organic Chemical Pollutants on Health

People spend most of their time in indoor environments such as schools, work places and homes thus, they get exposed more to pollutants present in the indoor than the outdoor environment (Mercier et al., 2011; Ali et al., 2011). Studies have found that organic chemical pollutant levels are generally higher in indoor than outdoor environments (Wang *et al.*, 2007a).

Many organic chemical contaminants are irritants to the eyes and mucous membranes; mixtures of different VOCs at low levels are capable of acting synergistically to elicit neural behaviours (Mølhave *et al.*, 1997; Hirvonen *et al.*, 2004). An association between phthalates exposure and endocrine disruption and cancer have been reported by several in- vivo studies (Falconer *et al.*, 2006; Rudel and Perovich, 2009; Hwang *et al.*, 2008). In an observational study by Lopez-Carillo et al., (2010), it was reported that indoor biological and chemical agents causing short term respiratory and inflammatory health effects may potentially lead to chronic, long term health impacts and health effects which may be experienced soon after exposure or, possibly, years later.

Much of the concern about health risks from dust is because of the organic compounds contained within it (Wilson et al., 2001). Phthalates and phosphate esters are SVOCs which may have both short term, and cumulative health effects (Weschler *et al.*, 2008; Langer *et al.*, 2010). The growing concern about the impact that chemicals in the household environment have on our health has led to increased studies over the years (carried out by organisations such as the Worldwide Fund for Nature (WWF) and Greenpeace) to assess the levels of chemicals in homes throughout Europe, and their potential consequences for individuals of exposure (Weber *et al.*, 2011). Both studies reported high levels of potentially harmful chemicals in household dust. Some of them can cause allergy, hypersensitivity, respiratory and toxicological problems (Clausen *et al.*, 2012). A number of negative health effects related to the inhalation and ingestion of dust have been identified which include decreased lung function, coughing, wheezing, and shortness of breath, chronic obstructive pulmonary disease, and lung cancer (Morawska and Salthammer, 2006a; Salo *et al.*, 2009).

Effects of Short term Exposure to Organic Pollutants: Immediate health effects of most organic chemicals found in indoor may show up after a single exposure or repeated exposures. These health effects include irritation of the eyes, nose, and throat, headaches, dizziness, and fatigue. Such immediate effects are usually short-term and treatable. Sometimes the treatment is simply eliminating the identified source of pollutants. Symptoms of some diseases, including asthma, hypersensitivity pneumonitis, and humidifier fever, may also show up soon after exposure to some indoor air pollutants. The likelihood of immediate reactions to indoor air pollutants depends on several factors; age and pre-existing medical conditions are two important influences. In other cases, whether a person reacts to a pollutant depends on individual sensitivity, which varies tremendously from person to person (Dong *et al.*, 2011).

Long-term Effects of Exposure to Organic Contaminants: Other health effects may manifest either years after exposure has occurred or only after long or repeated periods of exposure. These include some respiratory diseases, heart disease, and cancer, which can be severely debilitating or fatal. While pollutants commonly found in indoor environments are responsible for many harmful effects, there is considerable uncertainty about what concentrations or periods of exposure are necessary to produce specific health problems. People also react very differently to exposure to indoor air pollutants (Dong *et al.*, 2011).

2.4.6.2 **Characterization of Organic Chemical Pollutants**

To determine organic chemicals in dusts researchers have used various methods of sample desorption; these include headspace, thermal desorption (Wilkins *et al.*, 2004; Brown and Crump, 2008), solvent extraction using dichloromethane and solid phase micro extraction (SPME) in combination with gas chromatography (GC). In separate comparative reviews of exposure assessment for organic contaminants in settled house dust by solvent extraction and thermal desorption methods, they reported that thermal desorption had reduced sample preparation time, less extraction procedures and eliminated use of residual hazardous solvent waste (Wallace *et al.*, 1985; Mercier *et al.*, 2011).

The most common methods of measuring VOC concentrations in air are by use of adsorbents and evacuated canister sampling, with increased overlap between the two methods over the years (Wallace *et al.*, 1985; Mercier *et al.*, 2011; Dimitroulopoulo *et al.*, 2005). Some researchers have used the method of trapping air vapour using multi-sorbent tubes (e.g. Carbotrap-70 mg / Carbo pack-100 mg) and a portable pump. Thermal desorption of air samplers is generally more favourable than solvent desorption because it involves less dilution of the collected VOCs and thereby has higher sensitivity. The sorbent

Tenax can be reused many times, although drawbacks include artefact formation of several chemicals (e.g. benzaldehyde, phenol) and an inability to retain very volatile organic chemicals (e.g. vinyl chloride, methylene chloride) with specific sorbents used for these chemicals.

Wilkins *et al.,* (2004) reported that VOC emissions from mould infected building materials (40 compounds) and VOCs desorbed from Danish house dusts (55 compounds) contained many known microbial volatile organic compounds (MVOCs) and/or their oxidation products, including alcohols, ketones, esters, carboxylic acids, as well as a few monoterpenes. The studies conducted by Hirvonen *et al.*, (2004) on thermal desorption of settled household dust samples showed organic emission from desorbed household dust is composed mainly of aliphatic aldehydes containing 6 to 13 carbon atoms (C_6-C_{13}), aliphatic carboxylic acids and their esters with 8 to 18 carbon atoms (C_8-C_{18}), n-alkanes with 1 to 30 carbon atoms (C_1-C_{30}), and phthalates. Some of the thermally desorbed volatile organics in indoor house dust are shown in Table 2.6.

Table 2-6 Thermally desorbed compounds in household dust (Hirvonen et al., 1994)

Compound		Compound	
1	Toluene	18	Phenanthrene
2	Hexanal	19	Octadecane
3	Heptanal	20	Pentadecanoic acid
4	Octanal	21	Phthalate, butyl-2- methylpropyl ester
5	Nonanal	22	Palmitic acid
6	Octanoic acid	23	Heptadecanoic acid
7	Trichlorobenzene	24	Eicosane
8	Decanal	25	Heptadecane, 2,6,10,15 tetramethyl
9	Nonanoic acid	26	Stearic acid
10	Decanoic acid	27	Docosane
11	Undecanoic acid	28	Tricosane
12	Ethanone, 1,1-(1,3-phenylene)	29	Tetracosane
13	Lauric acid	30	Pentacosane
14	Diethyl phthalate	31	Phthalate, diisooctyl ester
15	Tridecanoic acid	32	Hexacosane
16	Heptadecane	33	Heptacosane
17	Myristic acid		

Phosphate esters, branched alkanes, n-alkenes, n-alkanones, monoterpenes, aromatic hydrocarbons, and aromatic and aliphatic alcohols were also well-represented groups in household dust samples. Polyaromatic hydrocarbons, nicotine, benzoic acid, naphthalene, amides, and chlorinated benzenes were also present in some samples. The study identified the presence of 95 organic compounds from the dust samples with the majority of detected compounds being typical for all analysed dust samples, and the relative distribution of the compounds in all samples was very similar. This suggested that the general sources in dwellings, which are similar from home to home, affect the composition of dust. It has been estimated that about half of the total volatile organic compounds concentration in the indoor air of homes may be generated by the occupants themselves or by their activities (Dimitroulopoulo *et al.*, 2005).

Many studies have shown that indoor dust is an important source of exposure to organic chemical pollutants (Hirvonen et al., 1994, Lioy et al., 2002, Mercier et al., 2011, Ali et al., 2011). House dust acts as a sink and repository for chemical organic compounds present in indoor consumer products (intentionally or non-intentionally added to the products) during their production to perform various desirable functions. These chemicals include phthalates, brominated flame-retardants, polyvinyl chloride and other SVOCs and VOCS. Exposure of humans to these chemicals may occur via inhalation, dermal absorption, and dietary intake (Guo and Kannan, 2011). For measurement convenience, the indoor VOC mixture is often characterized as total volatile organic compounds (TVOC) and used as an indicator of building air healthiness. The effectiveness of using TVOC as an indicator of indoor air quality, however, has been increasingly questioned, given that large differences in health effects exist among different individual VOCs and that different indoor environments may comprise distinct VOC mixtures (Wilkins *et al.*, 2004; Wolkoff and Wilkins, 1994; Wolkoff and Wilkins, 1994). Housing characteristics have been attributed to increased exposure to indoor pollutants as reported by Bornehag et al. (2005) who found that age of a building, type, and quality of furniture, furnishings as well as paintings and floorings are associated with pollutant concentrations in the indoor dust. Eight phthalates were analysed in 21 household dusts in Kuwait and the variation of the contaminants between homes was reported as being the result of possible differences in the types of products used in each household (Gevao *et al.*, 2012).

Phthalates are a group of organic chemicals that are used in a large variety of products, from enteric coatings of pharmaceutical pills and nutritional supplements to viscosity control agents, gelling agents, film formers, stabilizers, dispersants, lubricants, binders, emulsifying agents, and suspending agents. End-applications include adhesives and glues, agricultural adjuvants, building materials, personal-care products, medical devices, detergents and surfactants, packaging, children's toys, modelling clay, waxes, paints, printing inks and coatings, pharmaceuticals, food products, and textiles. Phthalates are easily released into the environment because there is no covalent bond between the phthalates and plastics in which they are mixed. As plastics age and break down, the release of phthalates accelerates. Phthalates in the environment are subject to biodegradation, photodegradation, and anaerobic degradation; therefore, in general, they do not persist in the outdoor environment. Outdoor air concentrations are higher in urban and suburban areas than in rural and remote areas. In general, indoor air concentrations are higher than outdoor air concentrations due to the nature of the sources. Because of their volatility, diethylphthalate (DEP) and dimethylphthalate (DMP) are present in higher concentrations in air in comparison with the heavier and less volatile DEHP. Higher air temperatures and PVC may result in higher concentrations of BBP and DEHP, which are more prevalent in dust (Rudel *et al.*, 2010), with phthalates frequently used in soft plastic fishing lures, caulk, paint pigments, and so-called jelly rubber (Schettler, 2005; Heudorf *et al.*, 2007). Phthalates are used in a variety of household applications such as shower curtains, vinyl upholstery, adhesives, floor tiles, food containers and wrappers, and cleaning materials. Personal-care items containing phthalates include perfume, eye shadow, moisturiser, nail polish, liquid soap, and hair spray. They are also found in modern electronics and medical applications such as catheters and blood transfusion devices (Fromme *et al.*, 2004).

The most widely used phthalates are di-2-ethyl hexyl phthalate (DEHP), diisodecyl phthalate (DIDP), and diisononyl phthalate (DINP). DEHP is the dominant plasticizer used in polyvinylchloride (PVC) due to its low cost. Benzylbutylphthalate (BBP) is used in the manufacture of foamed PVC, mostly used as a flooring material. Phthalates with small R and R' groups are used as solvents in perfumes and pesticides (Kolarik *et al.*, 2008). Phthalates and other SVOCs in settled dust have been ranked based on their specific health effects in the indoor environment (ranging from reprotoxic or developmental effects, endocrine disrupting mechanisms, and neurotoxic effects) which may pose a global concern, considering the most susceptible populations at risk which are women, children and the elderly (Bonvallot *et al.*, 2010). Some of the commonly used phthalates are shown in Table 2.7.

Table 2-7 Common phthalates used in household products

Name	Acronym	Structural formula	CAS no.
Dimethyl phthalate	DMP	$C_6H_4(COOCH_3)_2$	131-11-3
Diethyl phthalate	DEP	$C_6H_4(COOC_2H_5)_2$	84-66-2
Diallyl phthalate	DAP	$C_6H_4\ (COOCH_2CH{=}CH_2)_2$	131-17-9
Di-n-propyl phthalate	DPP	$C_6H_4[COO(CH_2)_2CH_3]_2$	131-16-8
Di-n-butyl phthalate	DBP	$C_6H_4[COO(CH_2)_3CH_3]_2$	84-74-2
Diisobutyl phthalate	DIBP	$C_6H_4[COOCH_2CH(CH_3)_2]_2$	84-69-5
Butyl cyclohexyl phthalate	BCP	$CH_3(CH_2)_3OOCC_6H_4COOC_6H_{11}$	84-64-0
Di-n-pentyl phthalate	DNPP	$C_6H_4[COO(CH_2)_4CH_3]_2$	31-18-0
Dicyclohexylphthalate	DCP	$C_6H_4[COOC_6H_{11}]_2$	84-61-7
Butyl benzyl phthalate	BBP	$CH_3(CH_2)_3OOCC_6H_4COOCH_2C_6H_5$	85-68-7
Di-n-hexyl phthalate	DNHP	$C_6H_4[COO(CH_2)_5CH_3]_2$	84-75-3
Diisohexyl phthalate	DIHxP	$C_6H_4[COO(CH_2)_3CH(CH_3)_2]_2$	146-50-9
Diisoheptyl phthalate	DIHpP	$C_6H_4[COO(CH_2)_4CH(CH_3)_2]_2$	41451-28-9
Butyl decyl phthalate	BDP	$CH_3(CH_2)_3OOCC_6H_4COO(CH_2)_9CH_3$	89-19-0
Di(2-ethylhexyl) phthalate	DEHP	$C_6H_4[COOCH_2CH(C_2H_5)(CH_2)_3CH_3]_2$	117-81-7

(From various sources including Fromme et al., 2004; Clausen et al., 2003)

2.4.6.3 Chemistry of the Indoor Environment

Surface chemistry greatly influences human exposure to reactants and products in indoor environments. Chemistry that occurs at interfaces is important because compared with outdoor settings, the available surface area is extremely large relative to the building volume; surface sorption extends the average residence time of reactants and increases the probability that conversions will occur; and unique compositions and morphologies at indoor surfaces can promote some reactions or promote selectivity in reaction pathways. Because many people spend 80–90% of their time indoors, this chemistry can have a dramatic impact on personal exposure (Morrison, 2008). One of the most notable reactions is that of ozone on indoor surfaces, which can result in a 2 to 10-fold reduction in indoor ozone concentrations while simultaneously increasing levels of the products of ozone reactions (Morrison, 2008). Ozone can occur indoors because of its occurrence in outdoor air, and its release from some indoor sources such as some electrical equipment e.g. photocopiers. Known ozone-reactive chemicals include nicotine from cigarette smoking, pesticides such as cypermethrin, and terpenes found in cleaning or other scented products. Researchers have shown that cleaning products and air fresheners enhance ozone uptake at surfaces and that sorbed compounds accounted for half of ozone reactions in some cases.

Early work on nitrogen oxides (NO_x) surface chemistry showed that NO_2 could react with water on smog chamber surfaces to generate nitric acid (HNO_3) and volatile nitrous acid (HONO) (Sakamaki *et al.*, 1983). A study by Sleiman *et al.* (2010) showed that this chemistry also occurs on indoor surfaces and can generate HONO levels that exceed outdoor levels of NO_x released from gas burners. Nitric acids are also said to possibly participate in chemistry and photolysis that releases nitric oxide (NO) and HONO making indoor surfaces act as sinks for NO_2, a reservoir for HNO_3, and a source of HONO and possibly NO (Sleiman *et al.*, 2010). Nitrate radicals are important oxidants in the low-light environments that are unique to indoor spaces (Weschler *et al.*, 1992).

Also of emerging importance is hydrolysis, which can generate toxins and odours. The plasticizer di-2-ethylhexylphthalate (DEHP) can be hydrolysed, generating monoethylhexylphthalate (Lundgren *et al.*, 2004), and the hydrolysis products may be associated with asthma (Norback *et al.*, 2000). DEHP and other plasticizers commonly found in vinyl flooring and adhesives, where highly basic concrete flooring and gypsum board may help in catalysis of the hydrolysis. In an intensive study of paint components, researchers identified hydrolysis products of Texanol isomers, including isobutyric acid (strong odour), emitted in the first few days after application to gypsum board (Levin, 2008). Hydrolysis reactions are slower than the ozone and NOx reactions and mediated by local pH and moisture conditions. New compounds can also result when VOCs react with hydroxyl nitrate radicals or ozone present in indoor environments.

2.4.6.4 **Health effects of Indoor Chemical Reactions**

The combined reactions of chemicals in the indoor environment are known to have health effects in which all chemicals in the mixture contribute to toxicity (Grudd *et al.*, 2011). Studies exposing animals to products of chemical reactions such as ozone mixed with limonene demonstrated that the reaction products had a significant impact on the breathing rate of the exposed animals when compared to the animals exposed to the reactants separately (Rohr *et al.*, 2003; Wilkins *et al.*, 2001). It has been reported that exposure of human lung cells to oxidized atmospheric environments can cause an increase in interleukin-8 mRNA, which is associated with an enhanced inflammatory response (Sexton *et al.*, 2004).

Epidemiological studies have also found that workers exposed to diacetyl (an oxygenated organic compound) have had twice the expected rates of physician-diagnosed asthma (Kreiss *et al.*, 2002; Mendell *et al.*, 2002). One possible connection between reaction products and health effects is that oxygenated organic compounds reduce the release of an epithelium-derived relaxing factor, which can lead to a damaged and thus more susceptible epithelium (Anderson *et al.*, 2007). A hazard assessment tool developed for asthma based on chemical structure concluded that chemicals with bifunctional reactivity (for instance, two carbonyl groups) were strongly associated with occupational asthma (Jarvis *et al.*, 2005). Reformulation of many household cleaners to include more green and plant-derived compounds such as α - and β-pinene, a-terpineol, citronellol, geraniol, and b-irisone is likely to cause increases in the concentrations of terpenes, terpene alcohols, and ethers in indoor environments. In addition, the investigations of the gas-phase chemistry of the chemicals mentioned above have identified oxygenated organic compound reaction products such as the a,b-dicarbonyls glyoxal, diacetyl, methylglyoxal, and the simple sugar glycolaldehyde (Hakola *et al.*, 1994). The results highlight that VOCs present in the indoor environment can be transformed into oxidized organic reaction products, and biological systems could be affected after exposure to these compounds. While indoor chemistry can be controlled by controlling the sources, reactants, and conditions that promote that chemistry, ozone has been identified as a clear target, with its removal from buildings predicted to lower indoor concentrations of aldehydes, ketones, organic acids, free radicals, and secondary organic aerosols (Weschler *et al.*, 2006).

2.5 Settled Dust Sampling

Although a lot of work has been done in the area of indoor environments and health with the analysis of pollutants in airborne and house dusts, there is currently no international standard method for settled house dust sampling. Various sampling techniques for settled carried out by different researchers include the most common methods that involved using vacuum cleaners and wiping of surfaces (Gordon *et al.*, 1999), but a variety of other methods have been used: collection of settled indoor dust on adhesive carbon spectrotabs (Vaughan et al., 2002) for particle characterisation by using a scanning electron microscope (SEM); collection on filters as carried by Horwell et al., (2003); and on pre-weighed petri dishes for photometric methods (Fullerton et al., 2009).

In a major survey to measure exposure to chemicals in Europe, the investigators used a vacuum cleaner with a dust filter bag (Santillo *et al.*, 2003).

A vacuum cleaner was also utilised in a pilot study carried out in Canada to identify different semi-volatile organic pollutants present in residential house dusts (Zhu and Aikawa, 2000), where six houses were included in the study and the dusts collected into vacuum bags, then sieved in order to separate the fine dust for analysing in the laboratory. A vacuum cleaner with modification was also used to collect dust in a study designed to investigate whether there was an association between asthma and allergic symptoms in children and phthalates in house dust (Bornehag *et al.*, 2005). In another study, dust samples were collected from household vacuum cleaner bags of 513 homes in a US study of pesticide levels (e.g. propoxur, chlorpyrifos, diazinon, permethrin, chlordane 2,4-dichlorophenoxyacetic acid and dicamba), and the participants were asked to complete questionnaires giving information about the their houses (Colt *et al.*, 2004). The authors reported that wipe sampling techniques have generally been found to give results with limited repeatability, and where adjacent areas have been sampled the results were variable. The use of a vacuum cleaner has been reported as having the disadvantage of not collecting some of the finer particles and these constitute the inhalable particle sizes, which are an important determiner of exposure (Butte and Heinzow, 2001). Vacuum cleaner dusts have been used in America for the development of a standard reference material for house settled dust (Bergh *et al.*, 2011; Poster *et al.*, 2007).

2.6 Collection of Airborne Samples

Diverse means of collecting airborne particles and vapours both passively and actively within the indoor/outdoor environments have been developed and employed by different researchers depending on the availability and suitability of the equipment for the sample and type of analysis to be carried out (Gordon *et al.*, 1999; Brown *et al.*, 1992).

The collection of airborne vapours for the analysis of organic chemicals have been carried out by the use of samplers such as sorbent tubes containing different sorbent materials such as Tenax TA, carbotrap, quartz wool, either singly or in combination (Woolfenden, 2010; Brown, 1996), and disc-type filters

(Yoshida *et al.*, 2004). For airborne particulates, approaches include personal measurement of PM_{10} using impactor-personal environmental monitors (PEM) (Janssen *et al.*, 1998), ultrafine particles counting by condensation particle counter (CPC) using P-Trak, and a Malvern APC 300 optical particle counter (OPC) (Afshari, 2005).

Biological monitoring in the indoor/outdoor environment has been carried out by using various sampling techniques for microbial spores with different analytical methods included culture, immunoassays, and bioassays. Examples of impact air samplers are Buckard biological monitors, Andersen-6 stage samplers and cassette filters (Martinez *et al.*, 2004).

2.7 Analyses of Settled Dust

Various techniques including gravimetric methods such as particulate counting, particulate size and shape determination, as well as international standard analytical techniques such as GC/MS and ICP/MS have been employed in order to characterize the heterogeneous constituents of house dusts.

2.7.1 Physical Characterization of Settled Dust

The investigation of sizes and shapes of dust particles conducted by researchers to determine the nature and source of the particles include the study of dust collected during a dust storm from the Bodele depression in 2002 and examined by SEM (Eckardt *et al.*, 2010). Further examples of the use of SEM images are a study of dust particulates collected from traffic junctions by Washington et al., (2003) and for characterization of settled dust collected from three University buildings in Wolverhampton, UK (Shilton *et al.*, 2002).

2.7.2 Analysis of Organic Chemicals in Dust

There are various methods used for analysing organics in dust samples. Generally, most studies have involved the dust samples sieved, solvent or thermally extracted and then analysed using gas chromatography combined with mass spectrometry (Leese *et al.*, 1997; Leese *et al.*, 1997; Mercier *et al.*, 2011; Norra and Stüben, 2009; Norra and Stüben, 2009; Nazaroff, 2008). In some instances researchers have used gas chromatography-UV spectrometry (Nilsson *et al.*, 2005), and LC-MS/MS (Vishwanath *et al.*, 2011). The majority of the literature reviewed used gas chromatography (GC) as their primary method of analysing the collected dust samples for organic chemicals. GC is a useful technique to use whereby the mixture of components is separated according to their volatility and their strength of interaction with the packing/coating material used in the GC column. The extraction process used in a number of studies is complex and resource intensive. In a study looking at pesticide concentrations in dust, the extraction consisted of numerous steps including, sieving the dust, spiking with a surrogate and Soxhlet extraction (Colt *et al.*, 2004). Solvent extraction was also carried out on the dust samples tested for phthalates in a study carried out to investigate the possible association between phthalates in their houses and symptoms of allergies and asthma in children (Bornehag *et al.*, 2005). However, if a dust sample is being analysed for VOCs, it has been suggested that thermal desorption is a useful alternative to using a solvent extraction process (Morawska *et al.*, 2001; Brown and Crump, 2008).

Thermal desorption has a number of advantages over solvent extraction including producing less chance of sample contamination due to lack of numerous stages, and being less time consuming. It is not applicable for all classes of compounds, notably those of low volatility such as brominated flame-retardants and higher PAHs, and if there is a possibility of decomposition of very high molecular weight compounds or polymers (Hirvonen *et al.*, 2004; Wolkoff and Wilkins, 1994).

2.7.3 Elemental Analysis of Dust

The elemental analysis of soils and dust have been performed using various techniques, the most common being acid digestion followed by atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP MS) or atomic fluorescence spectrometry (AFS). The ICP MS method has been described as the most versatile multi-elemental analysis approach (Al-Rajhi *et al.*, 1996; Rasmussen *et al.*, 2013; Rasmussen *et al.*, 2001; Brenner, 2010). Other methods include using flame atomic absorption spectrometry (FAAS) and X-ray fluorescence (XRF) (Tokalıoğlu and Kartal, 2006).

2.8 Chapter Summary

The increasing recognition of the importance of the indoor environment in the developed as well as the developing countries has led to a wide range of studies that investigated the impact of air pollution on health. There is a lot of work reported about activities such as cooking and electricity generation using biomass fuels and fossil fuels producing high amounts of environmental pollutants that cause high levels of human exposure to the various pollutants. There is also evidence of health effects associated with weather events that produce high concentrations of particulate matter and heavy deposition of dust.

Research findings about the pollutants contained in household dusts from most parts of the world show a variation in the composition of dusts in different regions, but the widespread presence of chemical and biological pollutants that may have adverse health effects on people. There is no report in the literature of a comprehensive study of the settled house dust composition and the possible risk to health in the West African sub-region and Nigeria in particular. Hence, there is a need for a study to characterise the nature of contaminants in the dust both indoors and outdoors (near homes) and to assess the possible risks to health.

The literature review highlighted the lack of well-developed and standardised methods for the characterisation of settled dusts in particular. In addition, some methods were not practical for application in the field in northeast Nigeria or were not possible within the resources available for the research. However the literature review identified a number of approaches to dust and air pollution sampling that can be used to characterise the physical, chemical (organics and metals), and biological components of dust and these were explored further in the initial phase of the current research. The increasing interest worldwide in the contribution that dust makes to the total exposure of people to hazardous substances was noted and therefore the experimental research focussed particularly on the investigation of organic compounds and toxic metals.

3 SAMPLING METHODOLOGY

This chapter contains the details of the field work carried out, in which various sampling methods were investigated as part of method development for the collection of settled and airborne particulates in the indoors and outdoors of UK and Nigerian homes. There are no standard methods for collecting settled dust. However, various methods used by other researchers investigated included; collection of settled indoor dust on adhesive carbon spectrotabs (Shilton *et al.*, 2002) used for particle characterisation by using scanning electron microscopy (SEM); collection on filters as carried by (Horwell *et al.*, 2003); on pre-weighed petri dishes for photometric methods (Fullerton *et al.*, 2008); use of a vacuum cleaner; and placing of ceiling boards on raised surfaces. Outdoor sampling was carried out with equipment such as a Frisbee dust deposition device (hanby.co.uk), as well as improvised methods such as a bucket-type collector.

Devices for the collection of airborne particulates such as the Buckard biological sampler model-PASA/B (Advanced instruments Co., Norwood), a personal environmental monitor (PEM) (SKC Inc., PA 15330 USA) for PM_{10} sampling, and an optical ultrafine particle counter (TSI P-TRAK® USA, www.tsi.com/p-trak-ultrafine-particle-counter-8525) were also investigated.

3.1 Sampling Techniques

Although the study is mainly concerned with settled dust, airborne pollutants were sampled in some instances in order to obtain more information about possible inhalation exposure and sources of settled dust constituents. The various methods investigated for collecting settled dust and airborne pollutants both indoors and outdoors were adopted or modified and some were improvised dependent upon their suitability for the type of analysis and consideration of the method of transportation of the samples from the field (in Nigeria) to the laboratory (in UK). Simple, portable, and affordable equipment types were used. The various equipment types used are illustrated in Appendix A. Table 3.1 shows the various types of sampling methods examined, samples collected and the analytical techniques performed.

Table 3-1 Summary of the sampling methods

S/N	Equipment	Description(sample parameters)	Sampling locations	Output
1	P-TRAK Ultrafine particle counter	Logged reading of real time airborne ultrafine particles	Indoor/ Outdoor	Ultrafine particle count
	ICOM CO monitor	Logged reading of Carbon monoxide	Indoor/ Outdoor	CO concentration
2	Personal Environmental Monitor (PEM)	Collection of airborne PM_{10}	Indoor/ Outdoor	Gravimetric analysis
3	Burkard Biological Air Monitor	Collection of airborne bacteria/fungi spores	Indoor/ Outdoor	Identification of microbial species
4	SpectroTabs on pin Stubs.	Dust settled on adhesive tapes	Indoor/Outdoor	SEM analysis
5	Tenax TA tubes	Passive sampling of airborne VOCs/SVOCs	Indoor/Outdoor	TD/GC/MS analysis
6	Q-Tenax tubes	Pumped sampling of airborne VOCs/SVOCs	Indoor/Outdoor	TD/GC/MS analysis
7	Petri dishes	Dust settled on petri dishes	Indoor	Gravimetric analysis
8	Vacuum cleaner	Collection of settled floor dust	Indoor/ Outdoor	VOC/SVOC analysis, SEM
9	Frisbee dust deposit gauge.	Collection of deposited dust	Outdoor	Gravimetric analysis
10	Bucket gauge	Collection of deposited dust	Outdoor	Gravimetric analysis

3.2 Sampling Periods

As one of the objectives of the study settled house dusts as well as airborne samples were collected from different sources and locations; indoor and outdoor settled dust samples were collected from homes in Damaturu, north-eastern Nigeria during two notable dust event seasons (Harmattan and Dust storm) and also in the period without a dust event (No-event period). Harmattan dust samples were collected in December 2009, and between December 2010 and March 2011 (duration of the event). Dust storm samples were collected between July and September 2010 (duration of the event), and ‘No-event’ samples were collected in April 2011. Surface sand was sampled (from a location away from the human dwellings) in Damaturu for comparison with the household dusts.

Dust samples were also collected from homes in the Damaturu community, Nigeria, based on different types of buildings (modern and traditional). Emissions of vapours and airborne particles (collected during anthropogenic activities) in both the indoors and outdoors around the homes were measured during the following events: cooking with firewood, cooking with kerosene stove, generating electricity with diesel, Harmattan haze, generating electricity with petrol and burning of incense. Ultrafine particles, carbon monoxide emissions and airborne microbial spores were also monitored.

Dust samples were also collected from household vacuum cleaner bags from UK homes and used for method development studies and for comparison with Nigerian dusts. Some airborne measurements were also conducted in UK homes. A summary of the settled and airborne particles sampling conducted during the study is shown in Table 3.2.

Table 3-2 Settled dust and airborne sampling conducted during the study

Phase of study	Samples collected	Date collected	Sampling method	Sampling source	Analytical method
Method development	Settled house dusts Standard reference dust	12/2009-01/2010 04/2010-11/2010 2011	Vacuum cleaner bags, petri dishes, ceiling boards Vacuum cleaner bags SRM 2585-dust purchased	Bedrooms, kitchens, living rooms of 5 Nigerian homes 5 UK homes NIST, USA	TD/GC/MS,SE/GC/MS, Microbial, ICP-MS, SEM analyses
	Outdoor settled dust	09/2009-04/2011	Bucket gauge Storm/Harmattan dusts	Outdoor of 3 Nigerian homes	TD/GC/MS,SE/GC/MS ICP-MS, SEM analyses
	Airborne VOCs/SVOCs	07/2010, 12/2010	Diffusive/pumped on Tenax/Q-Tenax tubes	Nigerian/UK homes: during dust events/ human activities	TD/GC/MS Analysis
Seasonal events	Settled dusts Surface soil (sand)	07/2010-09/2010, 12/2010-01/2011, 04/2011	Vacuum cleaner bags	Indoor and outdoor of 5 Nigerian homes ~500 metres away from homes	TD/GC/MS,SE/GC/MS, ICP-MS, SEM analyses
House type		04/2011-05/2011	Vacuum cleaner bags	Indoor and outdoor of 26 Nigerian homes	TD/GC/MS,SE/GC/MS, ICP-MS analyses

3.3 Settled Dust Collection

The settled dust samples are required in substantial amount to be able to carry out the different analyses (chemical, metal, microbial and physical analysis). Hence about 15 g of sample is preferred to be collected from each sampling location to carry out all the analyses.

During the method development phase dust samples were collected from the bedrooms, kitchens, and living rooms of five homes in Damaturu by different sampling methods: on petri dishes, on ceiling boards, on pin stubs, and by sweeping the floors at the sampling locations. In UK homes, five indoor samples were collected from household vacuum cleaner bags (collected from different types of vacuum cleaners over different periods), and one outdoor sample was collected by sweeping a concrete surface in a rear garden with a soft broom for validation of methods. The initial aim of employing the various methods was to ascertain which method is optimum for a particular analysis.

3.3.1 Collection of Settled Dust on Petri dishes

Four petri dishes (90 mm) diameter were weighed and placed on raised undisturbed places (between 1-1.5 metres high) in bedrooms, living rooms, and kitchens in each of the five Nigerian homes sampled for the duration of the two dusty weather events (2 -3 months). On completion of sampling, the closed petri dishes were conveyed to the laboratory and re-weighed. In the UK, pre-weighed petri dishes were placed on raised places in the living room and bedroom of 2 homes and kept open continuously to get settled ambient dust particles for two months after which the petri dishes were closed and re-weighed in the laboratory (Appendix A). The dust on all the four petri dishes in each of the sampling sites were combined by brushing the settled dust on one of the dishes and then on to a sheet of pre-weighed foil. The total combined samples for each house were weighed and the quantities were 3.6 g, 2.98 g, 3.76 g, 5.67g, 4.09 g, and 4.43 g for each of the sampled locations. The Nigerian samples were littered with rodents' excreta and after the removal of the visible excreta the quantities were not enough to carry out full laboratory analysis. The UK samples were collected differently with Petri dishes being kept opened for 3 months and others for 4 months and 6 months, but these did not collect substantial amounts of the settled dusts.

3.3.2 Ceiling board

Ceiling boards were measured (2 by 4 metres) and placed on bedroom cupboards, wardrobes, and television stands in the living rooms and on smooth-polished surfaces in kitchens for 3 months during Dust storm and Harmattan dust periods (Appendix A). The settled dusts were collected by brushing down onto pre-weighed sheets of aluminium foil paper, then contained in resealable bags, and brought to the laboratory. The dust samples were weighed (Table 3.3) but amounts were not adequate for the experimental study, though it gave a measure of indoor dust particles that settled on the surface. The weights were recorded after removing the coarse particles (such as rodents' excreta).

Table 3-3 Settled dust collected on ceiling board

House code Sample set1*	**mass (g m^{-2})**	**House code Sample set2****	**mass (g m^{-2})**
A1	5.26	A2	7.57
F1	11.65	F2	13.76
L1	4.78	L2	3.87
M1	3.91	M2	5.45
Y1	10.96	Y2	8.74

*Sample set1 collected during Harmattan **Sample set2 collected during Storm period

3.3.3 Spectrotabs with Pinstubs

Settled dust samples were collected on Spectro tabs mounted on pin Stubs and placed alongside the petri dishes in the sampling sites (Appendix A). The dust trapped on the adhesive surface of the carbon tape was reported to be suitable for SEM analysis (Shilton et al., 2002). The pin stubs were then placed in carriers and taken to the laboratory. Unfortunately, some of the sampled specrotabs became stuck to the cover of the containers during transportation, and the dust particles became moist and were considered unsuitable for further investigation.

3.3.4 Frisbee-type Dust deposit Gauge

The Frisbee-type dust deposit gauge is equipped with a frisbee-shaped collecting bowl made of anodized, spun aluminium, supported by a tripod 1.7 m above ground level with an opening through a drainpipe leading from the stem down to a rainwater-collecting bottle on the ground. The collecting bowl is lined with a 10-mm thick, 240-mm diameter, disc of black, open-celled (10 pores per inch) polyester foam. The gauge incorporates a bird-strike preventer in the form of a ring of fine (1-mm thick) plastic fishing line (left slightly slack) supported 5 cm above the collecting bowl on six stainless steel struts (see Appendix A for picture). The device is designed to collect outdoor dust deposition, usually quoted in units of mg m^{-2} day^{-1}. Outdoor dust particles are deposited on the Frisbee collection disc and are washed into a collector by rainwater. The solid matter is filtered using micro glass fibre filter paper (pre-weighed G/F-grade), and then dried and weighed to determine the mass of solid material.

Procedure: The device was mounted in a garden of a house located on the Cranfield University campus. The gauge was placed on a horizontal surface (at secured location) away from obstructions such as buildings, trees, and over-head wires on which birds might perch. (The device is not to be placed close to large objects, within 5 metres of the gauge, and as a rule, the top of any obstructions should subtend less than a 30° angle with the horizontal at the sampling point). At the end of each collection period (one month), 100 ml of distilled (or deionized) water was poured onto the Frisbee (with foam disc still in place) into the top of the pipe connecting to the collecting bottle. The bottle was removed and taken to the laboratory, and replaced with a clean one for the next sampling period.

Recovering the dust: A pre-weighed Whatman glass microfiber filter (9-cm diameter) was placed on a glass petri dish, dried in the oven at 80^0C for 1 hour and equilibrated in a desiccator for 2 hours. Using tweezers, the filters were re-weighed (Vallack, 1995). This method seems to be good for the determination of dust deposition but the recovered dust during each sampling period of one month was not enough for conducting a series of laboratory analyses (Table 3.4).

Table 3-4 Outdoor dust collected with Frisbee gauge

Sample	Initial weight (g)	Final weight (g)	Dust deposited(g)
F1	1.89	4.05	2.16
F2	1.87	4.09	2.22
F3	1.87	4.89	3.02
F4*	1.88	6.96	5.08

*- was sampled for 2 months

3.3.5 Bucket gauge

Equipment was devised to use as a dust gauge for the collection of deposited dust in Nigeria. This was made up of a bucket covered with mosquito wire mesh and placed on a constructed 1.7-metre wrought iron tripod stand. This provided a low cost and practical gauge constructed locally. In addition, it provided a wider surface area for collecting more deposited dust than the Frisbee-type gauge. The buckets were kept in the courtyard (garden) of four sampling locations for four months (December to March) during the Harmattan period with no rainfall (Location 1- FH house garden; location 2- LH house garden; location 3-YH house garden; location 4- AH house garden). After that time, the buckets were rinsed with water and the solid particles were filtered on pre-weighed glass fibre filter papers and dried in an oven at 100^{o}C for 1 hour. The filters were labelled based on the sampling location for identification. The filter papers were kept in a desiccator overnight to ensure complete dryness, re-weighed, folded, kept in resealable polythene bags, and transported to the laboratory. The amounts collected were not adequate for the planned chemical analysis, whilst the finer particles were stuck to the surface of the filter papers. The buckets were placed back again from April to September 2011. A substantial amount of dust was then collected (Table 3.5).

Table 3-5 Dust collected with bucket gauge (Apr.-Sept. 2011)

Sample	Initial weight (g)	Final weight (g)	Dust deposited (g)
A1	0.85	7.51	6.66
F1	0.87	10.09	9.22
L1	0.89	8.72	7.83
M1	0.78	9.64	8.86
Y1	0.86	10.51	9.65

Two of the samples, A1 and L1, were insufficient, but metal analysis was performed with the remaining three samples. The buckets were set again for more sampling from October to September (1-year plan) but the sampling could not continue due to the onset of civic unrest in Damaturu. Therefore, there was no repeat sampling but the metal results could be compared with Harmattan dust, Storm dust and sand samples (result presented in chapter 4). During Storm and Harmattan episodes, the deposited dusts were collected from the windscreen of cars and on window vanes by scooping with a brush.

3.3.6 Vacuum cleaner

Settled indoor/outdoor dusts were collected from the floors, carpets, and mats of living areas with a vacuum cleaner (Morphy Richards^{TM} model-37164). All the samples from the Nigerian homes were collected with the same vacuum cleaner. After sampling each home the dust bag was removed, sealed and the suction hose cleaned by turning it on and drawing only air for 3 minutes between sampling. Sampling was done in the carpeted locations for 15 minutes and on the cement floor for 10 minutes, due to more settled dust on the cemented floors. Substantial quantities of the dusts were collected for investigation in the laboratory. The samples contained many coarse particles, hair strands, and other larger particles e.g. pieces of toys. The samples were sieved with 150 μm meshed laboratory sieve in order to remove the coarse particles (stones, pieces of fabric etc.) and the fractions were kept in glass jars. The UK samples collected were from individual household vacuum cleaners, and 10 g of sieved 150 μm fractions were kept in glass jars, leaving the remainder in their original dust bags. The gross weights of the vacuum cleaner bags sampled dust and the weight of the sieved 150 μm fractions were as shown in Table 3.6.

Table 3-6 Dust collected from vacuum cleaner bags in Damaturu

S/N	**Sample location**	**Gross weight (g)**	**150 μm sieved fractions (g)**
1	AH House	29.657	19.873
2	FH House	32.543	24.876
3	LH House	34.216	21.973
4	MH House	28.098	14.675
5	YH House	35.986	16.986
6	FH-O	24.976	12.649

The vacuum cleaner bag dust samples were all labelled by a building code based on the locations where they were collected, with two UK samples, DH1 and DH2, collected from the same home at different times (Tables 3.7 and 3.8). Many researchers have used different vacuum cleaners in settled dust sampling (Ali *et al.*, 2012; Mercier *et al.*, 2011; Wilkins *et al.*, 2004), and have commented that it gives a better representation of the household dust than the other sampling methods. In this study, the vacuum cleaner method of collection of settled dust samples was adopted because of the practicality and because the quantity of the dusts collected were enough to carry out different types of analysis. More settled dust samples were then collected from Damaturu during the two dusty weather events (Harmattan, Dust storm, and no dust event periods). Samples collected from each sampling location were enough to perform several analyses; organic chemical analysis by TD/GC/MS and SE/GC/MS; metal analysis; and SEM.

Table 3-7 Dusts collected during method development in Nigerian homes

Sample code	Description	Comment
AH	A traditional township home built in 1999	Located at the new settlement site
FH	A modern detached house built in 1957	Pets and domestic animals in the compound
LH	A modern semi-detached building built in 1991	Located at the outskirt
MH	A traditional township home building built in 1983	Located in the main township
YH	A modern detached house built in 1995	Outskirt + more than 10 occupants
FHO	Frontage of FH house	Where cars and generator are kept

Table 3-8 Settled dust sampling locations in the UK homes

Sample	Description	Comment
AKH	A semi-detached house built in 1940s	Located on campus with 6 occupants
DH1& DH2	A semi -detached house built in the 1935	Located in a semi-rural environment
VH	A flat built in 1961	Located in an urban environment
FH-UK	A semi-detached house built in the 1940s	Located on Cranfield campus with 3 occupants
SH	A semi-detached house built in the 1940s	Located on Cranfield campus with 7 occupants
UKO	Backyard of FH-UK house	

3.3.7 Dust Sampling from different Building Types

Fifty-two settled dust samples were collected (26 indoor and 26 outdoor) during a no-event period in April-May 2011 from Damaturu, Nigeria. The samples collected were from thirteen modern and thirteen traditional types of buildings and the basic information about the type of buildings and building occupants recorded are shown in Tables 3.9 and 3.10.

Table 3-9 Demographic information of modern type houses sampled in April-May 2011 in Damataru

Ward	Type of building	Age (yrs.)	Flooring	No. of residents	Cooking fuel	Pets
BK-Estate	Detached	19	Cement/carpet	9	kerosene/firewood	Pets
BK-Estate	Detached	19	Cement/tiles	5	kerosene/firewood	Pets
BK-Estate	Detached	19	Cement/carpet	6	kerosene/firewood	None
BK-Estate	Detached	19	Cement/carpet	5	Gas	None
BK-Estate	Detached	19	Cement/carpet	5	kerosene	None
BK-Estate	Detached	19	Cement/tiles	5	Gas/kerosene	None
AM-Estate	Semi-detached	22	Cement/tiles	6	Gas	None
AM-Estate	Semi-detached	22	Cement/carpet	7	Gas/kerosene	None
AM-Estate	Semi-detached	22	Cement/carpet	4	Kerosene	None
AM-Estate	Semi-detached	22	Cement/carpet	3	Kerosene	None
Poly-Estate	Detached	28	Cement/carpet	8	Gas/firewood	Pets
WI-Estate	Semi-detached	22	Cement/carpet	3	Kerosene	None
WI-Estate	Semi-detached	22	Cement/tiles	2	Gas	Pet

Table 3-10 Demographic information of traditional type houses sampled in April-May 2011 in Damataru

Ward	Type of building	Age(yrs.)	Flooring	No. of residents	Cooking fuel	Pets
Abasha	Detached	56	Cement	18	Firewood	None
Sabon fegi	Attached	21	Cement/carpet	12	Firewood	Pets
Abasha	Attached	48	Cement	13	Firewood	Pets
Abasha	Attached	52	Cement	8	Firewood	Pets
Nassarawa	Detached	21	Cement/tiles	7	Firewood/kerosene	None
Nassarawa	Detached	21	Cement/tiles	4	Firewood	None
Abasha	Attached	55	Cement	5	Firewood	None
Abasha	Attached	56	Cement	3	Firewood	None
Sabon fegi	Detached	21	Tiles/carpet	7	Firewood/kerosene	None
Abasha	Attached	54	Cement	9	Firewood	Pets
Sabon fegi	Semi-detached	21	Tiles/Carpet	11	Firewood/charcoal	Pets
Gwange	Attached	56	Cement	8	Kerosene	None
Gwange	Semi-detached	54	Cement	2	Kerosene/charcoal	None

3.4 Airborne Particles and Vapours

3.4.1 Collection of chemical emissions on sorbent tubes

A standard method of sampling and analysis of volatile organic compounds in air was adopted from the international standard BS EN ISO 16017-2 using sampling tubes loaded with sorbent that is analysed by TD/GC/MS (BS EN ISO 16017-2, 2003). Sorbent tubes packed with Tenax TA were used for collecting gases and vapours from the air. Tenax® TA is a porous polymer resin based on 2,6-diphenylene oxide specifically designed for the trapping of volatiles and semi-volatiles from air or purged from liquid or solid sample matrices.

Samples were collected passively by opening the grooved end of the tube and placing on raised undisturbed indoor locations for 2 weeks to allow the sampling of the VOCs and SVOCs by diffusion. Each tube was closed after the sampling period, wrapped in foil paper, and transported to the laboratory for analysis.

Active sampling was undertaken by opening a pre-conditioned sorbent tube (quartz-Tenax), connecting it to a sampling pump, and pulling air through the tube with the pump at a flow rate volume of 200 ml min^{-1} for 10 minutes during each sampling. Airborne chemicals were trapped onto the surface of the sorbent and the tubes were sealed with push-on caps. The method was in accordance with an international standard (BS ISO 16000-6, 2011). The airborne samples were collected during various human activities in the same homes that settled dusts were collected. The sampling locations are listed in Tables 3.11 and 3.12.

Table 3-11 Airborne samples from Nigerian Homes

Samples	Description	Method
FK	Kitchen of FH house	Diffusive
LK	Kitchen of FH house	Diffusive
MK	Kitchen of FH house	Diffusive
YK	Kitchen of FH house	Diffusive
FLR	Living room of FH house	Diffusive
LLR	Living room of FH house	Diffusive
MLR	Living room of FH house	Diffusive
Kerosene stove	During cooking	Pumped
Gas cooker	During deep frying	Pumped
Fire wood	During cooking	Pumped
Petrol generator	During electricity generation	Pumped
Diesel generator	During electricity generation	Pumped
Dust storm	During dust storm episode	Pumped
Harmattan haze	During Harmattan period	Pumped

Table 3-12 Airborne samples from UK homes

Samples	Description	Method
AKB	Bedroom of AK house	Diffusive
FLR-UK	Living room of FH-UK house	Diffusive
AKLR	Living room of AK house	Diffusive
FBR-UK	Bedroom of FH-UK house	Diffusive
DHK	Kitchen of DH house	Diffusive
DHLR	Living room of DH house	Diffusive

3.4.2 Diffusive (Passive) Sampling

Duplicate Tenax tubes were exposed diffusively for 2 weeks during storm (July 2010) and during Harmattan (December 2010), and in UK homes at different periods with a typical sampling rate equivalent to 0.5 to 1 ml min^{-1} (depending on the compound). The sampling tubes were placed on 1.5-metre high positions in the Nigerian homes. Two tubes were kept closed as field blanks. The tubes were tightly closed after sampling, wrapped in foil, placed in airtight containers, and returned to the laboratory for chemical analysis. The equivalent of approximately 10.8 litres of air was sampled by each Tenax tube although transport of chemicals into the tube is by diffusion rather than airflow.

If 0.5 ml min^{-1} of air is sampled;-

In 14 days the equivalent air volume sampled = 0.5 X 60 X 24 X 14 = 10,080 ml = 10.08 litres.

3.4.3 Active (pumped) sampling

Air was pumped through Q-Tenax sorbent tubes using a TSI-side-pak pump (sp-700) at a rate of 200 ml min^{-1} for 20 minutes. The sampling was done in duplicate during the following events: cooking with firewood, cooking with kerosene stove, generating electricity with diesel, Harmattan haze, generating electricity with petrol and at ambient environmental condition. All the samples were collected in Damaturu, Nigeria (July 2010 and December 2010). The tubes were tightly closed after sampling, wrapped in foil, placed in airtight containers, and returned to the laboratory for chemical analysis.

200 ml X 20 min. = 4 litres of air was sampled through the sorbent tubes.

Twenty-one samples were collected by the Tenax (diffusive) and the pumped (Quartz wool/Tenax) sorbent tube sampling methods to determine organic chemical concentrations during various events in July 2010 and December 2010.

3.4.4 Investigation of Chemical Emissions from other sources

In order to investigate possible sources of chemicals in the indoor environment, laboratory tests were conducted on some consumer products used in homes in Damataru. This involved enclosing samples in a bag of clean air and sampling the headspace using sorbent tubes. Nalophane sheet was cut from a roll of 21cm width.

Procedure: A 50 cm length of Nalophane was used to form a bag by folding one end of the bag and sealing using a cable tie. Pesticides and incense samples were each placed in a bag. The open end of each bag was closed with polyethylene tubing and connected to a sorbent tube. The bags containing the samples were filled with zero grade air and allowed to equilibrate for 10 minutes. Chemicals emitted by the samples were collected from each bag in duplicate by attaching a Q-Tenax tube to a sampling pump and drawing 100 ml per minute of air from the bags for one or two minutes. The open end of each bag was closed with polyethylene tubing and connected to a sorbent tube (Q Tenax). The tubes were then analysed by TD/GC/MS. Emissions from burnt incense were collected on Q-Tenax tubes and analysed.

3.4.5 Ultrafine particles and Carbon monoxide Monitoring

The ultrafine particles (UFP) and CO were determined simultaneously while sampling for organic chemicals during human activities. The monitoring of UFP and CO was done during the household activities; cooking with kerosene stove, cooking with firewood, electricity generation with fossil fuels. The monitoring was also done when there was no activity-taking place. The equipment was placed on wooden stools 1.5 metre high during electricity generation with petrol, diesel (both outdoors), and during cooking with a gas cooker and kerosene stove (indoors). The stools were in each case positioned 2 metres away from the particles source. In the case of the cooking with firewood, the equipment was placed on wooden frame in the kitchen (about 1 m high). When there was no activity, the P-Trak and the ICOM were placed on a long bench in an open compound (outdoor) about 1 m apart.

Procedures: The UFP monitoring was carried out with a P-TRAK which is a portable hand held device capable of detecting and counting ultrafine particles (smaller than 1 µm in aerodynamic diameter) with a continuous read out of particles of up to 500,000 particle counts expressed as a concentration in air (particles/cc). Real time data was logged over a 10-minute period at 15 seconds interval for each activity to determine the particle concentration in indoor air during anthropogenic activities.

The UFP in air were drawn through the P-Trak Ultrafine Particle Counter(P-Trak^{TM} tsi inc. USA) using a built-in pump. Upon entering the instrument, the UFP pass through a saturator tube where they mix with an alcohol vapour. The particle/alcohol mixture is then drawn into a condenser tube where alcohol condenses on the particles causing them to grow into droplets that can be counted more easily. The droplets then pass through a focused laser beam, producing flashes of light. The light flashes are sensed by a photo detector and counted to determine the particle concentration. The results obtained presented are in chapter 4.

The carbon monoxide (CO) concentrations were monitored with an ICOM-carbon monoxide monitor (Sigma^{TM} Limited) which is equipped with an electrochemical (diffusive cell). The device monitors levels of CO (0.5–500 ppm) and is fitted with an inbuilt memory that was used for logging real time data during monitoring. The data of CO emission were logged (every 15 seconds) for 10 minutes during each sampling period (expressed as ppm concentration in air). The logged data were stored in the device memory and retrieved via ICOM radio-terminal software. The results are shown in chapter 4.

3.4.6 Airborne PM_{10} sampling

The PM_{10} particles monitoring was done with a personal environmental monitor (PEM) which is an impactor-containing device. SKC-225-1709 (2.0µm, 37mm) filters were conditioned and weighed before fitting them on to the PEM device. Air was drawn through the perforated device and particles trapped on the pre-weighed and pre-conditioned filters contained in the PEM impactor by the use of an air sampling Sidepak pump (SP700) at a flow rate of 2 litres per minute for 8 hours and 24 hours respectively. The airborne PM_{10} particles were collected on the filter and the filter was re-weighed using the analytical top-loading six-figure balance (Sartorius). The filters sampled were largely invalidated due to the effect of environmental parameters such as atmospheric moisture and the low weight of the samples collected. The process was repeated several times but in all instances, and even though discoloration was visible, no detectable weight gains were recorded in all the sampled filters.

Procedure: Filters were conditioned for 3 to 4 days before sampling. The filter papers were conditioned by placing in a petri dish half opened and these were kept in the balance room with daily weighing in order to allow equilibration of the parameters in the room with the filter paper for a reliable weighing.

Procedure: The conditioned filter paper was positioned into the PEM and air sucked through the PEM at a flow of 1 l min^{-1} for 8 hours with an air-sampling pump (480 litres of air) and the filter removed and taken to the laboratory. The airborne PM_{10} particles collected on the filter were weighed using the analytical top-loading balance (Sartorius). The process was repeated several times but in all instances, even though discoloration was visible, no detectable weight gains were recorded. Examples of the results obtained are shown in tables 3.13 and 3.14. For this technique to be used successfully there is a need for a balance room with controlled parameters (temperature and humidity) for the weighing of the filters, and for the sampling to be over a longer period of 12 to 24 hours.

Table 3-13 Conditioning of quartz filter paper

Day	**Initial weight (mg)**		**After 30 secs. W (mg)**		**Difference W (mg)**		**Comment**
	F-1	F-2	F-1	F-2	F-1	F-2	F=Filter paper
1	69.531	69.492	69.520	69.496	-(.11)	+(.4)	Weight gain
1	68.875	68.890	68.873	68.882	-(.2)	-(.8)	Weight loss
3	67.578	67.687	67.566	67.618	-(12)	-(.69)	Weight gain

Table 3-14 Sampling of PM_{10} using personal environment monitor (PEM)

	Initial weight (mg)	After Sampling	Difference (mg)	Comment
Filter 1	67.687	67.085	-(0.602)	Sample collected during and after cooking (8 hrs)
Filter 2	67.618	67.056	-(0.562)	Sample collected while asleep (8 hrs)

3.4.7 Microbial Spore Sampling

Airborne microbial spores were collected by impaction using a pump connected to a Burkard biological air monitor by placing the sampling device on a 1 m high stool while sampling outdoors. During indoor sampling, the sampler was placed on structures such as cupboards, room dividers or a fridge located in the building. Agar media plates were placed between the impactor within the sampler and the perforated lid was replaced. Air was then aspirated through the agar plates at the flow rate of 2 litres per minute for 4 minutes during each sampling period. Cultivable airborne bacteria and fungi spores were collected on the agar media plates contained in the device and the agar plates were cultured in the laboratory. The growth of the microbial species were monitored and recorded as shown in chapter 4.

3.5 Chapter Summary

- Among the various sampling methods investigated, collection by vacuum cleaner was deemed the most suitable because a substantial quantity of the sample was obtained in the vacuum cleaner bags for further chemical analysis, whereas with other methods only small quantities were collected.

- Researchers have been reported to have used different vacuum cleaners for settled dust sampling (Ali *et al.*, 2012; Mercier *et al.*, 2011; Wilkins *et al.*, 2004), and have commented that it gives a better representation of the household dust. In this study, collection of settled dust samples from vacuum cleaner bags was adopted because of the practicality and the quantity collected was enough to carry out different types of analysis.

- The dust samples collected from vacuum cleaner bags of each of the homes sampled was enough to perform all the constituent analyses: scanning electron microscopy, elemental analysis (ICP-MS), and organic chemical analyses (TD/GC/MS, SE-GC-MS) as reported in the subsequent chapters.

- The airborne samples were mainly collected in order to ascertain the presence of various air pollutants in the indoor/outdoor environments associated with particular activities.

4 INITIAL INVESTIGATIONS

4.1 Introduction

This chapter contains the results of initial investigations employed for method development: by using, various techniques described in 3.2 in order to obtain a broad idea about the characteristics of the dust components, and to develop and adopt suitable dust sampling methods. To investigate the possible contribution of other sources to pollutants in the indoor and outdoor environment, airborne samples were also screened alongside the dusts.

4.2 Physical (SEM) Analysis of Dusts

The scanning electron microscopy (SEM) was carried out in the School of Applied Sciences laboratory (building 39), Cranfield University, with an environmental scanning electron microscope (Philips -XL30 ESEM).

4.2.1 Methods

Vacuum cleaner bag dusts collected (as described in 3.3.6) during the method development phase from 5 indoor and Nigerian and UK homes, as well as outdoors including Harmattan and Storm dusts (Table 3.2) were used. The dusts were sieved and the ≤150 µm size particles fraction examined.

An adhesive carbon tape fixed on pin stubs usually used for mounting samples was used to prepare the sample for analysis. The adhesive surface was gently pushed into each of the bulk dust samples and then the stub with adhered dust particles was positioned into the carousel in the sample chamber of the SEM. The samples were placed at labelled coordinates for ease of identification of sample images and spectra. The microscope chamber door was screwed tightly to enable a vacuum (without a sufficient vacuum, the electron beam generated by the electron gun would encounter constant interference from air particles in the atmosphere, blocking the path of the electron beam).

The microscope was turned on from the attached computer and the vacuum pressure checked. Electrons then accelerate onto the samples from the in-built electron gun resulting in interactions with the atoms of the target samples. The characteristic x-rays of different elements in the samples were detected and separated as energy spectra by energy-dispersion. The images of samples generated from detection of the scattered electrons were viewed and adjusted to the required magnifications. In some instances, points of interest on a particular particle were magnified and saved. The element spectra of individually chosen particles were examined, and in some instances, the general spectrum of the complete visible sample surface micrograph was recorded.

4.2.2 SEM of Nigeria and UK Dusts

The scanning electron micrographs of both the Nigerian and UK dust samples revealed that the dusts contain a variety of particle sizes and shapes that included PM_{10} and sub-PM_{10} particles, which are considered as the respirable fractions that can potentially cause health hazards as described by Horwell et al., (2003). The element spectra also showed the presence of numerous elements of various origins.

The sizes of the particles observed from the sieved Nigerian settled dust ranged between ~100 µm and ~2 µm. Filamentous particles were seen in the Nigerian samples AH, FHO and YH with those in MH dust shown to be segmented which might have originated from hair strands, dead plants, or clothes. LH dust contained a spongy (mass) shape that resembles soot or other organic cells such as skin flake (Plate 4.4b). Representative micrographs (100 µm) are shown in Plates 4.1, 4.2. The spectra captured by the SEM showed predominantly peaks of silica (Si) and iron (Fe) followed by other elements - calcium (Ca), magnesium (Mg), sodium (Na), titanium (Ti), potassium (K), sulphur (S), and aluminium (Al). An example of the elemental composition is shown in Table 4.1 (details in Appendix B).

The images of UK samples were mostly amorphous, puffy, sheet-like and clustered, and spongy masses with irregular shapes. The particles from different dusts have different elemental compositions, indicating differences in nature and sources of the particles. The presence in UK dusts of particles dominated by carbon (C), phosphorus (P), potassium (K), and copper (Cu) that were not observed in the Nigerian dusts indicates a variation in the elemental composition of the dusts from the different geographical locations (Plate 4.3 and Table 4.2). Further images are presented in Appendix B.

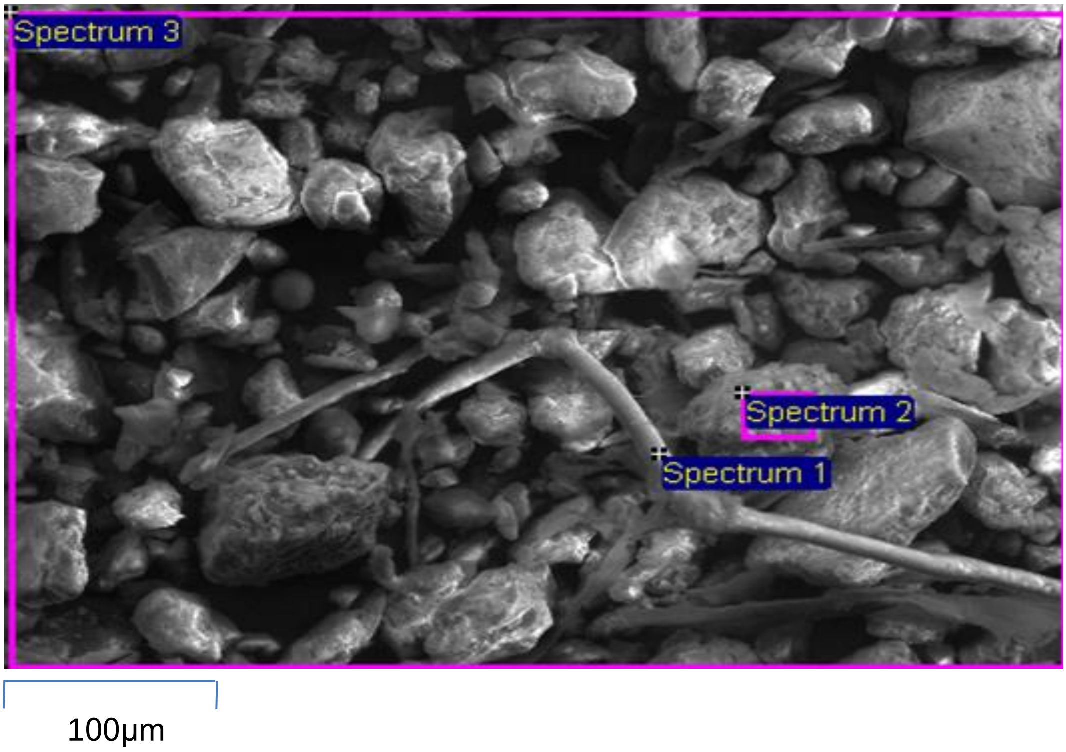
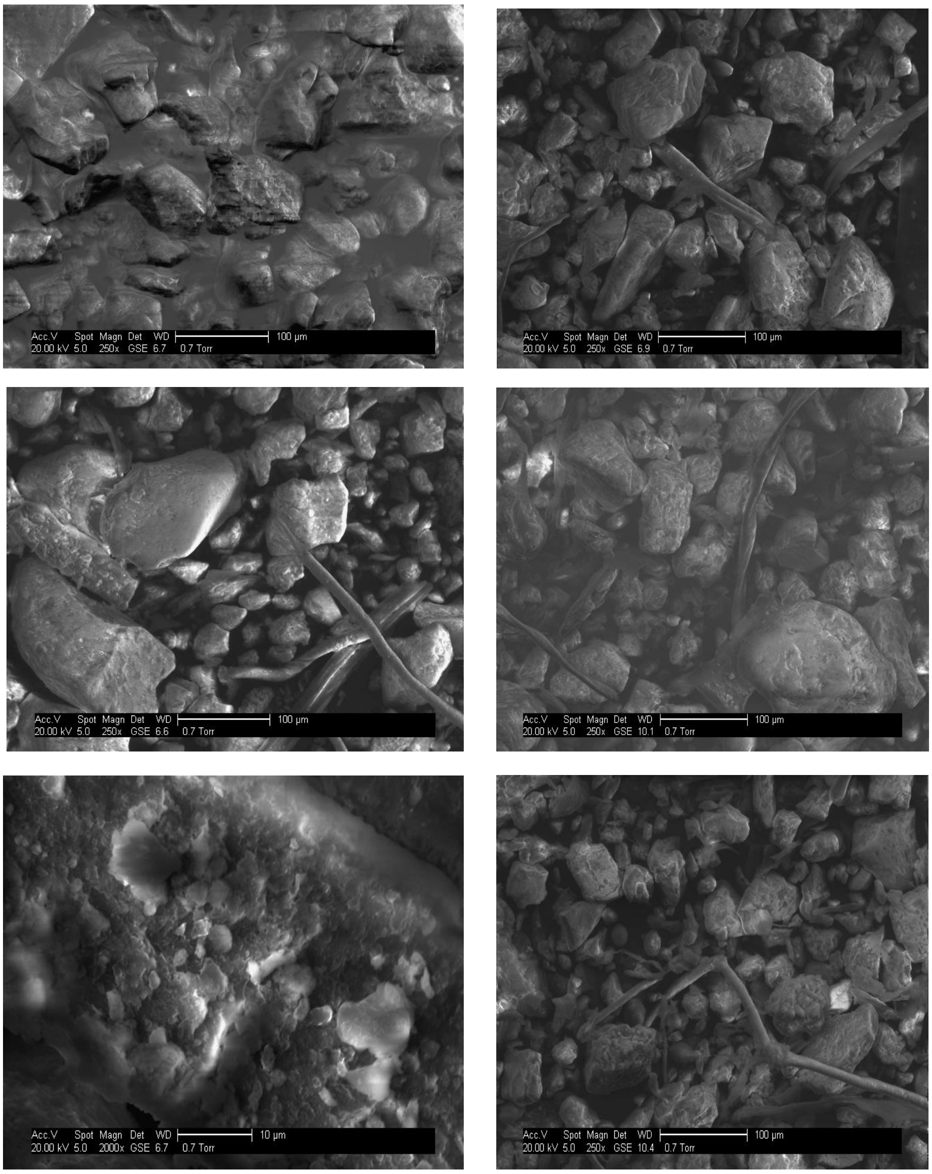


Plate 4-1 SEM image of MH (Nigerian) Dust

Table 4-1 Element composition of particles spectra in MH dust

	Amount of elements in weight (%)											
Spectrum	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Ti**	**Fe**	**Total**
1	76.2		0.8	3.4	12.7		0.3	0.7	1.4	2.4	0.7	1.6	100
2	60.2	0.7	1.4	8.4	18.1	0.4	0.2	0.3	1.2	4.3	0.4	4.5	100
3	59.7	0.7	0.8	4.8	24.1	0.3	0.4	1.0	2.2	3.4	0.1	2.5	100



FH Dust

FHO Dust

AH Dust

YH Dust

LH Dust

MH Dust

Plate 4-2 SEM images of settled dust samples from Nigerian homes

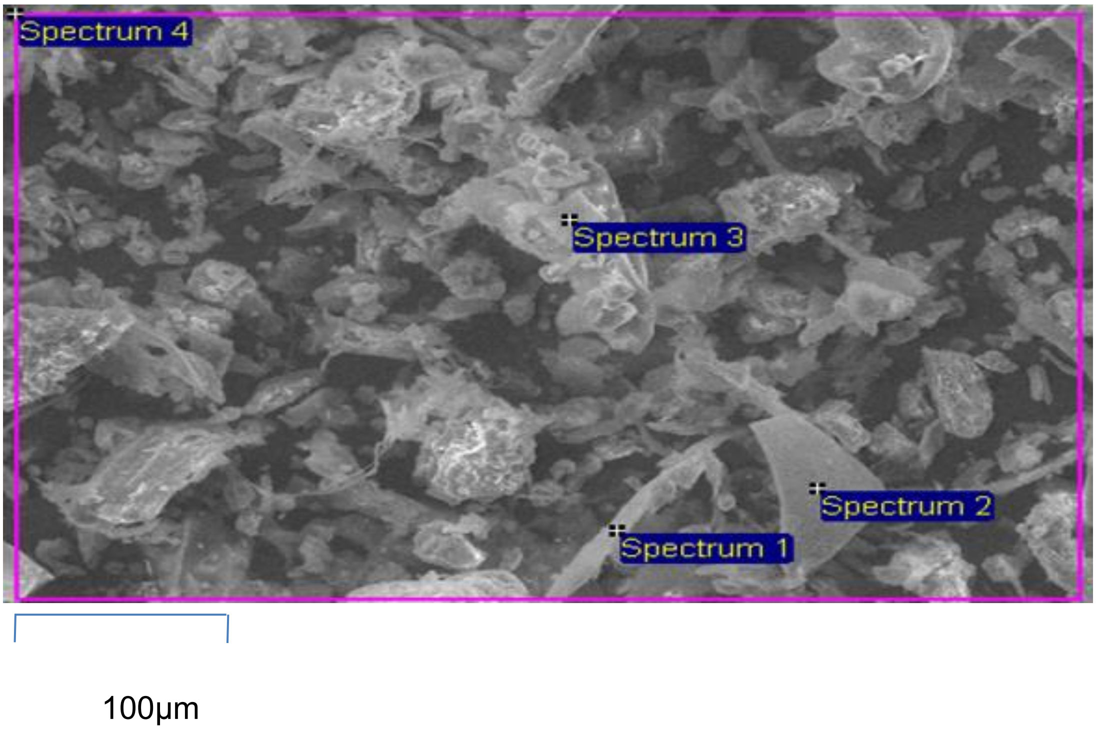
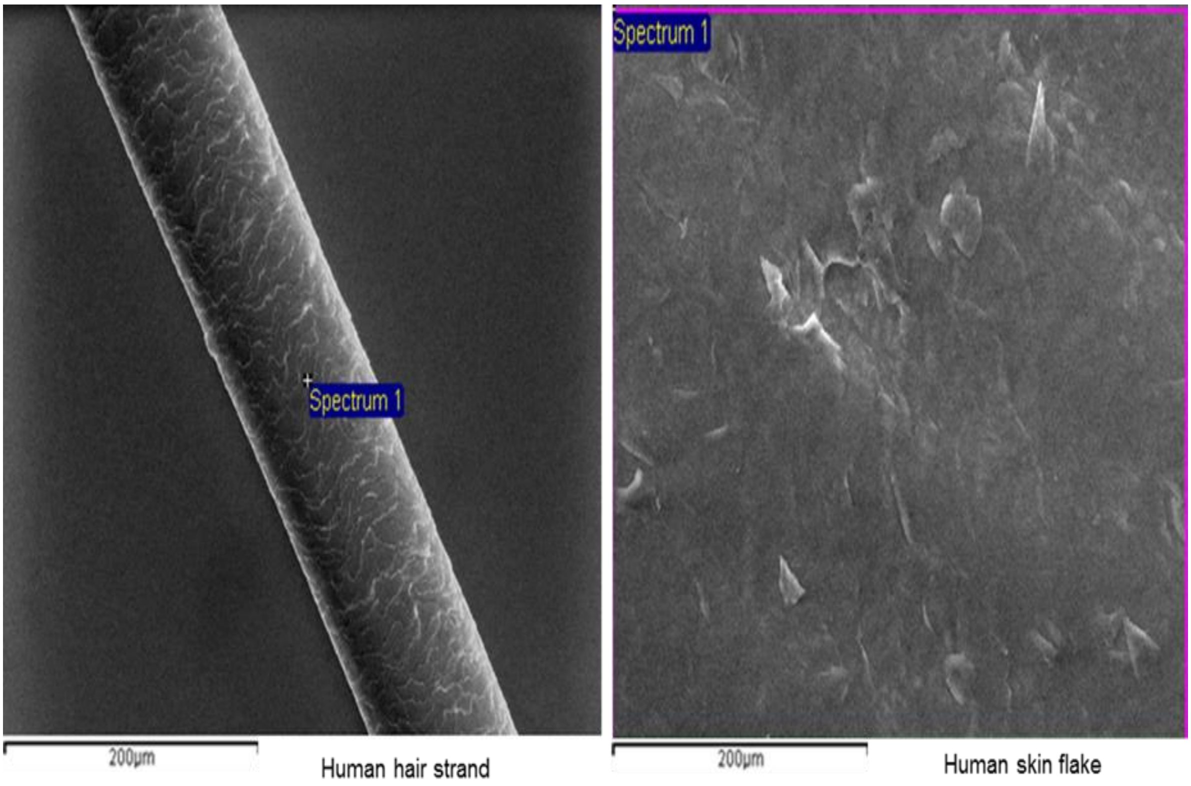


Plate 4-3 SEM picture of particles in DH (UK) dust

Table 4-2 Elemental composition of DH dust particles

	Amount of elements in weights (%)												
Spectrum	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Fe**	**Cu**
1	51.2	38.3	0.4		2.0	4.4		1.2	0.5	0.3	1.3	0.4	
2	26.2	53.3		0.1	1.3	17.3		0.1	0.1	0.1	1.0	0.2	0.2
3	58.1	32.2	0.9	0.4	1.9	2.3	0.1	0.8	0.8	0.4	1.4	0.7	
4	48.9	36.2	0.4	0.2	3.2	6.1		0.7	0.4	0.7	1.9	1.3	

For comparison of the SEM images of the dust particles, images of known samples (hair strand and skin flakes) were also taken. The images of LH dust showed some resemblance with that of the skin flake. The SEM images of skin flake and hair strand are shown in Plates 4.4a and 4.4b. The elemental compositions of the two known samples (hair strand and skin flake) were found to be similar to the particles in spectrum 1 of DH dust.



(a) (b)

Plate 4-4a SEM image of hair strand and 4.4b image of skin flake

Table 4-3 Elemental composition of hair and skin

	Amount of elements in weights (%)										
	C	**N**	**O**	**Al**	**Na**	**Si**	**S**	**Cl**	**K**	**Ca**	**Total**
Skin flake	58.8	9.7	29.2	-	0.3	0.1	0.9	0.5	0.5	-	100
Hair strand	67.6	5.7	20.8	0.2	-	-	5.2	-	-	0.5	100

4.2.3 SEM analysis of Harmattan Dust and Storm Dusts

The SEM images of Harmattan dust particles were dominated by perforated cylindrical-shaped particles of 2 to 50 µm in size (Plate 4.5). The elemental spectra of these particles are shown to contain the elements carbon (C) and oxygen (O), potassium (K), calcium (Ca), sulphur (S), iron (Fe), titanium (Ti), silica (Si) and sodium (Na) (Table 4.4). The distribution of the elements signifies that the particles were from organic sources. The appearance of images shown in the Harmattan sample were similar to those reported by Eckardt et al., (2005), and were suspected to be possibly of the crushed diatoms from dried lakes (Vaughan et al 2002; Todd et al., 2005). The Harmattan particle sources are believed to originate from the Bodele depression around the dried Lake Chad. The SEM picture (Plate 4.5) was found to be similar to that of the sample collected from the Bodele depression (Plate 4.6) by Todd et al., 2005.

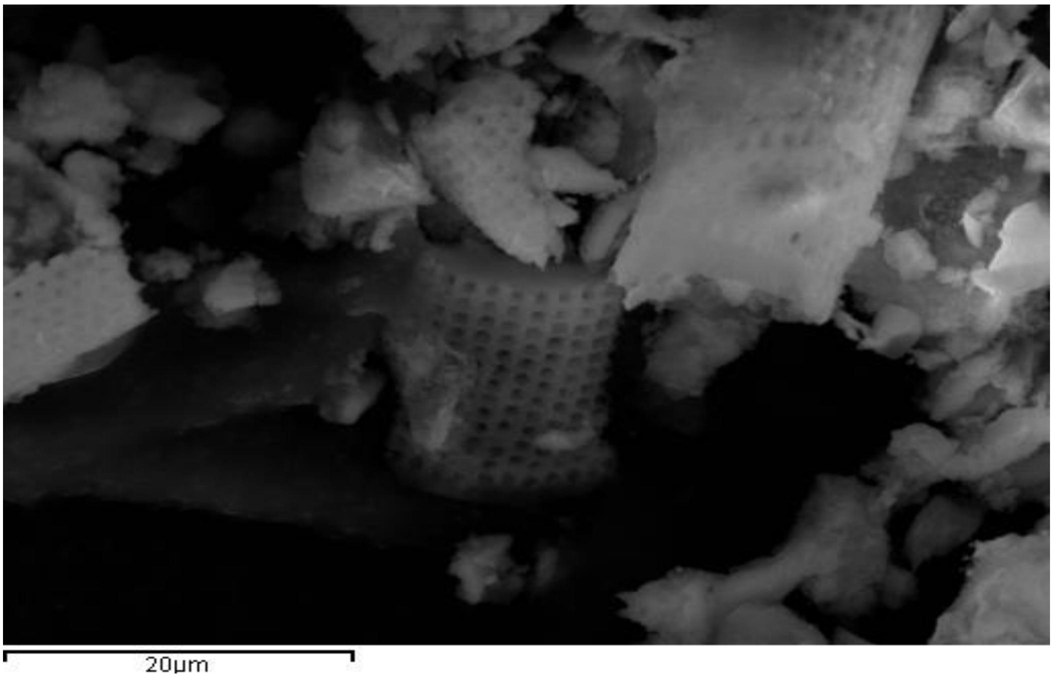


Plate 4.5 SEM image of Harmattan dust sample

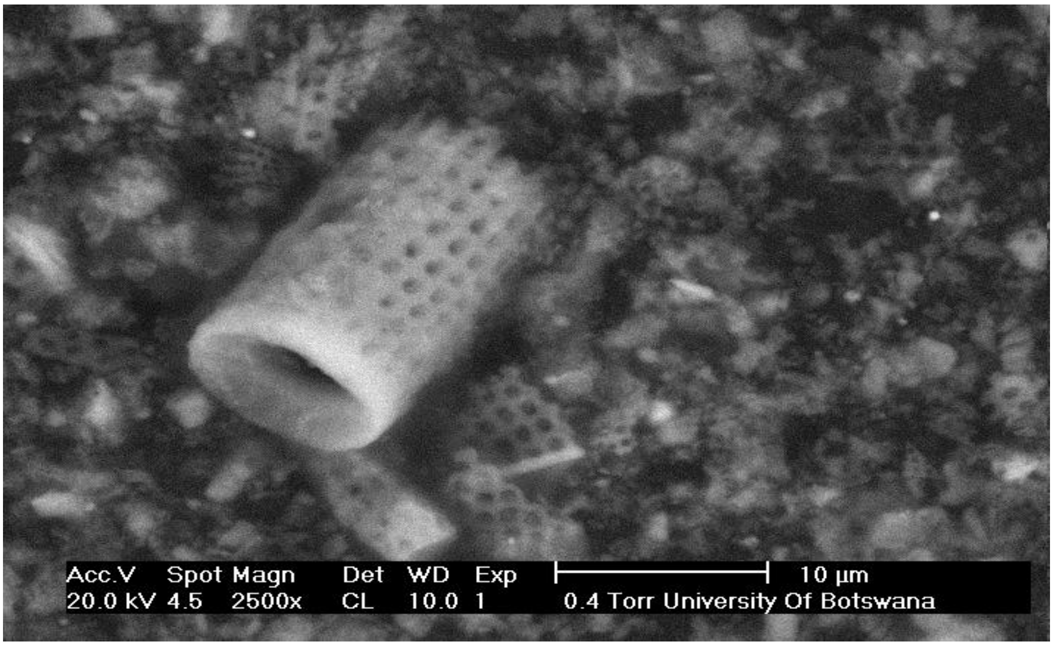


Plate 4.6 Crushed diatom fragments (Todd et al., 2005)

Table 4-4 Elemental composition of Harmattan dust particles

	Amount of elements in weights (%)									
	C	**O**	**Na**	**Si**	**S**	**K**	**Ca**	**Ti**	**Fe**	**Total**
Total	39.9	34.1	0.7	0.2	2.4	5.1	3.3	1.2	2.4	100

The images of the storm particles are mostly unclustered rectangular sharp-shapes of quartz (sand) particles (Plate 4.7). The elemental content of these particles shows the element O, dominating followed by Si, Al, Ca and Fe (Table 4.4 and spectrum 2). The Spectrum 1 in Plate 4.7 may be from an organic source.

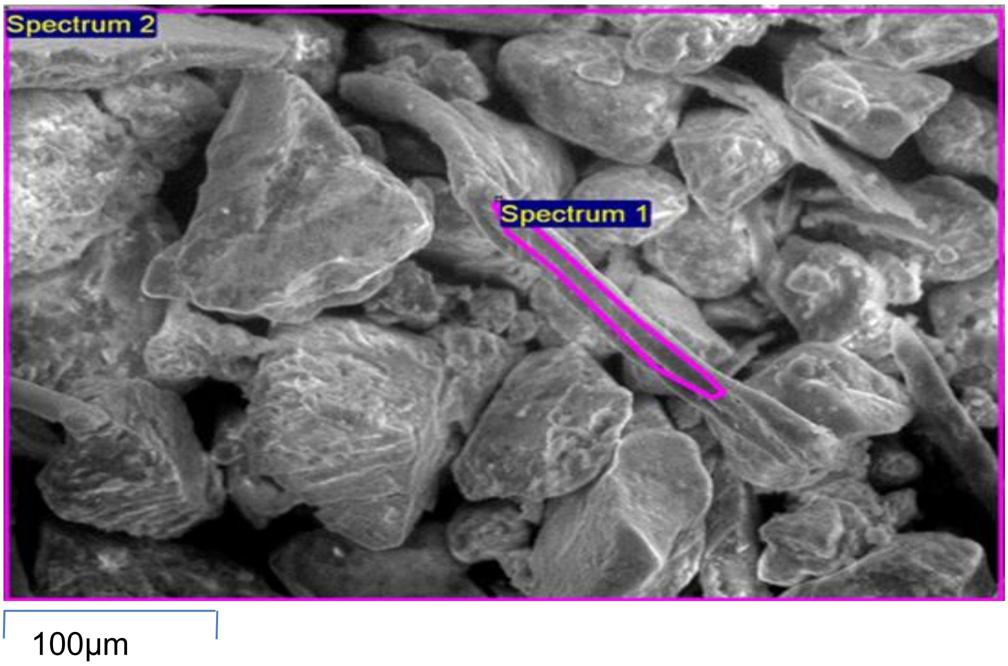


Plate 4.7 SEM image of Storm dust

Table 4-5 Elemental composition of Storm dust particles

	Amount of elements in weights (%)											
Spectrum	C	O	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe
1	31.7	46.5	0.7	4.2	11.8	0.4	1.1	1.1	1.2	0.2	1.1	
2		54.7	0.9	0.2	6.8	27.9		1.1	1.8	3.7	0.6	2.3

The dust particles were found to contain mixtures of particles of different shapes and sizes which may have originated from different indoor and outdoor sources. The strong winds that blow during the dusty events may be the cause of the high presence of sand fractions in the Nigerian dusts. The presence of soot on the other hand is probably from the fossil fuel combustion and wood burnt during cooking and various activities. The Harmattan particles were found to contain the crushed diatoms believed to be transported over hundreds of kilometres from the Bodele depression by the seasonal north-eastern trade wind that blows during the Harmattan season as reported by Todd et al., (2005).

4.2.4 Ultrafine Particles (UFPs) and Carbon monoxide (CO)

The various household activities (anthropogenic) were found to generate substantial concentrations of ultrafine particles depending upon the type of activity. The ultrafine particle counts ranged of 5,940 to 500,000 cm^{-3} (maximum measuring capacity of the instrument). The least particle counts were observed at the ambient condition (11,081 cm^{-3}). A continuous high particles count was recorded during electricity generation with diesel; 321,400 to 500,000 cm^{-3} throughout the sampling period (Table 4.6). Generally higher concentrations of UFP counts were observed during burning fossil fuels than when there was no activity. The UFP counts were high throughout the sampling period (10 minutes) in each case indicating the continuous release of the particles during the process.

Diesel combustion showed the highest UFP counts, cooking with firewood had the second highest, followed by kerosene combustion, which showed fluctuations of the UFP levels through the sampling period. The UFP level at ambient condition (when there was no household activity) was found to be low and steady through the first five minutes of the sampling period, but it kept fluctuating through the remaining sampling period (Figure 4.2). The fluctuations may be because of some activities taking place in the neighbouring household as the UFP count was done outdoors (in an open compound).

Table 4-6 Ultrafine particles monitored during activities in Nigerian Homes

ACTIVITY	**Location**	**Minimum pt/cc** (cm^{-2})	**Maximum pt/cc** (cm^{-2})	**Time min**
Firewood cooking	Indoor	321,400	500,000	10.00
kerosene stove	Indoor	213,456	500,000	10.00
Gas cooking	Indoor	97,201	384,600	10.00
Diesel generator	Outdoor	348,200	500,000	10.00
Petrol generator	Outdoor	61,366	500,000	10.00
Harmattan haze	Outdoor	205,793	498,766	10.00
Ambient condition	Outdoor	11,081	369,333	10.00
UK -Gas cooking	Indoor	5,940	7,550	10.00

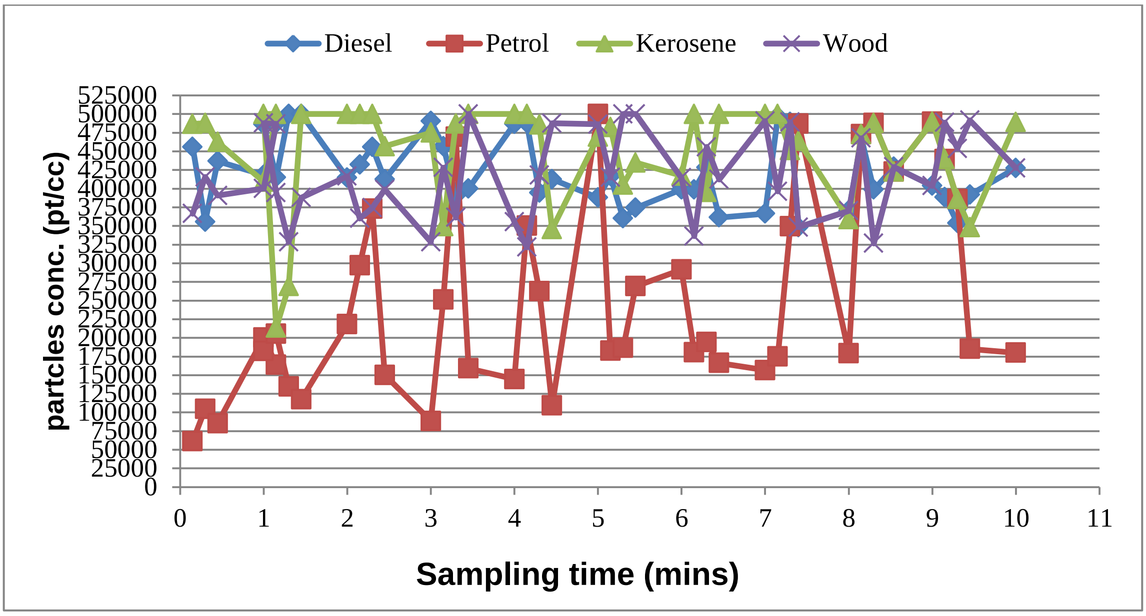


Figure 4.1 UFP concentrations during various household activities

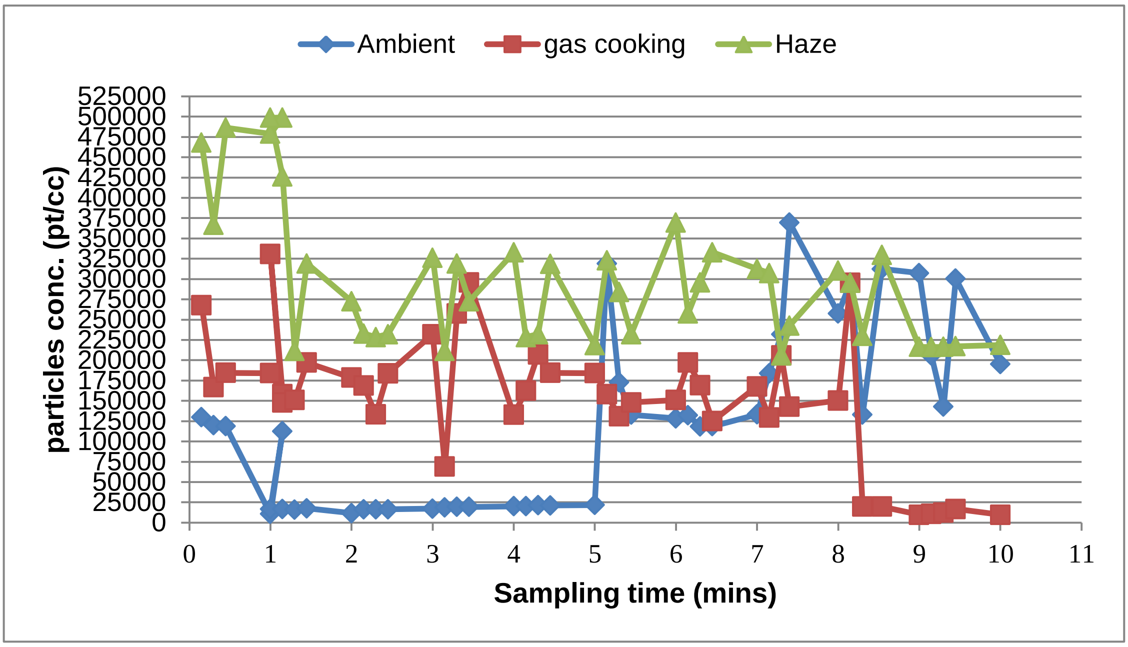


Figure 4.2 UFP concentrations during Harmattan haze, gas cooking and ambient condition

The CO levels found were higher during electricity generation with diesel than the other household activities. The CO concentrations observed were found to be higher during outdoor electricity generation with diesel with 176 ppm (217 mg m^{-3}), followed by cooking with kerosene in the indoor with 98.6 ppm (113.0 mg m^{-3}) and the lowest concentration of 4.0 ppm (4.6 mg m^{-3}) was observed at the ambient condition outdoor (Table 4.7). The lower CO concentration when there was no activity suggests that the various household activities resulted in the increased emission of carbon monoxide.

The mean CO concentrations were found to be above the WHO (2010) guideline of 100 mg m^{-3} or 87.29 ppm for 15 minutes average. The highest 10 minutes average CO concentration was observed during electricity generation with diesel of 110.6 ppm (126.7 mg m^{-3}) (Table 4.7). The high CO emission is an indication of incomplete combustion. High CO concentrations associated with electricity generation using fossil fuels with their potential health effects have been a cause of concern in Nigeria. This is due to the persistent power shortage and increased need of electricity as reported in many studies across the country. In most cases the portable generators were kept on verandas or in hallways leading to very high exposures and worst case scenarios often result in sudden death (Akande and Owoyemi, 2008; Mbamali *et al.*, 2012; Stanley *et al.*, Unpublished). The sudden increase in ambient CO emission after 5 minutes could be because of the onset of cooking in the neighbouring household.

Table 4-7 CO concentrations during household activities in Nigerian Homes

ACTIVITY	Location	Minimum ppm	Maximum ppm	Average		Time min
				ppm	mg m^{-3}	
Firewood cooking	Indoor	20	87	51.1	58.5	10
kerosene stove	Indoor	45	98.6	80.0	91.7	10
Gas cooking	Indoor	20	67.8	33.8	38.7	10
Diesel generator	Outdoor	16.3	176	110.6	126.7	10
Petrol generator	Outdoor	4.9	96.6	57.5	65.9	10
Harmattan haze	Outdoor	4.2	56	11.3	12.9	10
Ambient condition	Outdoor	4	11	6.0	12.6	10

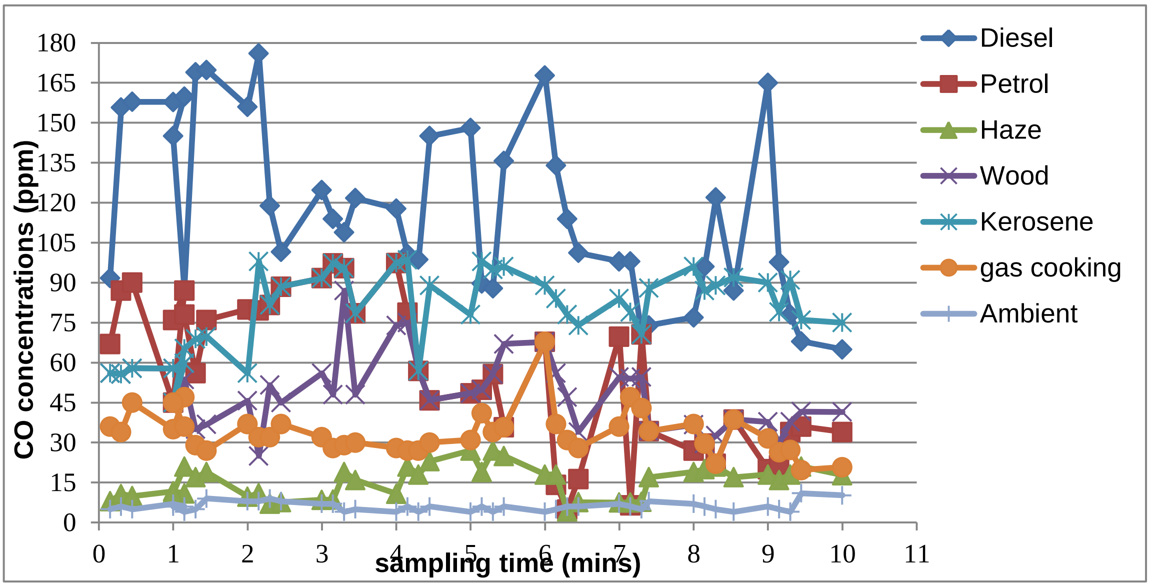


Figure 4.3 CO concentrations during household activities

4.3 Microbial analysis of settled dust and airborne particles

4.3.1 Microbial culture

Malt extract agar (MEA) was prepared by weighing 50 grams of MEA and dissolving in 1 litre of water and Nutrient agar (NA) was prepared by weighing

23 grams of the NA and dissolving in 1 litre of water. Each of the solutions were separately autoclaved for 10 minutes, the prepared media were each dispensed on petri dishes and allowed to set. One gram of each of the sieved settled dust samples were diluted in 9 ml of distilled water and 200 µml of each suspension were inoculated on the petri dishes containing the prepared media (in triplicates). The inoculated media of the settled dusts were then incubated at 25^{o}C for 3 days. The airborne samples were collected for 4 minutes each with the Buckhard biological monitor on agar plates and the plates were incubated at 32^{o}C for 3 days. Visible colonies were observed after 24 hours on all the cultured plates. The airborne samples collected in Nigeria were cultured and the fungi species were identified in the microbiology laboratory of the Science laboratory technology department at the Federal Polytechnic Damaturu, while the bacterial plates were sub-cultured and mounted on slides. The mounted slides were then stored in resealable plastic bags, transported to the Cranfield Health laboratory, and observed under the microscope.

The cultured media for both fungi and bacteria were observed for microbial growth and the colonies formed were counted with a Gallenhamp colony counter, where the numbers of colonies were recorded as colony forming units.

4.3.2 Fungi species

Fungal cultures were physically observed and various species present were identified based on their morphology (Plate 4.5). The fungi colonies identified in both the dust and airborne cultures include *Alternaria spp, Aurobaridium*, *Aspergillus niger, Aspergillus flavus, Cladosporium Fusarium, Penicillium*, *Pink yeast, White yeast* and some unidentified white and yellow colonies. *Clodosporium* was more abundant on all the cultured plates. A representative cultured Fungi plate is shown in Plate 4.5. Most of the fungi species identified have been reported in the literature as being commonly isolated from plant debris, soil, wood, textiles, and indoor air. *Alternaria* and *Clodosporium* were reported as the most prevalent fungal particles in dust while *Aspergillium spp* are said to thrive well in hot geographical regions due to their thermal tolerance (Sterflinger *et al.*, 2012).

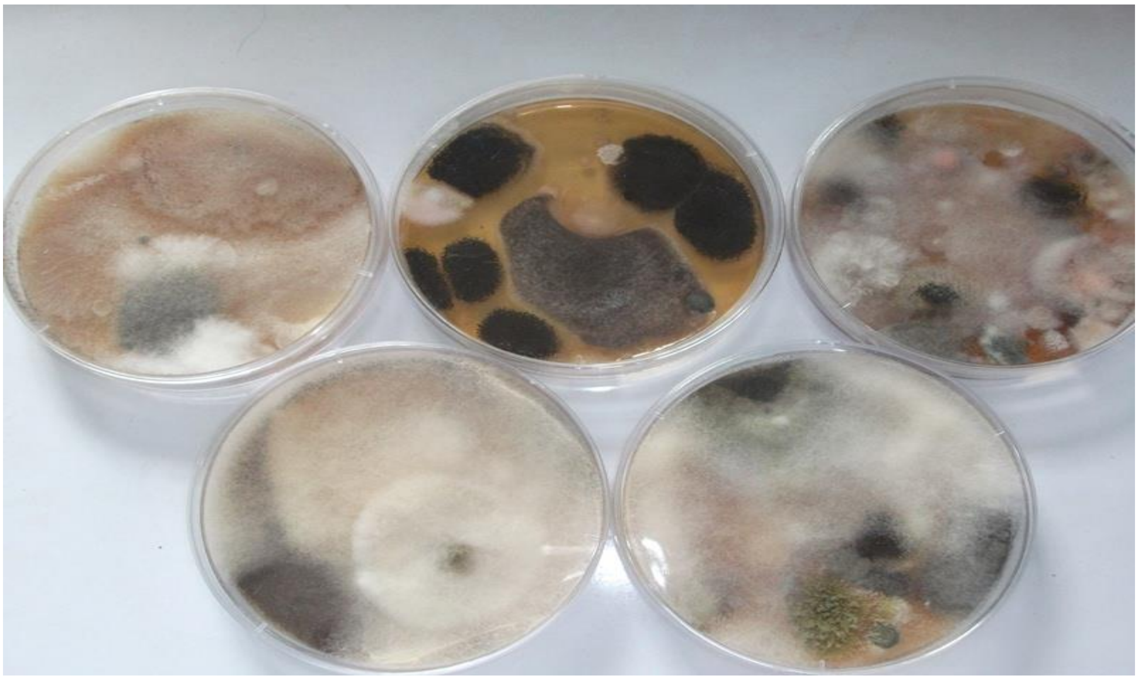


Plate 4-5 Fungal growth of cultured dust sample

The fungi colonies were found to be more in the dust samples collected from the indoors of homes than was observed in the Harmattan dust sampled outdoors (Table 4.8). The mean colony forming units were 1.97 x 10^5 cfu g^{-1} for dust and 1.44 x 10^5 cfu ml^{-1} in the airborne cultures. The maximum observed fungal growth was 2.74 x 10^5 cfu g^{-1} in FH house dust and 1.83 x10^5 cfu ml^{-1} in the airborne samples from LH house (Table 4.9). This is an indication of abundance of the culturable microbial spores in the indoors compared with the outdoor environment. The fungal colonies in the airborne samples were more than the range of <100 CFU m^{-3} to >1000 CFU m^{-3} reported in a previous study (Rao *et al.*, 1996). However no reported dust measurement was found for comparison.

4.3.3 Bacterial Species

The cultured NA media for both the settled dust and airborne samples were observed and visible bacterial colonies were counted. For further identification of bacterial species present, strands from the various colonies formed were sub-cultured, mounted on slides and a gram staining technique carried out. The prepared slides were observed under the microscope. The following colonies were identified; large rod and long filamentous gram positive B*acilli,* small pink gram negative *Cocci, Staphylococcus aures* (gram negative), unidentified pink and spread colonies and *yeast* in all the sub-cultures (airborne and dust). The bacterial species identified were predominantly gram positive and are *Cocci spp* with only one gram negative species identified (Plate 4.5). The abundance of more gram positive *cocci spp* of bacteria in both dust and air has been reported (Pakarinen *et al.*, 2008; Su *et al.*, 2001).

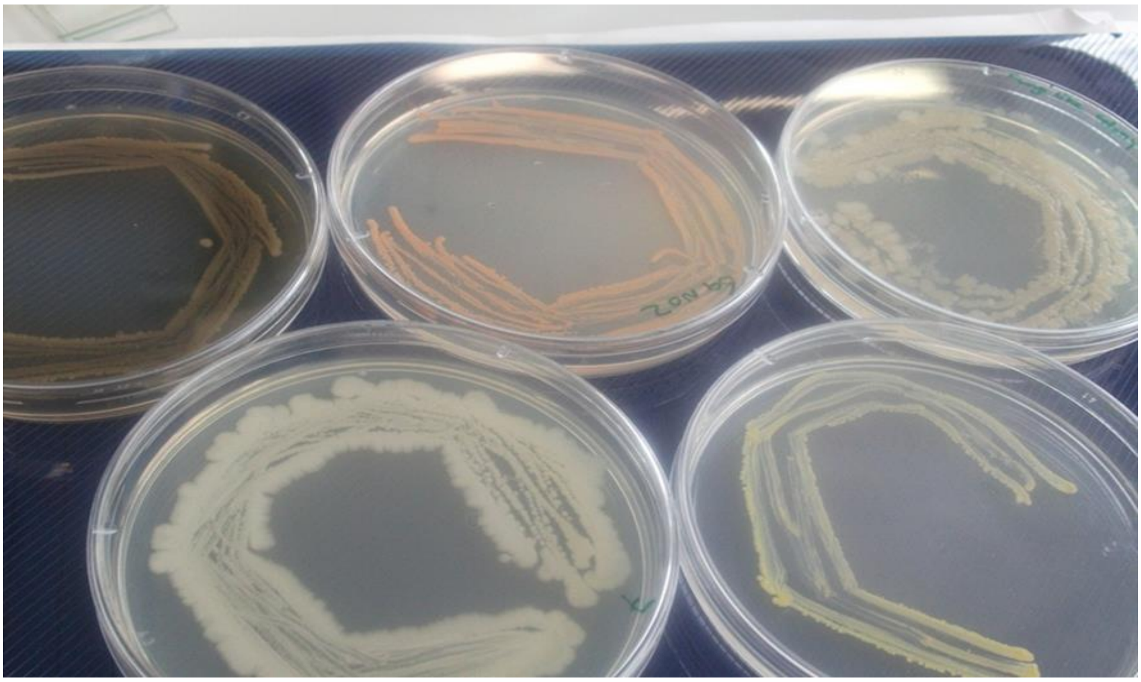


Plate 4-6 Smears of bacterial species in settled dust samples

The mean colony forming units counted in the airborne samples was 1.27 x 10^4 cfu ml^{-1} with minimum of 1.90 x10^3 cfu ml^{-1} and maximum of 1.45 x 10^4 cfu ml^{-1} (Table 4.9). The colony forming units for both bacteria and fungi in the air were found to be higher than the concentrations in human dwellings of Polish homes that were without mold problems (Gorny and Dutkiewicz, 2002). There was an indication of a host of species of microbial flora present in both air and dust, which can pose health effects such as allergies and pneumonia.

Table 4-8 Microbial colony forming units in dusts and airborne samples

	Fungal colonies (total)		**Bacterial colonies (total)**	
Sample	(CFU g^{-1})	(CFU ml^{-1})	(CFU g^{-1})	(CFU ml^{-1})
	Dust	Airborne	Dust	Airborne
AH	1.66 x 10^{5}	1.39 x 10^{5}	7.70 x 10^{4}	1.90 x 10^{3}
FH	2.74 x 10^{5}	1.79 x 10^{5}	9.80 x 10^{4}	4.50 x 10^{4}
LH	2.19 x 10^{5}	1.83 x 10^{5}	8.80 x 10^{4}	6.60 x 10^{4}
MH	1.95 x 10^{5}	1.15 x 10^{5}	1.22 x 10^{5}	9.80 x 10^{4}
YH	2.26 x 10^{4}	1.07 x 10^{5}	1.61 x 10^{5}	1.02 x 10^{5}
Storm	Not sampled	1.67 x 10^{5}	Not sampled	1.45 x 10^{5}
Harmattan	1.02 x 10^{5}	1.19 x 10^{5}	9.90 x 10^{4}	1.21 x 10^{5}

Table 4-9 Mean, maximum, and minimum of fungal and bacterial colonies

	Fungal colonies		**Bacterial colonies**	
	Dust (CFU g^{-1})	Airborne (CFU ml^{-1})	Dust CFU g^{-1})	Airborne (CFU ml^{-1})
Mean	1.97 x 10^{5}	1.44 x10^{5}	6.51 x10^{4}	1.27 x10^{4}
max	2.74 x10^{5}	1.83 x10^{5}	9.90 x10^{4}	1.45 x10^{5}
min	1.02 x 10^{5}	1.07 x10^{5}	1.22 x10^{4}	1.90 x10^{3}

The presence of livestock (sheep, cows, goats and poultry) in the households living together with humans which is a common practice in Damaturu could be a source of increased microbial flora in the air and dust. Many studies have reported the association between bacteria in house dust with health effects such as allergies, asthma, and increased hospital admissions especially among children (Kanatani *et al.*, 2010; Horak, 1987; Jo and Seo, 2005; Gorny and Dutkiewicz, 2002; Jaffal *et al.*, 1997), asthma and wheezing (Karvonen *et al.*, 2012).

4.4 Chapter Summary

The vacuum cleaner bag dusts were used for the SEM and the microbial analysis and the results obtained made it the best choice of sampling method. The preliminary results obtained gave a profile of what is contained in the dust. Furthermore, the airborne samples analysis gave additional information on the exposure risks to household dust in the indoor environment and evidence of risks to human health.

The physical characterization of the settled dust samples has revealed the various shape and sizes, and elemental composition and the presence of particles of respirable size. There was also the presence of sand and particles of derived from diatoms transported during the dust events from the dried Lake Chad. The microbial analysis has also indicated the presence of a host of fungi and bacterial species. The possible contributions of household activities to the increased production of pollutants (UFP and CO) was also ascertained.

5 ORGANIC CHEMICALS ANALYSIS

5.1 Introduction

The growing concern about the impact of chemicals in the household environment on our health has led to increased studies over the years to assess the levels of the chemicals in homes and the potential consequences for human exposure (Weber *et al.*, 2011). A widely occurring group of organic chemical compounds in both the gas phase and condensed phases are commonly referred to as semi-volatile organic compounds (SVOCs) which include pesticides, plasticizers and flame-retardants. SVOCs, especially phthalates that are widely used as plasticisers, have been investigated in this study because they have been reported as being among the most ubiquitous synthetic chemicals in the environment found in all types of environmental and many biological samples (Fromme *et al.*, 2004). As discussed in section 2.4.6.1 the non-dietary exposure to SVOCs via inhalation and dust ingestion has been identified as an important exposure pathway for humans. Therefore, phthalates in household dust is an important aspect of understanding the health risk associated with dust exposure.

The investigations reported in this chapter involved the determination of organic chemicals (VOCs and SVOCs) in house dusts and airborne samples by the analytical techniques of thermal extraction combined with thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) and by solvent extraction/gas chromatography/mass spectrometry (SE/GC/MS). The studies included method development work, particularly with respect to the measurement of organics in dust using thermal extraction.

5.2 Analysis of Organic Chemicals in House Dust by thermal extraction and TD/GC/MS

5.2.1 Sample preparation and instrumentation

The household dusts collected in vacuum cleaner bags as described in chapter 3 were subject to a novel method of investigating chemical content.

This involved heating of the dust directly in a micro chamber thermal extractor (µ-CTE) (Markes International Ltd., Llantrisant, UK), and collecting the chemical emissions released using sampling tubes containing a sorbent (Q-Tenax). The tubes were subsequently analysed by TD/GC/MS.

The sampled dusts were sieved through a laboratory sieve of 150-µm aperture with a stainless steel mesh (using a clean brush to exhaust dust particles through the sieve mesh). The sieving was carried out in a fume hood, wearing eye and mouth protection to avoid possible inhalation of the dust particles. The <150 µm fractions retained were kept in labelled glass jars and used for analysis. Weighed aliquots of dust were placed in the µ-CTE.

The µ-CTE comprises of six individual micro-chambers (28 mm deep x 45 mm diameter) designed for the collection of bulk or surface emissions of SVOCs and VOCs from a variety of materials. Six samples were tested simultaneously at temperatures from ambient to 120°C. A controlled flow of pure air / inert gas (10-500 ml min^{-1}) was passed through all chambers simultaneously to sweep emitted vapours onto attached sorbent tubes.

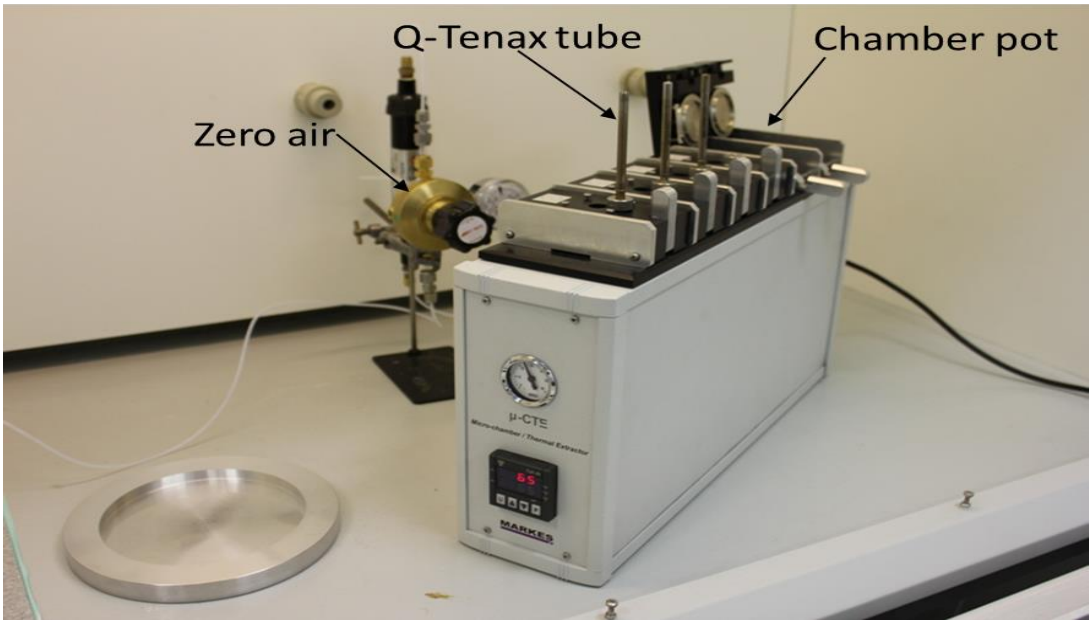


Plate 5-1 µ-CTE heating of dust and collection of emissions on Q-Tenax tubes

The TD/GC/MS assembly used consisted of a TD-100^{TM} thermal desorber (Markes International Ltd.), gas chromatograph (GC) (Agilent 6890^{TM}) and mass selective detector (MSD) (Agilent 597^{TM}) located in the IEH Volatiles Laboratory, Cranfield University. The use of TD/GC/MS analysis for the determination of organic compounds allows identification of unknown components and can separate the objective components from interfering materials (Yoshida *et al.*, 2004). The analysis was based on a method developed within the IEH Volatiles Laboratory for the determination of VOC emissions from construction and consumer products with the following instrumental conditions:

Thermal Desorber (TD): Thermal desorption involves the use of heat and a flow of inert (carrier) gas to extract volatiles from a solid or liquid matrix directly into the carrier gas and this transfers them to the analytical column of a GC. No solvent is required. Sorbent tubes were desorbed at 300°C for 8 minutes in a flow of helium with the split flow of 50ml min^{-1}. The desorbed compounds were then trapped in a ‘Materials Emission’ (Markes International Ltd.) cold trap at -10°C, followed by fast heating of the cold trap to 300°C with a split of 10 ml min^{-1} and a cold trap high temperature hold time of 3 minutes.

Gas Chromatography (GC): A 60-metre DB5 column of internal diameter 0.25 mm and film thickness 0.5 µm was used. A constant flow of 1.3 ml min^{-1} helium was set and a thermal gradient applied; oven temperature 35°C for 1 minute, then 2°C min^{-1} to 76°C, 5°C min^{-1} to 140°C ,10°C min^{-1} to 300°C and a 12 minute hold time.

Mass Spectrometer (MS): Scan range 20-450 amu, MS transfer line 280°C, MS source temperature 230°C, MS quad temperature 150°C. The TD/GC/MS assembly is shown in Plate 5.2.

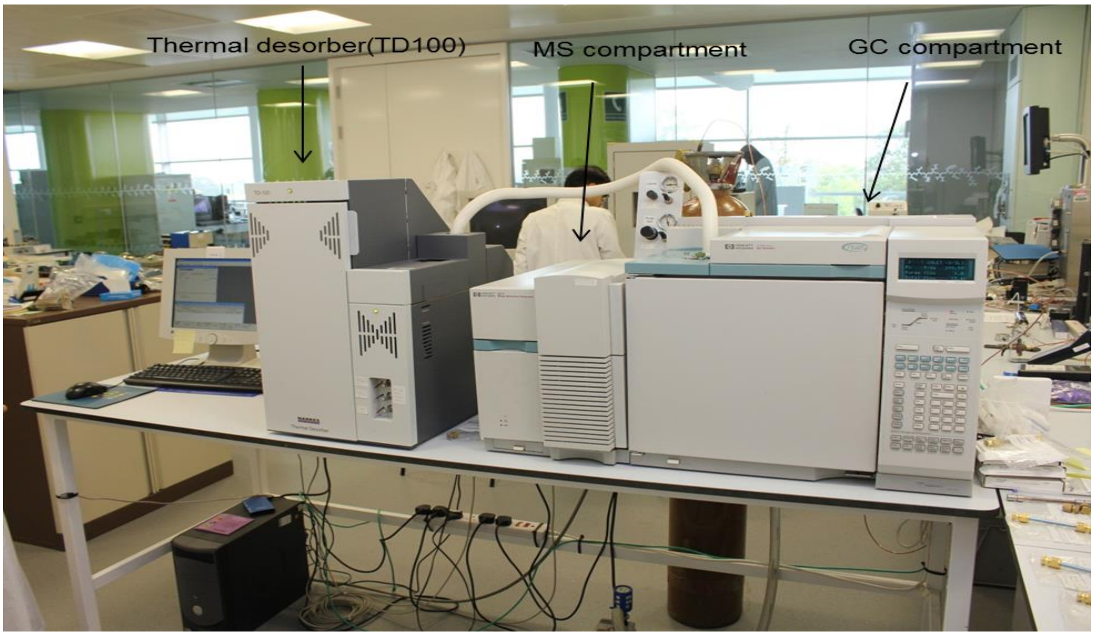


Plate 5-2 The TD/GC/MS assembly

5.2.1.1 TD/GC/MS Procedure

The sampled tubes and the blank were in turn loaded onto a solution-loading rig. A flow of clean air was set at 80 to100 ml min^{-1} through the tubes and with a glass micro syringe each of the tubes were spiked with 0.5 µl D-toluene solution as internal standard. The tubes were purged for approximately three minutes (it takes about 4 minutes for each tube to be spiked) and the tubes were closed by fitting silcosteel analytical caps and then loaded on the TD trays.

In the TD, desorption of tubes takes place (1 tube at a time) followed by fast heating of the cold trap. The vaporized sample is swept by the carrier gas through the coiled 60 m GC column situated in an oven that regulates the GC temperature. The column is coated with a porous stationary phase in which the separation occurs. Vaporized molecules are separated (and eluted) based primarily on their volatility; compounds with high vapour pressure (lower boiling points) travel faster, have low retention time and are eluted earlier than the higher boiling compounds, which take longer to travel through the column into the interface and to the MS. The separated gaseous molecules then pass into the MS compartment and are ionized by electron beams, and then through the mass analyser and ion detectors. Molecular spectra are produced and the data are accessed via an attached PC. The process is outlined in a schematic diagram (Figure 5.1).

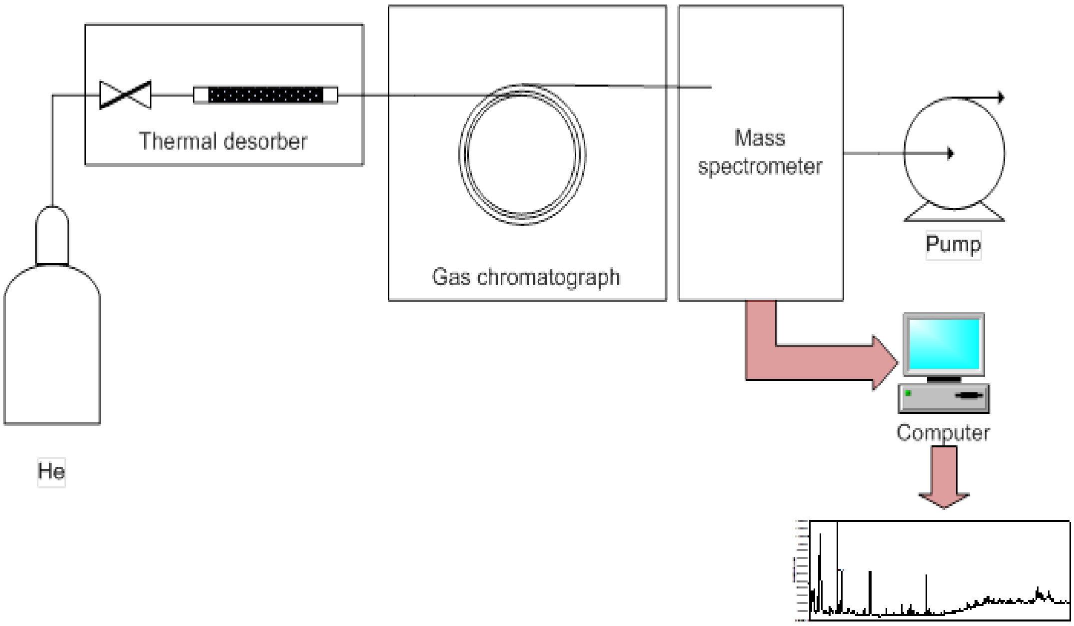


Figure 5.1 Schematic diagram of TD/GC/MS process

5.2.1.2 The initial µ-CTE Procedure

The initial procedure of heating the dust in the µ-CTE was adapted from the work of Brown and Crump, (2008) with some modifications. For this method, approximately 5 g of each dust sample (<150 µm fraction) was accurately weighed with a 5-figure balance (SartariousTM) into a µ-CTE pot lined with glass micro-fibre filter paper (GF/A) which had been conditioned in a laboratory oven at 200°C for one hour. A second piece of conditioned filter paper was placed over the dust with the aim of preventing the possibility of dust suspension in the airflow and being sucked onto the sampling tubes, as well as contaminating the µ-CTE pots through direct contact. Each dust sample was placed in duplicate pots and these were loaded into the µ-CTE chamber, including one pot containing filter paper alone to act as control. The instrument was heated at 120°C (the maximum temperature for the instrument) with a flow of about 70 ml min^{-1} of clean air through each pot. The sorbent tubes containing quartz wool and Tenax (Q-Tenax) were attached to the outlet of each pot via the grooved end from the start of heating. The heating was undertaken for 2 hours with the sampling tubes replaced after each 40 minutes. The sampled tubes were analysed by TD/GC/MS.

5.2.2 Method Development

A standard stock solution containing eight (8) chemicals (as described in 5.2.5) was prepared by weighing 0.4 g of each of the chemicals into a 10 ml volumetric flask and making it up to 10 ml with methanol (solvent). The stock was diluted to varying concentrations that were used to calibrate the analytical instrument. The stock was diluted serially down to 40 mg ml^{-1} and 1μl of each of the diluted standard solutions was spiked onto a Q-Tenax tube followed by 5 μl of d-Toluene (as internal standard). The spiked tubes were then run on the TD/GC/MS system prior to running of the analytes. Calibration curves were obtained for the target chemicals which were used to determine the concentration of the chemicals in the analytes using the accompanied software (Agilent GC-MSD ChemStation). The calibration curve is a plot of the instrumental response against the concentration of the analyte standards. An example of a calibration curve is shown in Figure 5.2.

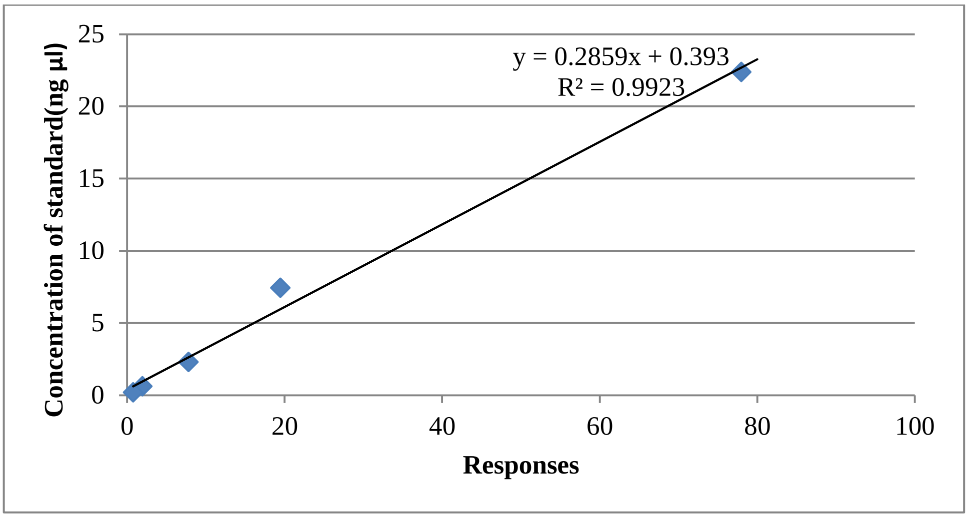


Figure 5.2 **Calibration curve of Hexanal for TD/GC/MS analysis**

5.2.2.1 Thermal extraction and TD/GC/MS (method A)

Experiments were undertaken to investigate the feasibility of using an existing analytical procedure of thermal extraction coupled with TD/GC/MS analysis. Method-A (µ-CTE-TD/GC/MS) used in the IEH volatiles laboratory for testing emissions from building materials was used to extract organic chemicals from dust. The initial experiments were carried out with two UK samples, DH1 and DH2, collected from the same house on different occasions during the method development phase (Table 3.2). The procedure as described in (5.2.1.2) was followed.

5.2.2.2 Chemical Analysis using Method B

In method A, as described in 5.2.1.2, filter papers were placed in the µ-CTE pots, which were subsequently thought to (possibly) interfere with the result by being a source of some chemical emissions. The procedure was altered by not adding the filter paper into the pots, 3g of each sample was heated instead of 5g, and the heating was done for 90 minutes over 3 periods of 30 minutes each**.**

Testing the repeatability of the µ-CTE thermal extraction of dusts was carried out with samples of one UK and one Nigerian (DH1 and FH) dust by putting 3 grams of each of the dusts in five pots and heating for 40 minutes. The similarity of chemical emissions in the five pots given by this repeatability test was determined. The results are shown in section 5.2.5.4.

Descriptive statistical analysis was carried out where the means of the replicates were taken and standard deviations determined. The differences between means of the chemical emissions in the analysed samples were calculated.

5.2.2.3 Investigation of Organic Chemicals in UK and Nigerian Dusts using Method C

To optimise the quantification limits for the samples the quantity of dust extracted was further reduced to 1 g, and more dust samples were analysed based on this procedure (method C). Indoor/outdoor Nigerian dusts collected in July 2010 (storm period), and UK dust samples (collected at different times) as described in chapter 3 were analysed. The samples were heated in duplicates for 60 minutes at a temperature of 120^{o}C. The heating was done over 2 periods of 30 minutes each, changing the sampling tubes after each period. Parameters such as temperature changes and airflow were observed. The airflow pressure was regulated at 11 psi and the rate of airflow through the μ-CTE pots was monitored. The sampled tubes were investigated for the presence of SVOCs and VOCs by TD/GC/MS. The results are shown in section 5.2.5.5.

5.2.2.4 Investigation of Chemical Emissions from Sand

Samples of sand were also collected from an outdoor location (dried waterway) about 500 metres away from township buildings in Damaturu (as described in 3.3.7) and were analysed by TD/GC/MS. Because of the low level of chemicals, this also acted as a check for the possible contamination of samples by the sampling method used or during transportation of samples to the laboratory (section 5.2.5.6).

5.2.2.5 Analysis of Chemicals in a Standard Reference Dust (SRM 2585)

A standard reference material for chemical analysis of household dust (SRM 2585) obtained from the National institute for standards (NIST) in the USA was analysed alongside the test samples. 1g of SRM 2585 was heated in the µ-CTE (in triplicates) for 60 minutes and emissions were collected on Q-Tenax tubes after every 30 minutes over 2 periods. The tubes were analysed by TD/GC/MS analysis (section 5.2.5.6).

5.2.3 Investigation of Chemicals in Dusts during Weather Events

More samples were collected using the same vacuum cleaner method of sampling during the notable dusty weather events; Harmattan and Dust Storm and when there was no dusty event (no-event period) (Table 3.37) and the dust samples were analysed by method C. The results are as shown in section 5.2.5.4

5.2.4 Determination of Chemicals in Dusts from Modern and Traditional Buildings

Dust samples were collected from indoors and outdoors of 26 Nigerian homes (13 modern and 13 traditional types of buildings) as described in section 3.3.7. The samples were treated as in the previous analysis and the results are shown in section 5.2.5.8.

5.2.5 Results of µ-CTE/TD/GC/MS Analyses

Based on the initial results using method A, it was apparent that a wide range of VOCs and SVOCs released were from dusts and therefore it was necessary to select a number of these for quantitative investigation that was practical within the available resource. The selection was done based on the health hazard of the chemicals as reported in other studies, their frequency of occurrence in the various samples, the suitability of the analytical method and the quantification limit of the analytical equipment used. The chemicals are benzene, hexanal, nonanal, limonene, diethyl phthalate (DEP), diisobutylphthalate (DIBP), dibutylphthalate (DBP), and diethylhexylphthalate (DEHP) (Table 5.1).

The lower quantification limits of selected chemicals ranged between 5 ng to 10 ng on the tubes and upper limits ranged from 1200 ng to 4000 ng as was established in the initial calibration of the TD/GC/MS (Table 5.2).

Table 5-1 Target organic chemicals quantified (various sources)

Chemical	Characteristics	Uses	Health effect
Alkyl aldehydes-Nonanal, Hexanal,	Ubiquitous constituents emitted into the atmosphere from the incomplete combustion of biomass and fossil fuels.	Used in the flavour industry to produce fruity flavours.	Eye and mucous membrane irritants
Benzene	Used mainly as an intermediate to make other chemicals used to make polymers and plastics.	Used in rubbers, lubricants, dyes, detergents, drugs, explosives, napalm, and pesticides. Benzene is formed during fuel combustion.	Carcinogenic
Phthalate esters-DBP, DEP, DIBP, DEHP (CDC, 2011; Mercier et al., 2011)	DBP has a faint, disagreeable odour and can be transferred from the plastics that contain it.	Used as additive to adhesives, printing inks, plasticizer in plastisols (for example in toothbrushes, textile paint, food packaging and toys), nail polish, explosive material and as solvent.	Produce toxic gases, irritants, and endocrine disrupters.
Limonene (monoterpene) (Nilsson et al., 1998)	Occurs in citrus peel, and it has a strong generic citrus smell.	Widely used as a flavour and fragrance additive in cleaning and cosmetic products, food and pharmaceuticals. It is also present in most of the essential oils.	Contact with limonene or limonene products can cause eye and skin irritation.

Table 5-2 Lower and upper quantification limits in the initial method A

LIMITS OF QUANTIFICATION (ng)		
Compound	**Lower limit**	**Upper limit**
Benzene	5	5000
Hexanal	5	4000
Nonanal	5	4000
Diethylphthalate (DEP)	5	4000
Diisobutylphthalate (DIBP)	5	1600
Dibutylphthalate (DBP)	5	1200
Diethylhexylphthalate (DEHP)	10	1200

Modifications to the method were made to prevent over loading of the sampling tubes to enable quantification and to achieve time saving and usage of fewer tubes, thus enabling available resources to be applied to a greater number of the dust samples. Because the sampled tubes were over loaded and the observed high concentrations of chemicals, the TD/GC/MS was re-set with a split of 10:1.

The Modified method B was adopted and the system was calibrated with higher quantification limits than in the former method due the fact that some of the compounds (nonanal, DIBP, and hexanal) in a number of samples were above their high quantification limits when the former method was used. The low limits in method B ranged between 26 ng and 410 ng and the high limits ranged between 30,000 and 42,000 ng (Table 5.3).

Table 5-3 Quantification limits in method B

LIMITS OF QUANTIFICATION (ng)		
Compound	**Lower limit**	**Upper limit**
Benzene	26	26,000
Hexanal	390	39,000
Nonanal	410	41,000
Diethylphthalate (DEP)	36	36,000
Diisobutylphthalate (DIBP)	39	39,000
Dibutylphthalate (DBP)	42	42,000
Diethylhexylphthalate (DEHP)	75	30,000

5.2.5.1 Chemicals determined by thermal extraction Method A

The chemical emissions on the sampled tubes are presented according to the two periods of 40 minutes during which the dust samples were heated in the µ-CTE (Tables 5.4 and 5.5). The chemicals quantified showed high concentrations (high emissions) compared with the content on the blank tubes during both heating periods. Nonanal and DIBP were quantified as being higher than their upper calibration limit in the first set of tubes; in the second set only DIBP emission was found to be above the upper limit of quantification.

Table 5-4 Chemical emissions during the first period of µ-CTE heating

Period 1 (Tubes set 1)

Compound	**Amount of chemicals on tube (ng)**					
	Pot 1 Blank Tube	**Pot 2 Control**	**Pot 3 DH1**	**Pot 4 DH1**	**Pot 5 DH2**	**Pot 6 DH2**
Benzene	<5	31	56	58	34	32
Hexanal	<5	89	2474	2789	1883	1885
Nonanal	<5	79	~8576	~8482	~6845	~6863
DEP	<5	73	149	155	148	145
DIBP	<5	130	~4676	~4654	1041	1082
DBP	<5	11	494	500	404	356
DEHP	<10	96	520	488	391	387

~ Approximate as amount is above upper limit of quantification (calculated by assuming linear relationship above upper calibration point).

Table 5-5 Chemical emissions during the second period of µ-CTE heating

Period 2 (tubes set 2)

Compound	**Amount of chemicals on tubes (ng)**					
	Blank Tube	**Pot 5 (Control)**	**Pot 1 DH1**	**Pot 2 DH1**	**Pot 3 DH2**	**Pot 4 DH2**
Benzene	<5	25	59	60	54	53
Hexanal	<5	<5	1285	1280	1140	1187
Nonanal	<5	20	3571	3531	~4081	~4013
DEP	<5	3	213	218	123	142
DIBP	<5	145	~6619	~6581	~2984	~2874
DBP	<5	6	952	986	870	885
DEHP	<10	12	~1268	~1230	~1161	~1185

~Approximate as amount is above upper limit of quantification

The presence of detectable amounts of the chemicals on the analysed tubes was a good indication of the potential of µ-CTE heating of the dust as a method of releasing chemicals from dust for TD/GC/MS analysis. However, the presence of chemicals on the control tubes indicated that the filter paper inserted in the µ-CTE pots might have significantly contributed to the chemical emissions observed. The quantity of the dust samples heated might have also contributed to the high emissions of some compounds relative to the upper calibration limit used.

5.2.5.2 Chemicals determined by thermal extraction Method B

In the modified method, the quantity of the heated dust was reduced from 5 g to 3 g; the filter paper was not inserted into the µ-CTE pots; and the heating period was 90 minutes over three periods (30 minutes each). The concentrations of chemical emissions in the analysed samples were then quantified (Table 5.6).

The TD/GC/MS system was calibrated with higher concentrations of the standard target chemicals so the quantification limits were higher than used in Method A. The chemical emissions from the sampled tubes were within the range of the lower and upper calibration limits shown in Table 5.3. Amounts in the control tubes were below the detection limits of the chemicals. The amounts present on each tube expressed as ng g^{-1} of dust during the 3 sampling periods are shown in Table 5.6.

Table 5-6 Chemical concentrations (ng g^{-1}) in DH1 and DH2 (method B)

Compound	**Total amount of chemicals on tubes in ng g^{-1}**							
	DH1 Dust				**DH2 Dust**			
	Period 1	**Perio d2**	**Period 3**	**AM**	**Period 1**	**Period 2**	**Period 3**	**AM**
Benzene	46	50	48	48	11	10	13	11
Hexanal	818	796	773	796	418	386	386	397
Nonanal	2587	2677	2262	2509	1258	1351	1346	1318
DEP	29	31	35	32	45	43	44	44
DIBP	1512	1552	1613	1559	811	928	913	884
DBP	262	301	290	284	223	231	291	248
DEHP	436	412	455	434	368	379	388	378

The results showed the presence of all the target chemicals in detectable amounts collected on the tubes from both samples during all the sampling periods. The amounts of chemicals in the two dusts (DH1 and DH2) were quite similar although they were collected at different times. An initial investigation of the repeatability of measurements was carried out by calculating the difference of individual values from the means of chemical emissions given by the replicate pots. The percentage difference from the means of chemical concentrations for the sampled duplicates were less than 15% during the 3 periods of heating indicating similarity between samples, and good repeatability of the method (Tables 5.7).

Table 5-7 Difference from the means of duplicate samples in DH1 and DH2 dusts (method B)

Mean concentration of chemicals on duplicate tubes and difference				
Compound	**DH1**		**DH2**	
	Mean (ng)	**Diff (%)**	**Mean (ng)**	**Diff (%)**
Benzene	48	8	11	5
Hexanal	796	3	397	8
Nonanal	2509	4	1318	7
DEP	32	6	44	5
DIBP	1559	2	884	13
DBP	284	13	248	3
DEHP	434	5	378	3

5.2.5.3 Repeatability Test of thermal extraction Method B

The quantified chemical emissions in all the 5 replicates from both DH1 and FH dust samples showed good repeatability of the analytical procedure (Figures 5.3 and 5.4). The relative standard deviations (RSD) of the replicates in both dusts were 10 to 27% with a higher value of 47% for benzene, which was present in low concentrations (Table 5.8). Benzene was not detected in FH dust. The percentage relative standard deviations from the mean of the 5 repeated tubes are further evidence of good repeatability of the micro chamber thermal extraction of chemicals from the dusts.

As in the previous experiment, there is evidence of continued emission over the 90-minute period and this is likely to continue beyond this time. In order to provide a comparative method that was time and resource efficient it was decided to fix the thermal extraction period to one hour, although still use two sampling tube periods to check the profile of emission and reduce the likelihood of overloading of tubes. Further, as there was adequate sensitivity for most analytes the use of 1 g of dust was adopted in the subsequent tests of further Nigerian and UK dusts.

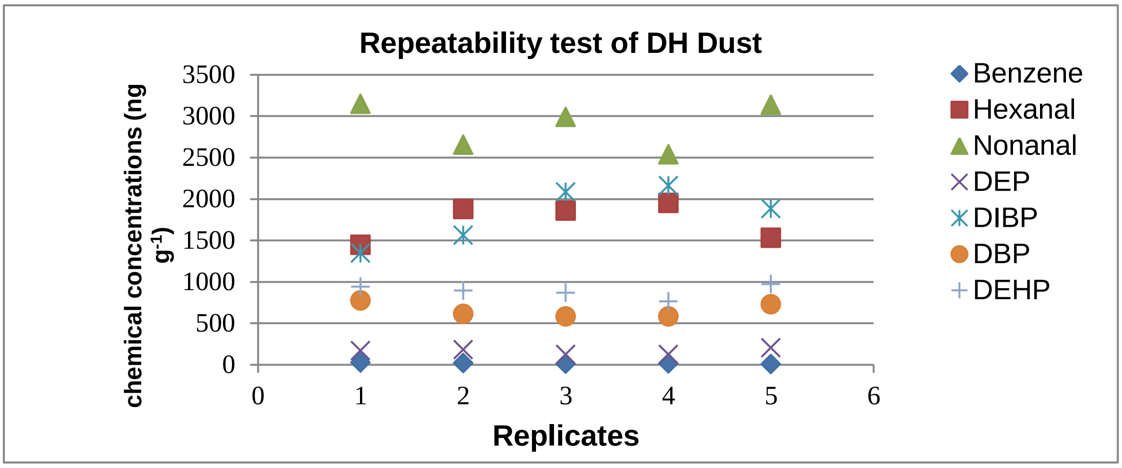


Figure 5.3 Chemical emissions (ng g^{-1}) for 5 replicates of DH Dust

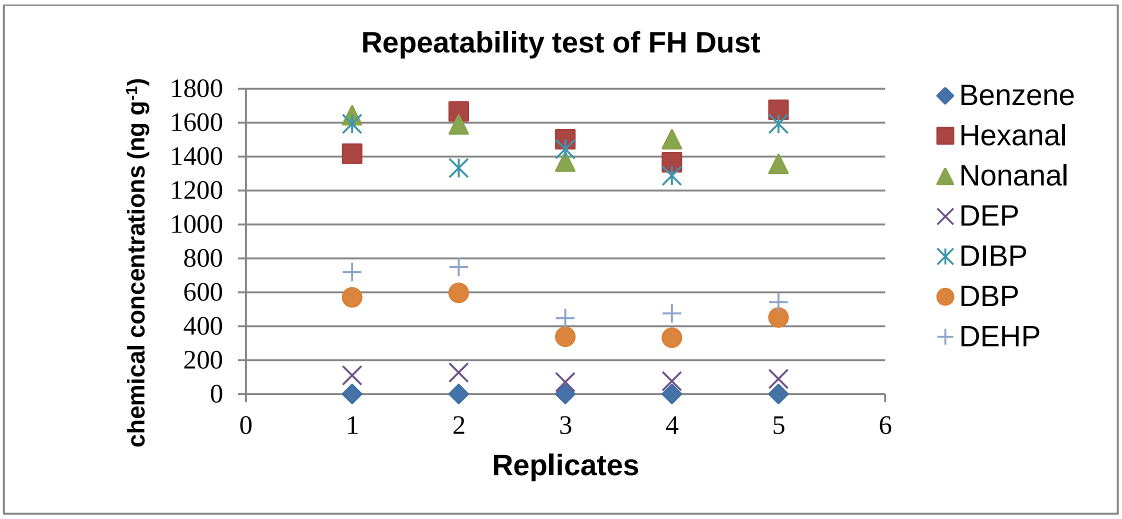


Figure 5.4 Chemical emissions (ng g^{-1}) for 5 replicates of FH Dust

Table 5-8 Chemical concentrations (ng g^{-1}) during the repeatability tests

	DH1 Dust			**FH1 Dust**		
Compound	**mean**	**SD**	**RSD%**	**mean**	**SD**	**RSD%**
Benzene	14	7	46.6	ND	-	-
Hexanal	1732	228	13.1	1524	281	9.7
Nonanal	2892	281	9.7	1491	128	8.6
DEP	157	36	23.0	94	24	25.4
DIBP	1805	346	19.2	1449	142	9.8
DBP	654	91	13.8	457	125	27.3
DEHP	886	80	9.1	586	139	23.8

ND= Not detected

5.2.5.4 Analysis of Nigerian and UK Dusts using Method C

1 g of each dust sample was heated in the µ-CTE and collection of emissions on Q-Tenax sampling tubes was undertaken over two periods of 30 minutes for Method C. This was used to carry out further experiments on 5 indoor and 1 outdoor sample collected in both Nigeria and the UK. As previously, the analysis revealed the presence of many organic compounds in the various dust

samples from the duplicate tubes as shown on the chromatograms (Figures 5.5 and 5.6).

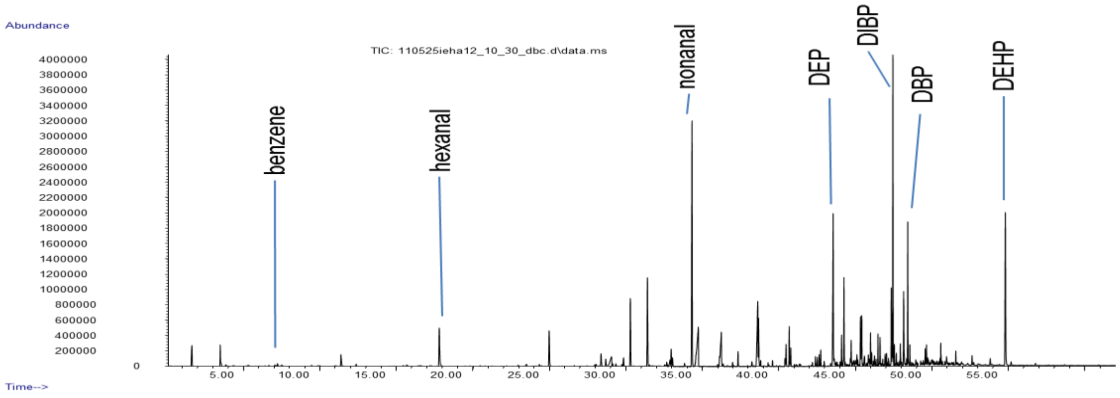


Figure 5.5 Chromatogram of a Nigerian Dust (FH) given by thermal extraction method C (abundance (MS total ion count) vs retention time)

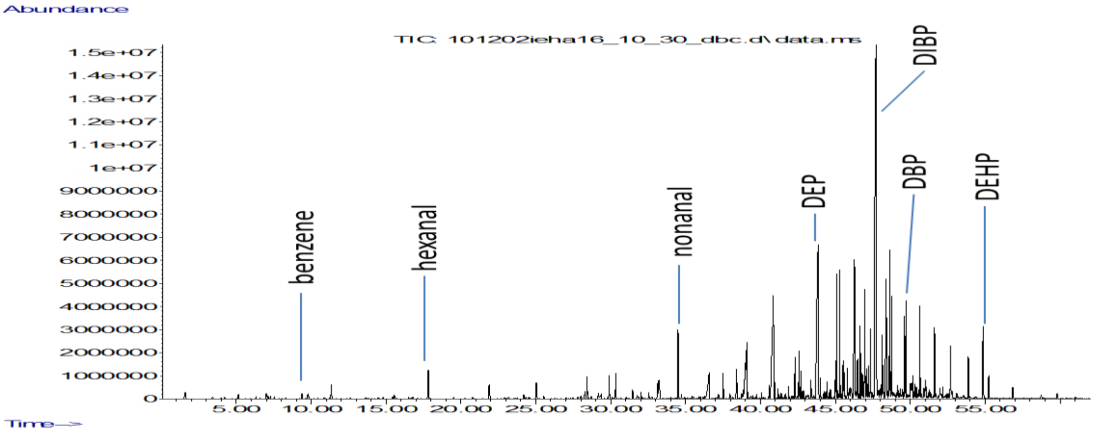


Figure 5.6 Chromatogram of a UK Dust (DH) given by thermal extraction method C (abundance (MS total ion count) vs retention time)

The concentrations of the target chemicals was quantified as ng g^{-1} of dust sample and each was analysed in duplicate. The mean concentrations of the duplicates ranged from <10 ng g^{-1} to 17,000 ng g^{-1} in the Nigerian dusts and <10 ng g^{-1} to 12,000 ng g^{-1} in the UK dusts (Figures 5.7 and 5.8). The chemical emissions from the individual household dusts were shown to be higher from the Nigerian dusts than the UK dusts, with only benzene being higher in the UK dusts than the Nigerian dusts.

Nonanal had the highest emission value for all chemicals in the Nigerian dust AH, followed by DIBP in a UK dust (DH). Chemicals were present in quantifiable amounts in the outdoor dusts sampled from UK and Nigeria, though in low concentrations compared to the indoor samples. The presence of chemicals in higher concentrations in the indoors than the outdoors conforms with findings of a US EPA study in 1985 that reported the levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside, regardless of whether the homes were located in rural or highly industrial areas (USEPA,1985). The higher concentrations of chemical pollutants indoors compared with outdoors have also been reported by other researchers (Rudel *et al.,* 2010; Shoeib *et al.*, 2005).

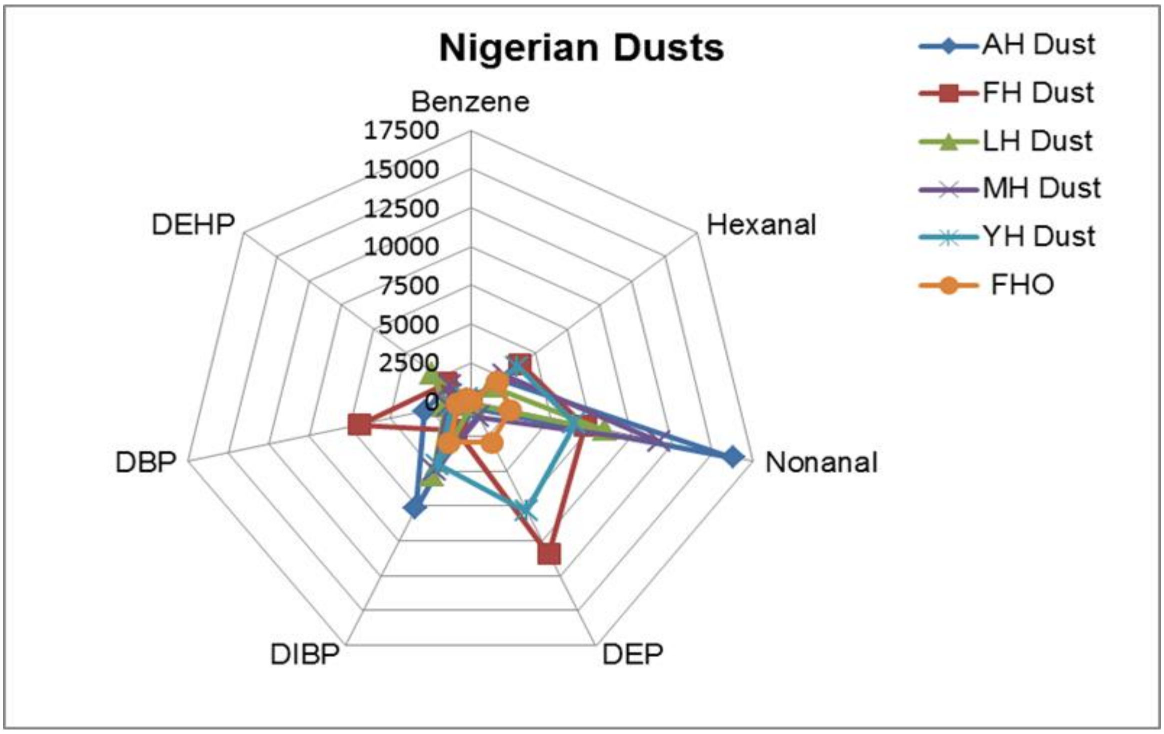


Figure 5.7 Mean Concentration of chemicals (ng g $^{-1}$) for 5 Nigerian dusts determined by thermal extraction Method C

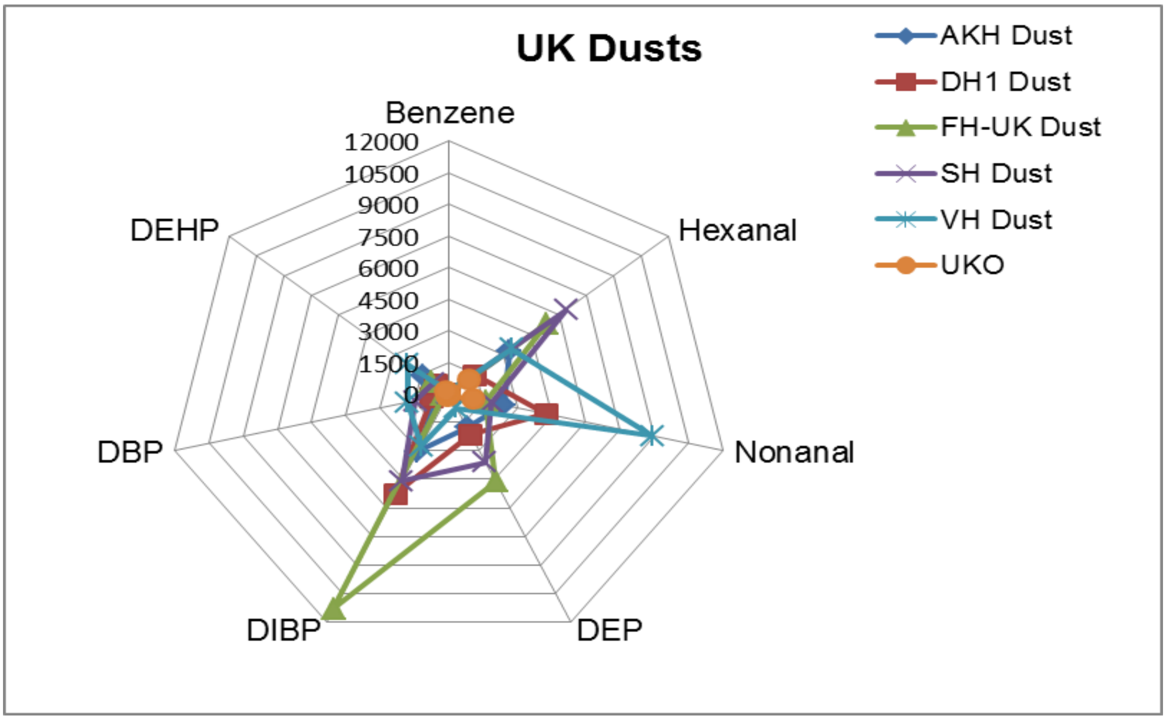


Figure 5.8 Mean Concentration of chemicals in (ng g $^{-1}$) for 5 UK household dusts determined by thermal extraction Method C

For comparison of the mean chemical emissions of the Nigerian and UK household dusts, arithmetic means (AM) of the individual chemical concentrations in the UK and Nigerian indoor dusts as well as their standard deviations (SD) and relative standard deviations (RSD) were calculated (Table 5.9). The geometric mean (GM) was also calculated because of the non-normal distribution of the data sets, which is typical of environmental data.

The mean emissions of benzene, hexanal, DEP and DIBP in ng g^{-1} of dust were higher in the UK samples, while the mean emissions of nonanal, DBP and DEHP were higher in the Nigerian samples than the UK samples. Benzene was not detected in both UK and Nigerian outdoor samples, all other were chemicals released in higher amounts in the Nigerian outdoor dust compared with that of the UK outdoor dust. The relatively high benzene and aldehydes concentration on the other hand, is typical of the result obtained in the indoor air of industrialised environments with high usage of fossil fuels as reported in a number of studies (Mercier et al., 2011; Grudd et al., 2011).

Table 5-9 Descriptive statistics of chemical emissions data for indoor and outdoor dusts

Chemical concentrations in ng g^{-1} in indoor settled dust									Outdoor Dusts	
	Nigerian Dusts (n=5)				UK Dusts (n=5)					
Compound	**AM**	**GM**	**SD**	**RSD %**	**AM**	**GM**	**SD**	**RSD %**	**UKO**	**FHO**
Benzene	14	3	22	156	33	7	41	125	ND	ND
Hexanal	2788	2646	960	34	3985	3547	1927	48	43	2098
Nonanal	9998	9406	4074	41	3814	3080	3033	80	8	2472
DEP	2329	1133	3166	136	2574	2160	1534	60	7	1955
DIBP	4905	4514	2007	41	5397	4700	3480	64	17	2934
DBP	2755	2152	2418	88	950	751	660	69	11	789
DEHP	1669	1348	936	56	1231	1119	636	52	177	309

For further comparison of the amount of chemical emissions from the UK and Nigerian dust samples, the percentage difference between the mean chemical emissions were calculated (Table 5.10). The differences for the six compounds were <40% with the exception of benzene.

The student's t-test was performed on the AM values. The calculated t-values of all the 7 target chemicals showed that there was no significant difference ($p=0.05$) in chemical emissions in the two sets of dust samples obtained in the UK and Nigerian homes (Table 5.10).

Table 5-10 Difference between the means of chemical concentrations in Nigerian and UK Dusts

Difference between emissions from Nigerian and UK dusts			
Compound	**%Difference**	**t-values**	**Sig. (2-tailed)**
Benzene	65.5	0.819	0.459
Hexanal	21.5	1.011	0.369
Nonanal	30.9	2.193	0.093
DEP	5.3	0.125	0.907
DIBP	5.0	0.263	0.805
DBP	32.8	1.482	0.212
DEHP	13.1	0.659	0.546

The indoor /outdoor ratios for all the chemicals in the Nigerian dusts were between 1 and 5. The indoor/outdoor ratios for hexanal and DEP were 1:1 with the DEHP ratio indicating indoor emission being 5 times the outdoor emission (Table 5.12). For the UK dusts however, the ratios were considerably larger ranging from 477 for nonanal emissions to 86 for DBP emissions with only DEHP having a lower ratio of seven, which was similar to the ratio for the Nigerian dusts (Table 5.11). These ratios indicate a greater influence of indoor sources of chemicals on the outdoors in Nigeria compared with the UK. Previous studies have also reported that organic chemical pollutants levels are higher in indoor than outdoor environments (Wilson *et al.*, 2001; Rudel *et al.*, 2010; Wilford *et al.*, 2004). The high chemical concentrations of hexanal and nonanal in Nigerian dusts could be because of their natural occurrence such as the presence in decaying woods used as pillars in the verandas.

Table 5-11 Indoor/outdoor ratios of chemicals in Nigerian and UK Dusts

	Nigerian Dust			**UK Dusts**		
Compound	**Indoor**	**outdoor**	**I/O ratio**	**Indoor**	**Outdoor**	**I/O ratio**
Benzene	14	ND	-	33	ND	-
Hexanal	2788	2098	1	3985	43	93
Nonanal	9998	2472	4	3814	8	477
DEP	2329	1955	1	2574	7	368
DIBP	4905	2934	2	5397	17	317
DBP	2755	789	3	950	11	86
DEHP	1669	309	5	1231	177	7

5.2.5.5 Chemical emissions in µ-CTE extracts of Sand and SRM 2585

The results of the chemical analysis of the surface soil (sand) samples using thermal extraction Method C did not show the presence of any chemicals at detectable levels. This shows a low level of chemical concentration in this sample collected away from human settlement in Nigeria. Further, it demonstrates the lack of any significant contamination from the sampling method involving the vacuum cleaner as well as the subsequent storage prior to analysis.

The chemicals in the standard reference dust material for analysis of organic chemicals in dust (SRM 2585) were investigated and the results are presented in Table 5.12. The phthalates emissions were more than that of the aldehydes. DBP had the highest concentration followed by DEHP, DEP and then DIBP. Benzene was found to be present in small amounts. The hexanal concentration was higher than nonanal, and limonene had the least concentration. The RSDs for all the chemicals analysed were between 5% and 29% in the 6 replicates, indicating similarity in the chemical emissions among the replicates (Table 5.12). During the development of the SRM 2585, phthalates and aldehydes were not analysed, thus their concentration in the house dust is not established. Bergh *et al.*, (2012) however reported the presence of 22 phthalates in the reference material when analysed by solvent extraction with GC/MS (discussed further in section 5.3.6).

Table 5-12 Amounts of chemical emissions (ng g^{-1}) of SRM 2585 Dust

Compound	Mean (n=6)	Median	SD	RSD%
Benzene	10	9	2	18
Hexanal	843	815	56	7
Limonene	23	24	2	7
Nonanal	182	160	53	29
DEP	1346	1414	107	8
DIBP	1272	1232	84	7
DBP	2134	2169	101	5
DEHP	2036	2089	105	5

5.2.5.6 Chemical Concentrations of Dusts during Weather Events

Analyses of the sampled household dusts that were collected during Harmattan and Dust storm, and the no-event period (when there was no dusty weather event) were carried out using thermal extraction Method C and the results compared to determine the influence of the dust events on the possible chemical exposure in the indoor environment. The results obtained are shown in Tables 5.13 to 5.15. Benzene was below the lower quantification limits in all the samples analysed.

Table 5-13 Chemical emissions of indoor/outdoor Dusts collected during Harmattan

Compound	Concentration of chemicals (ng g^{-1}) of dusts during Harmattan								
	AH	**FH**	**LH**	**MH**	**YH**	**Mean**	**Median**	**FHO**	**I/O**
Benzene	ND	ND	ND	ND	ND	ND	-	ND	-
Hexanal	4138	1090	1829	1344	1829	2046	1829	63	32
Nonanal	26,695	18,044	8993	19,333	9246	16,462	18,044	989	17
DEP	517	3599	61	425	1416	1204	517	234	5
DIBP	2059	2632	638	3085	1760	2035	2059	383	5
DBP	1962	2965	168	1517	1353	1593	1517	332	5
DEHP	2443	767	2369	5493	30978	8410	2443	2257	4

ND=Not detected

Table 5-14 Chemical emissions of indoor/outdoor Dusts collected during No-event

	Concentration of chemicals (ng g^{-1}) of dusts during no event								
Compound	**AH**	**FH**	**LH**	**MH**	**YH**	**Mean**	**Median**	**FHO**	**I/O**
Benzene	ND	ND	ND	ND	ND	ND	-	ND	
Hexanal	714	510	859	195	1419	739	714	195	4
Nonanal	4034	1052	6263	205	12,199	4751	4034	205	23
DEP	298	286	11	18	551	233	286	18	13
DIBP	1039	743	83	22	1044	586	743	20	29
DBP	266	146	12	27	1600	410	146	21	20
DEHP	1408	707	2575	859	592	1228	859	1541	1

ND=Not detected

Table 5-15 Chemical emissions of indoor/outdoor Dusts collected during Storm

	Concentration of chemicals (ng g^{-1}) of dusts during Dust storm								
Compound	**AH**	**FH**	**LH**	**MH**	**YH**	**Mean**	**Median**	**FHO**	**I/O**
Benzene	ND	ND	ND	ND	ND	ND	-	ND	
Hexanal	1100	550	260	1672	2084	1133	1100	1003	1
Nonanal	27	1166	1272	7960	5272	3139	1272	1404	2
DEP	12	1446	23	400	3176	1011	400	46	22
DIBP	72	1282	386	1708	1733	1036	1282	756	1
DBP	6	526	84	428	346	278	346	197	1
DEHP	33	86	87	420	129	151	87	20	8

ND=Not detected

The mean chemical emissions in the dusts during the different weather event periods showed that generally, the mean chemical concentrations were higher in the Harmattan period samples followed by the no-event samples and then the Dust storm samples had least concentrations of the quantified chemicals. Nonanal had highest mean concentrations in all the dusts followed by DEHP and DIBP. The nonanal concentration was higher in the dusts sampled during

Harmattan followed by no-event dusts (Figure 5.9). The data were log transformed because the concentrations of the target chemicals quantified in the dusts collected over the three periods were not normally distributed and the geometric mean (GM), geometric standard deviation (GSD), and geometric relative standard deviations of the log-transformed data were calculated (Table 5.16). The mean individual chemical emissions in Harmattan dust samples were found to have geometric relative standard deviations (GRSD) of less than 1% indicating similarity in concentrations of the chemicals emitted in the dust samples collected from 5 different homes during 3 different weather events. The GRSD of emissions in the two events were 5% and below in both the No-event and storm samples. Box plots showing the distribution of and variations in the chemical concentrations during the different weather events were plotted (Appendix C-4).

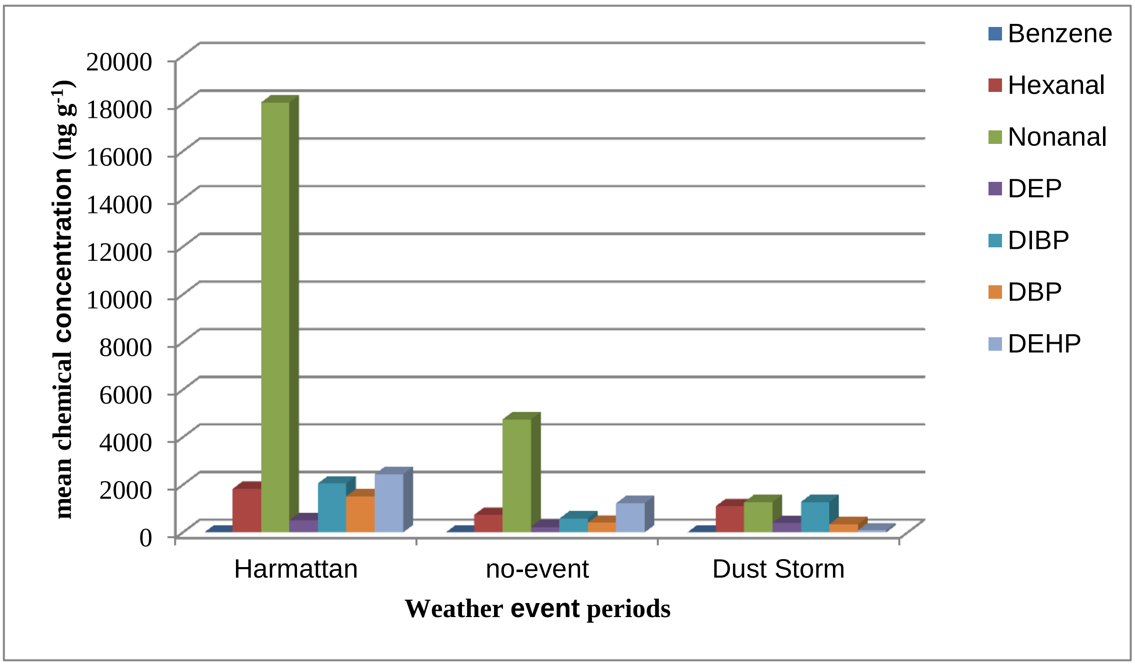


Figure 5.9 Arithmetic means of chemical (AM) emissions in Dusts during weather events

Table 5-16 Concentrations of the target chemicals in Dust during weather events

	Chemical concentrations (ng g^{-1}) of Dust							
		Benzene	**Hexanal**	**Nonanal**	**DEP**	**DIBP**	**DBP**	**DEHP**
Harmattan period	**AM**	ND	2046	16462	1204	2035	1593	8410
	Median	-	1829	18044	517	2059	1517	2443
	GM	ND	1826	15059	585	1798	1149	3764
	GSD	-	1.66	1.62	4.60	1.86	3.05	3.94
	GRSD%	-	0.09	0.01	0.79	0.10	0.27	0.10
No-event period	**AM**	ND	739	4751	233	586	410	1228
	Median	-	714	4030	286	743	146	869
	GM	ND	613	2315	99	271	115	1054
	GSD	-	2.09	5.08	6.08	5.79	6.89	1.81
	GRSD%	-	0.34	0.22	6.16	2.14	5.99	0.17
Dust Storm period	**AM**	ND	1133	3139	1011	1036	278	151
	Median	-	1100	1272	400	1282	346	87
	GM	ND	887	1109	219	638	131	106
	GSD	-	2.23	9.43	11.93	3	92	2.51
	GRSD%	-	0.26	0.85	5.44	0.61	4.93	2.37

ND= not detected

To understand whether there are significant differences in the concentrations of individual chemicals during the three event periods, paired t-tests were performed to compare the chemical concentrations during Harmattan and No-event period; Dust storm and No-event period; and then Harmattan and Dust storm periods. The Harmattan samples had higher chemical emissions than the Storm and No-event samples as indicated by the AM and the GM of the chemical concentrations in the different dusts (Table 5.16), but the differences in the concentrations of DEP, DBP, and DEHP in the dusts were not statistically significant (Table 5.17). Significant differences were observed in nonanal and DIBP emissions between Harmattan and no-event dusts, and Harmattan and Dust storm samples. Hexanal emission was found to be significantly different in Harmattan and No-event samples, but the emissions in dust storm and no-event, and Harmattan and Dust storm were not significantly different.

Table 5-17 Significance of differences (p values) between the means of chemical emissions during different weather events

Compound	**Harmattan & No-Event**	**Dust-storm & No-Event**	**Harmattan & Dust-Storm**
Benzene	ND	ND	ND
Hexanal	0.047*	0.534	0.222
Nonanal	0.079*	0.570	0.028*
DEP	0.182	0.210	0.774
DIBP	0.036*	0.350	0.054*
DBP	0.820	0.291	0.368
DEHP	0.296	0.116	0.262

ND = Not detected *****= significant difference

5.2.5.7 Chemicals in μ-CTE extracts of Dusts from Modern and Traditional Homes

The results of the analysis of the 52 dusts collected from the indoors/outdoors of 26 modern and 26 traditional type buildings using thermal extraction Method C indicated the presence of a wide range of chemicals. The target chemicals were quantified and only limonene was not detected in some samples (both groups of outdoor dusts) (Figure 5.10). Arithmetic means (AM) of the chemical emissions, median concentrations, standard deviations as well as the relative standard deviations (RSD) and geometric means (GM) were computed based on the dusts sampling locations/ building type (Table 5.18).

Indoor dusts concentrations from modern homes showed nonanal as having the highest concentration followed by DEHP, DBP, hexanal, DIBP, DEP, and limonene had the lowest mean concentrations. The relative standard deviations from the means of the chemical concentrations were all above 50% with only limonene having less RSD, indicating differences of chemical emissions among all the samples (Table 5.19). In the modern outdoor dusts the chemical concentrations were in the order nonanal>DEHP>DIBP>DBP>DEP>hexanal (while limonene was not detected) with RSD below 50% for 3 phthalates and 60% for DEP. The high nonanal concentrations may be due to the presence of decayed materials in the surroundings of the homes. The chemical emissions were more than five times more in the indoor samples than the outdoor samples. In the traditional indoor dusts nonanal was higher than the other chemicals in the order; nonanal>DEHP>DIBP>DEP>DBP>hexanal>limonene. The RSD was above 50% for the phthalates and less than that for hexanal and limonene. In the traditional outdoor locations the order is; nonanal>DEHP>hexanal>DBP>DIBP>DEP with RSD above 50% in the chemicals quantified with the exception of nonanal which was 32% (Table 5.19).

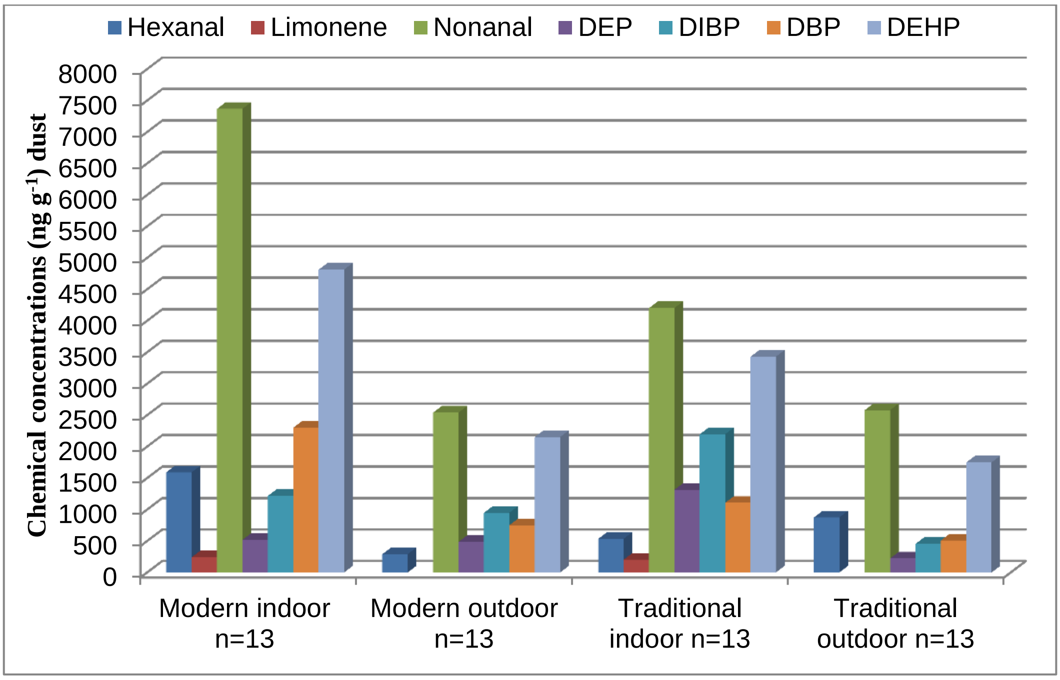


Figure 5.10 Mean chemical emissions in thermally desorbed Dusts

Table 5-18 Chemical concentrations from thermal (μ-CTE) extraction of Dusts from modern and traditional homes

Chemical concentrations (ng g^{-1}) emitted from dusts								
source		**Hexanal**	**Limonene**	**Nonanal**	**DEP**	**DIBP**	**DBP**	**DEHP**
Modern Indoor (n=13)	**AM**	1591	241	7368	518	1217	2300	4813
	GM	1281	235	6277	270	675	2035	4421
	Max	3570	323	23566	1712	4675	5816	9127
	Min	290	134	3410	36	139	1242	1985
	SD	920	54	5402	563	1403	1356	2050
	RSD%	58	22	73	109	115	59	43
	Median	1293	239	5527	183	494	1574	4575
Modern Outdoor (n=13)	**AM**	321	ND	2540	486	948	751	2152
	GM	290	-	1980	189	789	993	1476
	Max	565	-	4743	990	1783	1635	4028
	Min	173	-	1234	132	252	318	1047
	SD	95	-	1114	290	520	364	943
	RSD%	30	-	44	60	55	48	44
	Median	290	100	2344	441	958	745	1932
Traditional Indoor (n=13)	**AM**	535	203	4202	1314	2196	1106	3429
	GM	500	226	2608	1498	1744	412	4155
	Max	883	320	9650	3441	6776	3903	8397
	Min	298	100	1245	161	347	84	1153
	SD	216	71	2805	1126	2063	1012	2038
	RSD%	40	35	67	86	94	92	59
	Median	456	219	3289	945	1322	721	3547
Traditional Outdoor (n=13)	**AM**	875	ND	2580	223	454	509	1749
	GM	392	-	1645	47	166	350	1180
	Max	6528	-	4034	715	1737	1420	6826
	Min	188	-	1410	36	39	42	545
	SD	1712	-	815	257	458	402	1633
	RSD%	196	-	32	115	101	79	93
	Median	290	-	2656	82	339	358	1438

The mean chemical concentrations were generally higher in the indoor than the outdoor dusts in the thermal extracts of modern buildings. In the traditional buildings however the mean concentration of hexanal was found to be higher in the outdoor dusts than in the indoor dusts (Figure 5.11). Large standard deviations were observed between the mean emissions of the indoors/outdoors in both the modern and the traditional type of homes which indicated possible differences in the sources of the chemicals in the dusts from individual homes. The variations in the chemical emissions between the individual houses dust is related to the difference in the environments, building type, household activities furnishings, geographical and anthropogenic conditions (Bornehag et al, 2004; Hsu et a., 2011).

In the thermal extracts of the dusts of the modern buildings, the aldehydes, hexanal and nonanal, had higher amounts of emissions than the phthalates. Nonanal was more in the indoor dusts while hexanal was dominant in the outdoor dusts. The ranking of the emissions were; nonanal>hexanal>DEHP>DBP>DIBP>DEP (Figure 5.11). The mean concentration of DEP indoors was found to be 6 times higher than the mean of the DEP in the outdoor samples while the mean hexanal concentrations had an indoor/outdoor ratio of 1:1. In the traditional buildings, the indoor/outdoor ratios ranged from 1 for hexanal, 2 for nonanal, DBP and DEHP, 5 for DIBP, and 6 for DEP (Table 5.19).

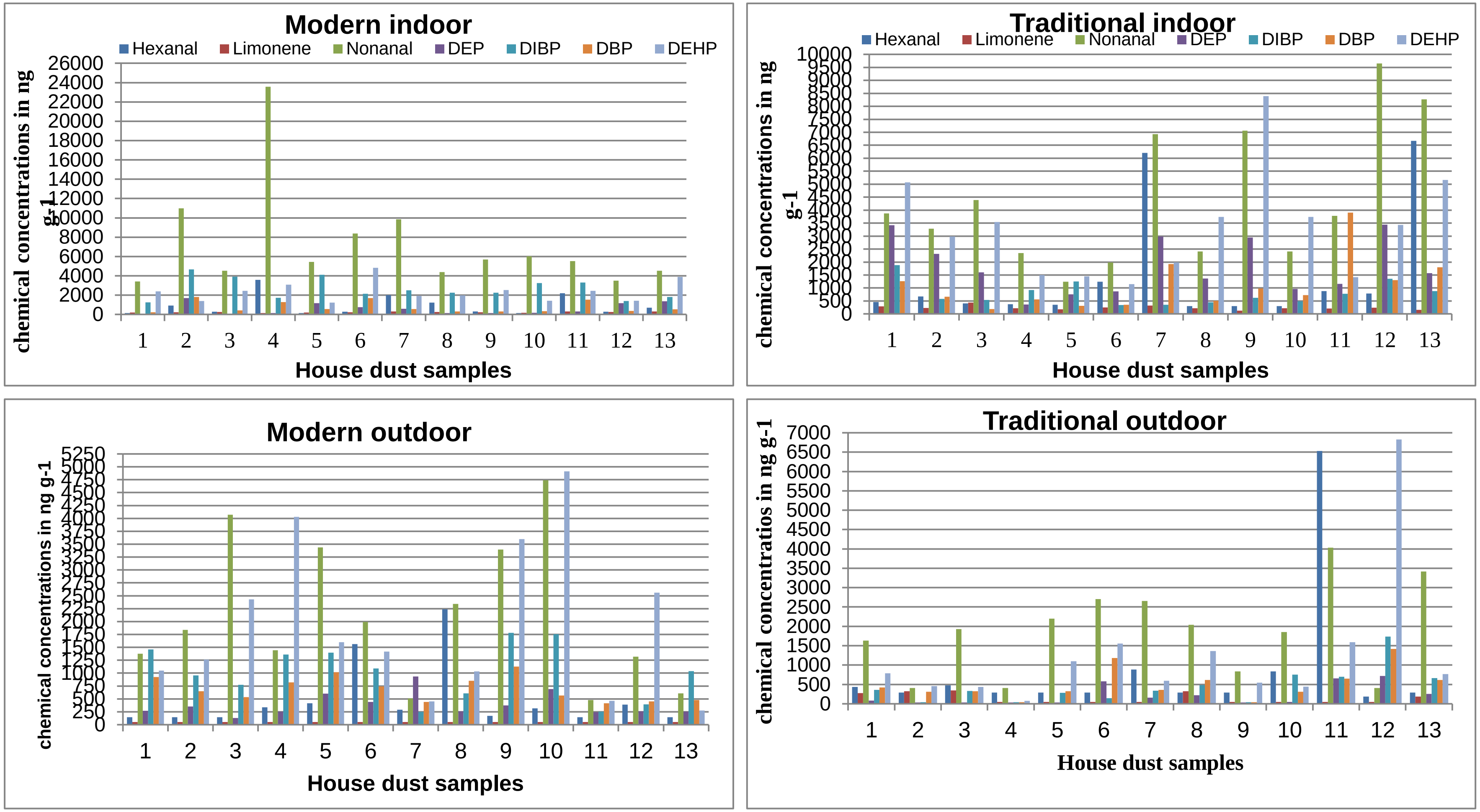


Figure 5.11 Chemical concentrations (ng g^{-1}) of individual dust μ-CTE extracts in traditional and modern homes

Table 5-19 Indoor/outdoor ratio of chemicals in µ-CTE Dust extracts of traditional and modern homes

Mean indoor/outdoor ratio of chemicals(ng g^{-1}) in µ-CTE extracts of house Dust						
Compound	**MI(n=13)**	**Mo(n=13)**	**I/O ratio**	**Ti(n=13)**	**To(n=13)**	**I/O ratio**
Hexanal	1591	321	5	535	875	1
Limonene	241	ND	-	203	ND	-
Nonanal	7368	2540	3	4202	2580	2
DEP	518	486	1	1314	223	6
DIBP	1217	948	1	2196	454	5
DBP	2300	751	3	1106	509	2
DEHP	4813	2152	2	3429	1749	2

Mi= Modern indoor Mo= modern outdoor Ti=Traditional indoor To= Traditional outdoor

5.3 Solvent Extraction/GC/MS analysis of Dust

This involved the extraction of phthalates and other SVOCs in house dust samples using solvent. The procedure was based on published studies (Gevao et al., 2012; Guney et al., 2010; Guo and Kannan, 2011) with modifications. The glass centrifuge tubes were replaced with Teflon (Oak ridge™) centrifuge tubes; orbital shaking was 300 rotations per minute (rpm) instead of 200; the centrifuge machine was set at 25°C (room temperature), this temperature was not mentioned in the previous studies.

5.3.1 Solvent Extraction of Dust

1g of each house dust sample (<150 µm fraction) was weighed into 10 ml Teflon (Oak ridge™) centrifuge tubes (duplicate per sample). 1 µl of 1000 µg l^{-1} of standard solution containing the mixture of 7 target chemicals (hexanal, limonene, nonanal, DEP, DIBP, DBP, DEHP) was placed in a separate tube. 6 ml of the solvent-hexane: acetone 4: 1 (v:v) was added to each of the tubes and the mixtures were agitated on an orbital shaker at 200 rotations per minute (rpm) for 30 minutes, followed by centrifugation at 4000 rotations per minute (rpm) for 5 minutes at 25°C. The content of each tube was decanted and the process repeated 3 times. The combined extracts were concentrated under a gentle stream of nitrogen to 1 mL and transferred into amber sample vials. The lids of the vials were tightened with a crimper and the samples were analysed by liquid injection GC/MS in duplicates.

5.3.2 Procedure for GC/MS Analysis of Dust solvent extracts

The solvent extract-GC/MS assembly used were the GC component**-** Autosystem XL **(**Perkin Elmer) connected to a Turbomass mass spectrometer (Perkin Elmer) located in the volatiles laboratory, IEH, Cranfield University. The amber vials containing the hexane: acetone extracts of the dust samples were arranged onto the carousel of the instrument's auto sampler. Each sample extract was injected via the GC sample injection port onto the capillary column, where the compounds present separated and were then detected by mass spectrometry. Instrument conditions were as follows:

Sample injection conditions: Sample extract (1.0 µl) is injected (via the auto sampler) in the GC sample injection port into the capillary column with a split of 49:1 and solvent delay of 1.5 minutes.

Gas Chromatography (GC) conditions: Width 0.25 mm id, 60 m column length and 25 µm film thickness. Maximum temperature of 300^{o}C with constant flow of 1.3 ml min^{-1} of helium. Oven temperature 50°C min^{-1}, then 12°C to 180°C min^{-1}, hold for 1 minute, followed by 6.8°C to 270°C min^{-1} no hold, and finally 30°C min^{-1} to 300°C and 12 minutes hold.

Mass Spectrometer (MS) conditions: TurboMass Mass spectrometer with scan rang of 50-300 amu, mass scan start 35 m/z and end 350 m/z, ionization mode-EI^{+}, scan duration 0.2 seconds, inter scan delay 0.1 sec.

The liquid injection/GC/MS assembly shown in Plate 5.3.

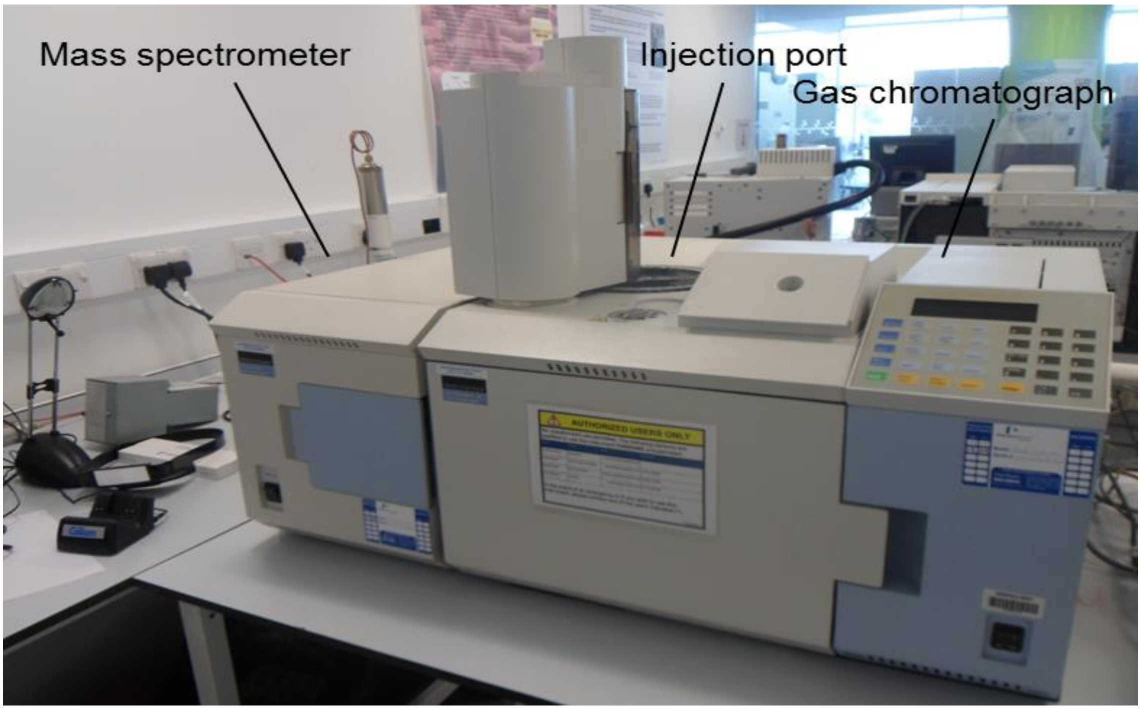


Plate 5-3 Liquid injection/GC/MS assembly

5.3.3 Investigation of Chemicals in Solvent extracts of Dusts

The analysis of the solvent extracted dust samples was carried out under the protocol described in 5.3.2. The set of 5 UK and 5 Nigerian indoor dusts were again used for the method development.

After setting up the procedure, the 52 samples collected from 26 indoors/outdoors of modern and traditional homes were analyzed. Samples collected during Dust storm and Harmattan and No-event periods, and the surface soil (sand) were also analyzed as well as the standard reference dust SRM 2585 using the adopted procedure.

5.3.4 Calibration Standards

A stock solution of the target chemicals was prepared in the hexane: acetone solvent and serially diluted across a range of concentrations within the expected concentrations of the target chemicals in the analyte, and run on the GC/MS for calibration. The dilution was done from 100 ng μl^{-1} down to 1.75 ng μl^{-1} in the initial run. Calibration curves were obtained for the target chemicals which were used to determine the concentration of the chemicals in the analytes. The calibration curve is a plot of the instrumental response against the concentration of the analyte standards. An example of a calibration curve is shown in Figure 5.12. The calibration standards were run with each samples run because an internal standard was not used.

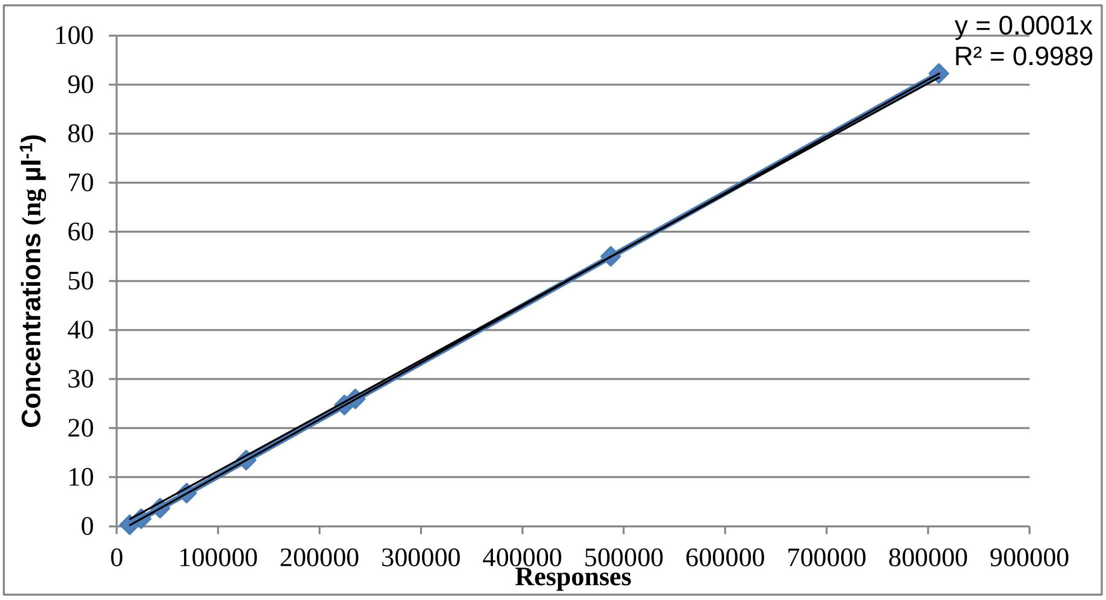


Figure 5.12 Calibration curve of DIBP for liquid injection GC/MS analysis

To determine the limit of detection, a standard solution of 100 ng µl^{-1} concentrations was run in triplicate and the limit of detection calculated by multiplying standard deviations of the triplicate concentrations by 3, which is an acceptable signal to noise ratio for calculating LOD (Shrivastava and Gupta, 2011). The calculated LOD for the chemicals is shown in Table 5.20. The % recovery of the varying dilutions were calculated by dividing the amount of the chemical quantified by the initial (known) concentration of the standard chemical and multiplied by 100. For instance, the percentage recovery for the 100 ng µl^{-1} standard solutions ranged from 99% in hexanal to 105% for DEHP, which is an indication of viability of the extraction method as well as the analytical method (Table 5.20).

Table 5-20 Limit of detection and % recovery using 100 ng µl^{-1} standards

	Hexanal	**Limonene**	**Nonanal**	**DEP**	**DIBP**	**DBP**	**DEHP**
1	98.11	99.96	99.95	98.27	99.45	101.5	99.35
2	99.68	95.64	101.92	98.64	103.76	97.84	111.78
3	99.41	99.54	98.76	108.1	99.54	103.56	103.54
Mean	**99**	**98**	**100**	**102**	**101**	**101**	**105**
SD	**0.8**	**2.4**	**1.6**	**5.6**	**2.5**	**2.9**	**6.3**
LoD	**2.4**	**7.2**	**4.8**	**16.7**	**7.4**	**8.7**	**19.0**
%Recovery	**99**	**98**	**100**	**102**	**101**	**101**	**105**

5.3.5 Results of Solvent extraction/GC/MS of Dusts

The solvent extracts of the 5 Nigerian and 5 UK samples were analysed for the initial method development and the presence of target chemicals in the dust extracts were detected and a repeatability test was carried out. After that the other test samples were run. The results are shown below;

5.3.5.1 Chemicals in method development samples

The analysis revealed the presence of the target analytes plus other chemicals in the 5 Nigerian and 5 UK extracts. Benzene was not detected in all the extracts and removed from the subsequent data analyses. The benzene may have been lost in the extraction process because of its volatility. The chemical concentrations generally were higher in the Nigerian extracts with only DEHP being higher in the UK dust extracts (Figures 5.13 and 5.14). However, some parameters were changed due to the high amount of the chemicals. A lower calibration standard of 0.65 ng µl was applied and benzene was removed from the target analytes. The revised procedure was adopted for subsequent samples analysed.

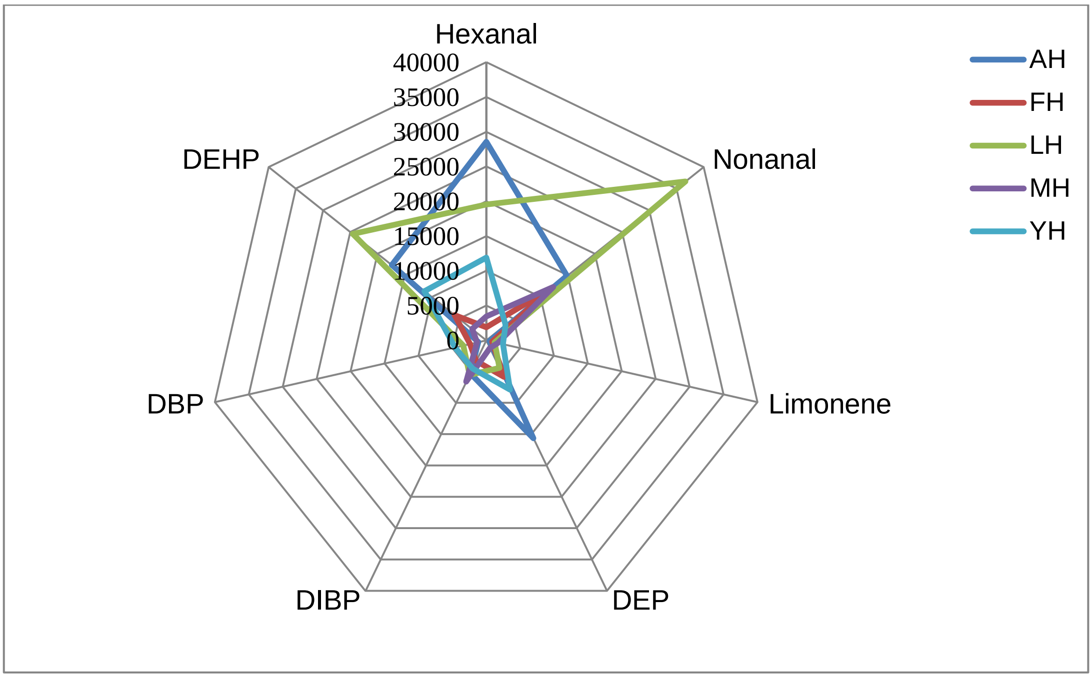


Figure 5.13 Chemical concentrations (ng µl^{-1}) in Nigerian dust extracts

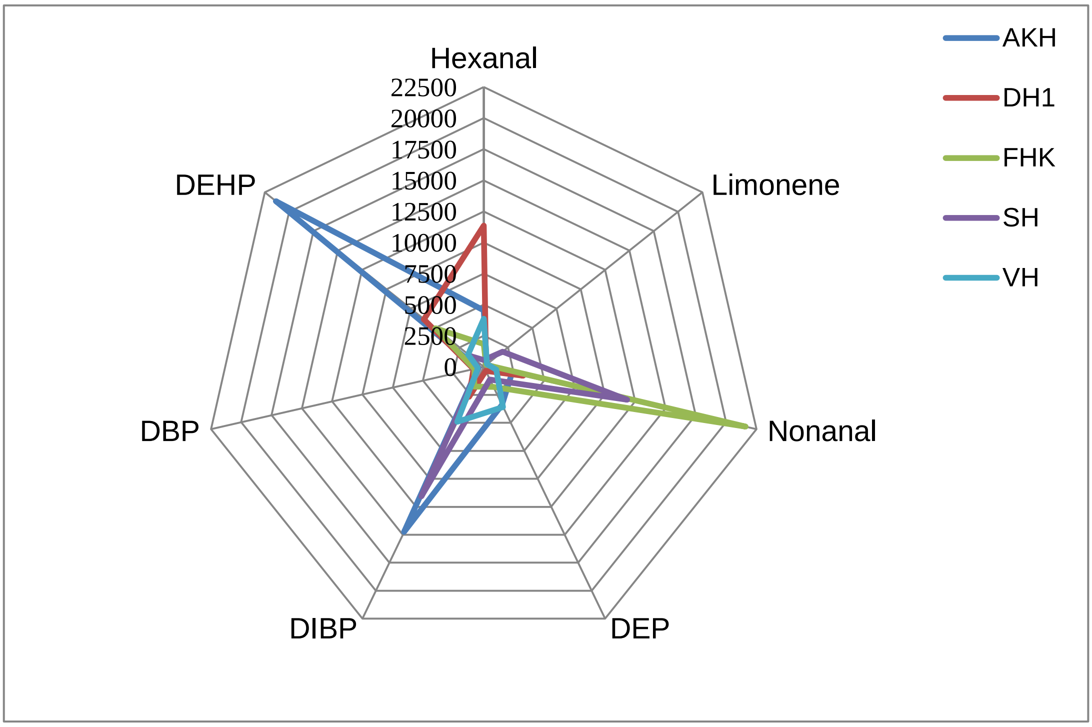


Figure 5.14 Chemical concentrations (ng µl^{-1}) in UK dust extracts

Repeatability of the test was assessed by 5 repeat analyses of the 50 ng µl^{-1} standards. Good repeatability was found with RSD of less than 10% for all the target analytes indicating similarity of the chemical concentrations in the replicates (Table 5.21).

Table 5-21 Repeatability of the test using 50 ng µl^{-1} standard solutions

	Replicates (n=5)						
	Hexanal	**Nonanal**	**Limonene**	**DEP**	**DIBP**	**DBP**	**DEHP**
Mean	39.4	64.2	58.0	62.0	68.2	54.1	59.4
SD	0.9	4.4	62.2	4.5	5.5	2.0	3.5
RSD%	2.3	6.9	3.2	7.3	8.1	3.7	5.8

5.3.5.2 Chemical concentrations in Sand and SRM 2585 extracts

Surface soil (sand) samples were extracted and analyzed together with the SRM 2585, but no chemical was detected in the sand extracts. Hexanal and limonene were not detected in the SRM extracts, but nonanal and the phthalates were detected in substantial amounts. There was no certified value for phthalates in the standard reference material for house dusts contaminants (SRM2585). Bergh *et al.,* (2011) also reported the presence of 7 phthalates in the reference dust. The mean concentrations of the phthalates in the SRM 2585 are shown in Table 5.22. All the chemicals were higher in the results reported by Bergh *et al.*, (2011) particularly for DEHP. Although the ratio of solvent: thermal for the indoor and outdoor dusts is consistent with the DEHP in SRM in this study. This difference may in part be due to differences in extraction methods. In this study simple extraction was carried out while Bergh *et al.*, (2011) did repeated ultrasonication which may result to more vigorous total extraction of the chemicals. Unfortunately it was not possible to undertake repeat analysis of the SRM dust in the present study because of the very limited amount of the sample available.

Table 5-22 Chemical concentrations in µg g^{-1} of SRM 2585 dust

Chemical	**Mean (n=6)**	**RDS%**	**Mean (n=6)**	**RDS%**
Nonanal	NA	NA	3.0	5
DMP	1.0	3	NA	NA
DEP	6.7	5	1.4	3
DIBP	6.0	4	2.7	6
DBP	31	4	13	7
BZBP	93	2	NA	NA
DEHP	570	2	47.8	3
DOP	17	5	NA	NA
Extraction method	Solvent: Acetone+ Hexane		Solvent: Acetone+ Hexane	
Analytical method	GC/MS		GC/MS	
Reference	Bergh et al., 2011		This study	

5.3.5.3 Chemical Concentrations in Modern and Traditional House Dust extracts

The results of the SE/GC/MS analysis of 52 dusts collected from indoors/outdoors of 26 modern and 26 traditional type buildings indicated the presence of a host of chemicals and the target chemicals were quantified. The chromatograms obtained showed the presence of many chemical compounds as is shown in the example of chromatograms analysed (Figure 5.14 and 5.15). A host of other chemicals that were commonly present in the analysed samples were also identified using the NIST library associated with the MS system software. These chemicals included naphthalene and C_{10}-C_{16} aliphatic and aromatic hydrocarbons (Figure 5.15) which need confirmation by running the pure compound samples. These compounds have been reported in a previous study as commonly present in household dusts (Hirvonen, 1991). The list of the chemicals identified is given in Appendix C. Hexanal and limonene were not detected in all the analysed samples while the phthalates were found in higher concentrations than nonanal (an aldehyde) with only the DEP concentration being lower than nonanal as shown in Figure 5.16.

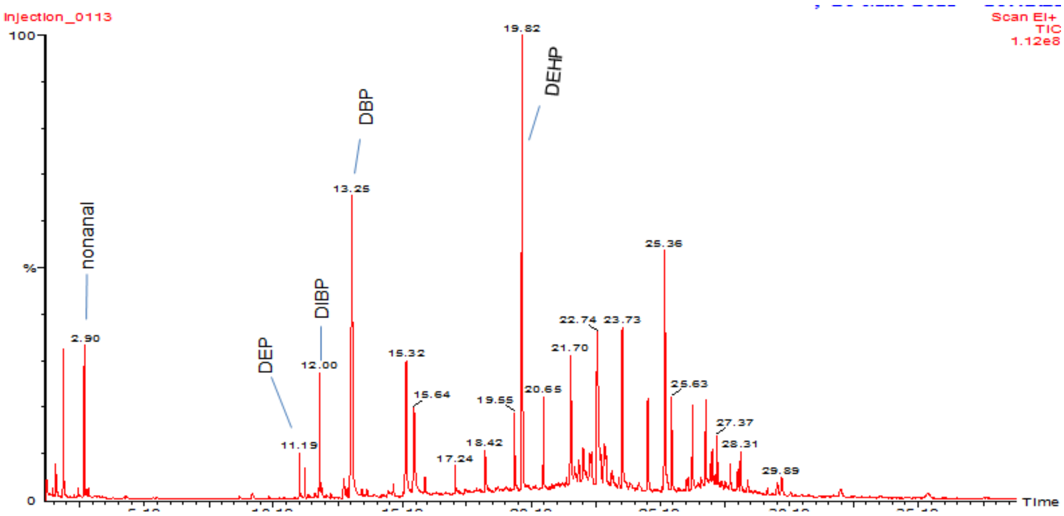


Figure 5.15 Chromatogram given by GC/MS analysis of the extract of a modern indoor dust

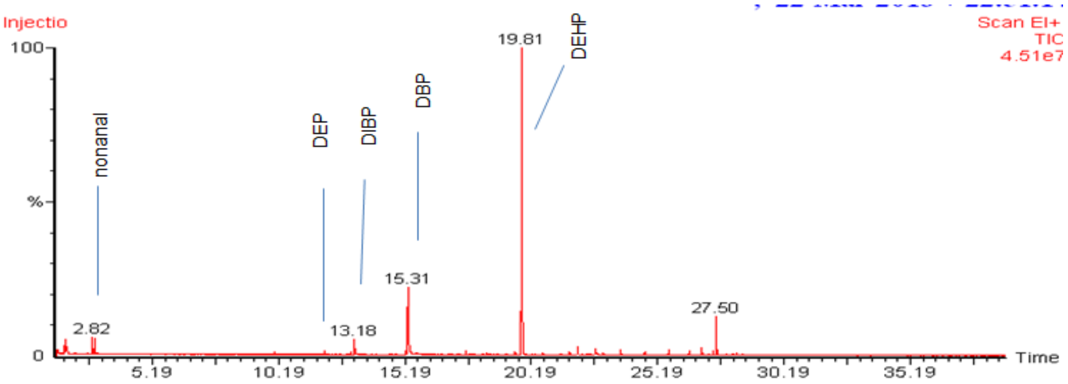


Figure 5.16 Chromatogram given by GC/MS analysis of the extract of a modern outdoor dust (abundance vs retention time)

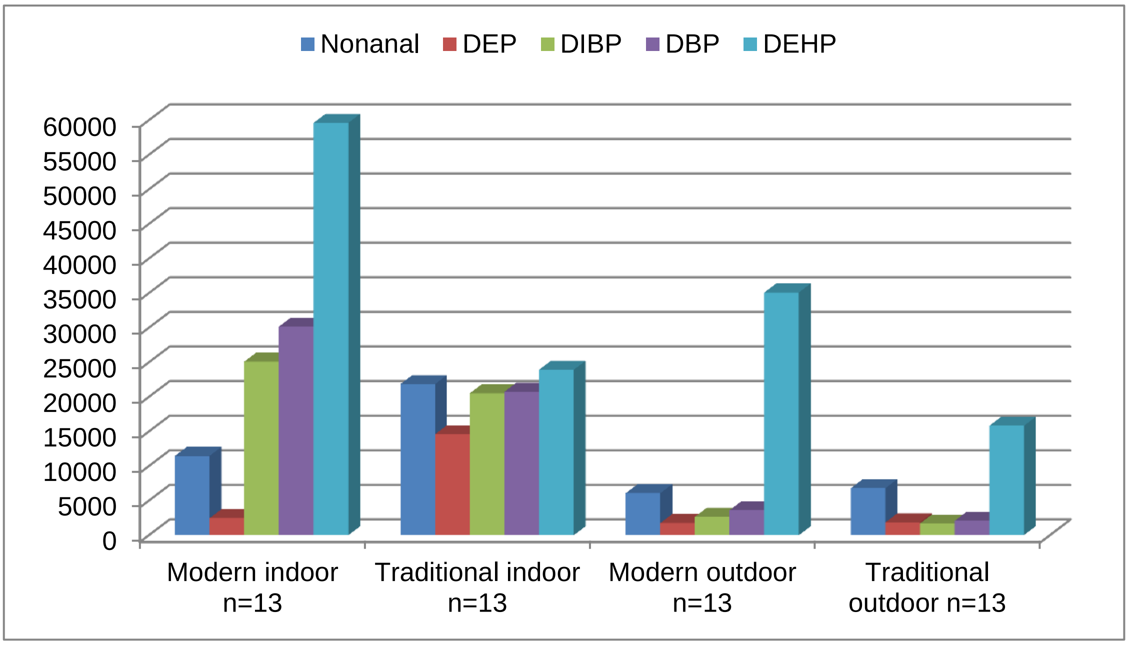


Figure 5.17 Chemical concentrations (ng g^{-1}) in solvent extracts of dusts from modern and traditional homes

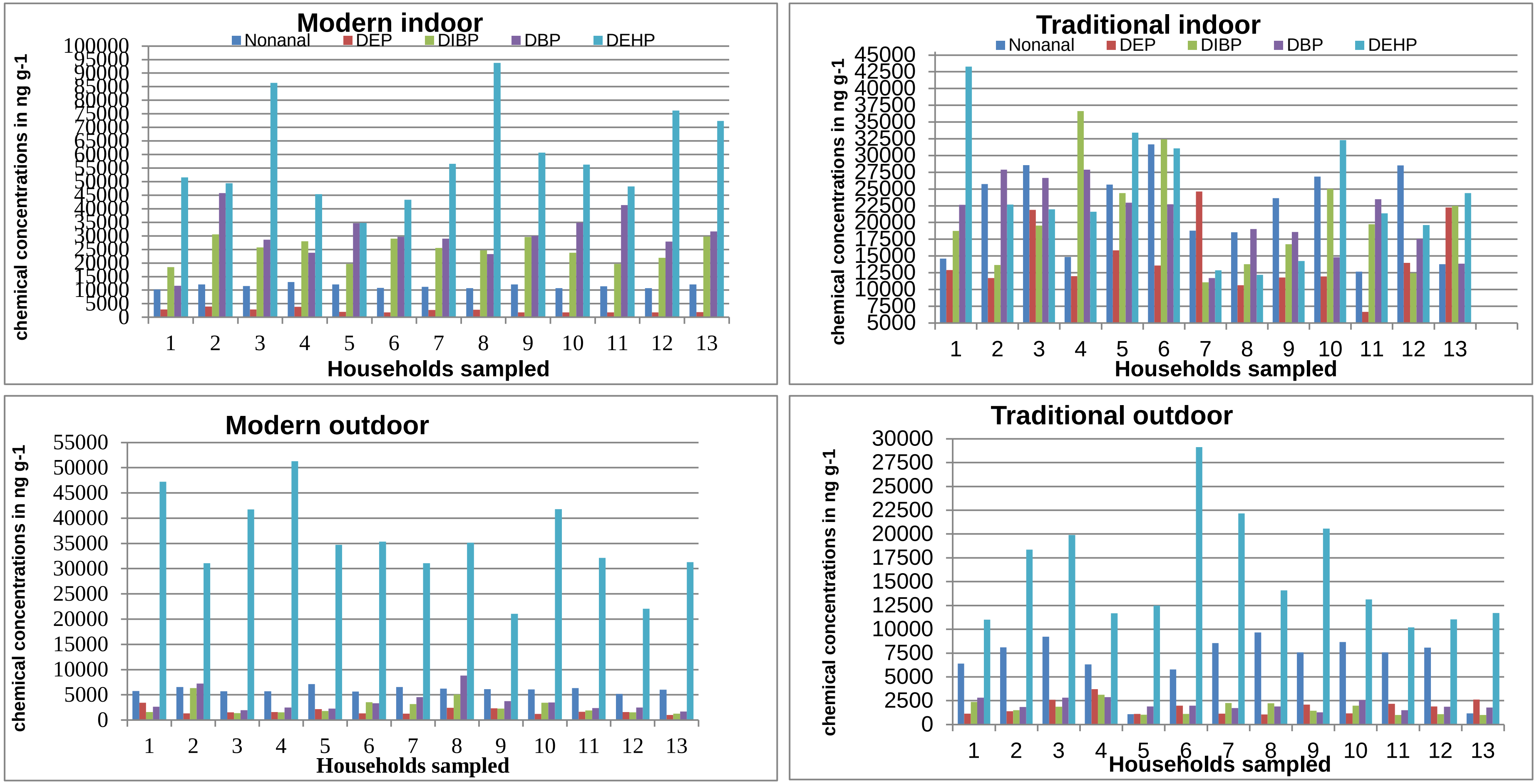
Arithmetic means (AM) of the chemical emissions, median concentrations, standard deviations as well as the relative standard deviations (RSD) and geometric means (GM) were computed based on the house types and sampling locations (Table 5.23). The arithmetic mean concentrations of the chemicals were in the order of DEHP>DBP>DIBP>nonanal>DEP. The trend also indicated higher mean chemical concentrations in the indoor dusts than the outdoors, and all the chemicals were higher in the modern indoors with only DEP being higher in the traditional indoors dusts as shown in Figure 5.17.

The emissions of the chemicals from all the sample extracts indicated high DEHP concentrations compared with the other chemicals with a maximum concentration of 73,730 ng g^{-1}; arithmetic mean of 59,614 ng g^{-1} in the modern indoor dusts. The chemical with the least concentration was DIBP in traditional outdoor dusts with maximum concentration of 3,120 ng g^{-1} and AM of 1,696 ng g^{-1} (Table 5. 23). The indoor/outdoor ratios for the chemical emissions ranged from a minimum of 1 for DEP in modern buildings; the indoor/outdoor concentrations of DEHP in both modern and traditional buildings were in the ratio of 2:1 as well as nonanal in modern buildings. The ratios for DBP in modern and DEP in traditional buildings were 8:1, other ratios are 3 for nonanal in traditional buildings, DIBP in modern is 9, DBP is 10 in traditional and the highest ratio was 12 for the indoor/outdoor concentrations of DIBP in traditional buildings (Table 5.24).

The occurrence of higher concentrations of DEHP in household dusts compared with other phthalates has been reported in previous studies (Gevao *et al.,* 2012; Guo and Kannan, 2011; Langer *et al.,* 2010).

Table 5-23 Chemical Concentrations in dusts of modern and traditional homes determined by solvent extraction

Chemical Concentrations (ng g^{-1}) in dust						
Dust source		**Nonanal**	**DEP**	**DIBP**	**DBP**	**DEHP**
	AM	11,463	2465	25,093	30,162	59,614
Modern indoor (n=13)	GM	11,438	2362	24,755	28,850	57,348
	MAX	12,980	3980	30,560	45,780	73,730
	MIN	10,230	1810	18,470	11,650	34,820
	SD	786	783	4194	8434	17,620
	RSD%	7	32	17	28	30
	Median	11,390	1950	25,540	29,670	56,250
Traditional indoor (n=13)	AM	21,839	14,595	20,511	20,745	23,923
	GM	20,872	13,784	19,287	20,064	22,396
	MAX	31,670	24,630	36,620	27,880	43,290
	MIN	12,650	6650	11,090	11,700	12,190
	SD	6560	5219	7669	5314	9021
	RSD%	30.0	35.8	37.4	25.6	37.7
	Median	23,640	12,900	19,540	22,650	21,965
Modern outdoor (n=13)	AM	6079	1760	2674	3617	35,075
	GM	6059	1663	2335	3190	34,039
	MAX	7140	3440	6350	8840	51,281
	MIN	5170	1020	1260	1670	21073
	SD	507	667	1572	2141	8751
	RSD%	8.3	37.9	58.8	59.2	24.9
	Median	6090	1564	1920	2620	34,742
Traditional outdoor (n=13)	AM	6782	1852	1696	2070	15,808
	GM	5742	1710	1581	2011	14,975
	MAX	9670	3700	3120	2870	29,120
	MIN	1080	1050	1001	1290	10,205
	SD	2751	797	670	523	5745
	RSD%	40.6	43.1	39.5	25.3	36.3
	Median	7560	1900	1510	1897	13,140


Modern indoor

Traditional indoor

Modern outdoor

Traditional outdoor

Figure 5.18 Chemical concentrations (ng g^{-1}) of individual dust solvent extracts

Table 5-24 Indoor/outdoor ratio of chemicals in solvent extracts of dusts from traditional and modern homes

Mean concentration (ng g^{-1}) and indoor/outdoor ratio						
Compound	**Mi(n=13)**	**Mo(n=13)**	**I/O ratio**	**Ti(n=13)**	**To(n=13)**	**I/O ratio**
Nonanal	11,463	6079	2	21,839	6782	3
DEP	2465	1760	1	14,595	1852	8
DIBP	25,093	2674	9	20,511	1696	12
DBP	30,162	3617	8	20,745	2070	10
DEHP	59,614	35,075	2	23,923	15,808	2

Mi= Modern indoor Mo= modern outdoor Ti=Traditional indoor To= Traditional outdoor

Researchers have collected household dusts by various sampling methods and have extracted phthalates by different techniques involving different solvents (Langer *et al.,* 2010; Bergh *et al.,* 2011; Guo and Kannan, 2011, Gevao et al., 2012). The results obtained in this study as compared with those obtained in other studies showed similarity in the dominance of DEHP among other phthalates in house dusts. The median concentrations of the phthalates found in this study were compared with those reported from various cities from different geographical locations. DEP was found as higher in the Nigerian dusts (this study) than those reported from other cities and the median for DEHP in this study was the least as compared to those reported from other studies (Table 5.25).

Table 5-25 Concentration (μg g^{-1}) of organic chemicals (phthalates) in house dusts from various studies

Location	Sampling method	Solvent type	Analytical method	DEP	DIBP	DBP	DEHP	Reference
Danish homes (500)	ALK dust filter	n-hexane: diethyl ether	GC/MS	GM-3.1 Med- 1,7	GM-16.6 Median- 27	NA	GM-220 Median-210	Langer *et al.,* 2010
Beijing (11)	Sweep/ wipe	Hexane : acetone	GC/MS	Med- 0.4 Range- 0.1-0.6	Median 12.6 Range- 7.2-84	Median 18.9 Range- 7-32	Median 156 Range- 47.6-883	Guo and Kannan, 2011
Shanghai (21)	Sweeping and wiping	Hexane : acetone	GC/MS	Med- 0.4 Range nd-46	Median 33.6 Range 7.0-86	Median 26.9 Range 1.5-96	Med-319 Range-117-1380	Guo and Kannan, 2011
Albany (33)	Vacuum cleaner bags	Hexane : acetone	GC/MS	Med-2.0 Range 0.7-11.8	Median 3.8 Range 0.7-34	Median 13 Range 4.5-94	Med-304 Range 37.2-9650	Guo and Kannan 2011
Kuwaiti homes (21)	Vacuum cleaner bags	Hexane : acetone	GC/MS	Median 1.8 Range-0.1–16 GM-1.5	NA	Median-45 Range-8–160 GM-51	Median-2256 Range-380–7800 GM-1700	Gevao *et al.,* 2012
Nigerian homes (26)	Vacuum cleaner bags	Hexane : acetone	GC/MS	AM-8.5 Median-4.0 Range-2-25 GM-5.4	AM-22.8 Median-24.8 Range-11-37 GM-21.8	AM-25.5 Median-26.7 Range-12-46 GM-24.6	AM-41.8 Median-43.3 Range-12.2-94 GM-36.4	This study

5.3.6 Comparison of emissions in µ-CTE and Solvent extracts of Dust

There was an observed higher concentration of the chemicals in the solvent extracts than the µ-CTE extracted dust samples including the SRM 2585 (Table 5.26). The ratios for the chemicals in the indoor dusts range between 3- 13 with DEHP in the solvent extracts being 13 times more than in the thermal extract. The concentration of nonanal in the solvent extract of the reference dust material was 15 times that in the thermal extract. The phthalates were between the ratios of 1 and 2 (Table 5.26). The higher concentration of the chemicals in the solvent extracts is expected due the aggressive removal of the chemicals by the organic solvent whereas in the case of thermal extraction only the readily available chemicals (loosely bound to the matrix) and that easily released by increases in temperature were removed.

Table 5-26 Comparison of chemical concentrations in solvent and µ-CTE extracted dusts from modern and traditional homes in Damataru

Mean concentrations (ng g^{-1}) ratios for Solvent Extracts and CTE extracts									
	Indoor Dusts (n=26)			**Outdoor Dusts (n=26)**			**SRM Dust (n=6)**		
Compound	**SE**	**µ-CTE**	**ratio**	**SE**	**µ-CTE**	**ratio**	**SE**	**µ-CTE**	**ratio**
Hexanal	ND	1063	-	ND	598	-	ND	857	-
Limonene	ND	222	-	ND	ND	-	ND	23	-
Nonanal	16,651	5785	3	6431	2560	3	2993	194	15
DEP	8530	916	9	1806	355	5	1343	1422	1
DIBP	22,802	1707	13	2185	701	3	2699	1169	2
DBP	25,454	1703	15	2844	630	5	12261	2073	6
DEHP	41,768	4121	10	25,442	1951	13	47,800	2075	23

SE= solvent extracts µ-CTE =thermal extracts ratio= SE/µ-CTE

An independent 2-tailed paired t-test was conducted to determine any significant differences between the means of chemicals in dusts from Modern and Traditional homes measured by the μ-CTE and solvent extraction methods. There were significant differences in all the chemical emissions between the two extracts with the exception of DEP, with p=0.718 for the two extracts of the indoor dust samples (Appendix C-2).

A non-parametric independent test (Mann Whitney U test) carried out indicated that only the distribution of DEHP is not significantly different for the μ-CTE (thermal) and solvent methods with a value of 0.143 while significant differences were observed for the other chemicals (Appendix Table C2).

The Spearman's rank-order correlation (*p*) was used to measure the strength of association between the chemicals in both the thermal and solvent extracts of the dusts. The statistical significance of the correlations was also calculated by two-tailed tests. For the indoor dusts thermal extracts, there were strong positive correlations between hexanal with limonene and the phthalates DIBP, DBP and DEHP (*p*=0.711, 0.535, 0.552, and 0.602) indicating the possibility of common indoor sources. Nonanal and DEP were strongly correlated (*p*=0.555), and negatively correlated with the other chemicals which suggested common sources for nonanal and DEP and differences in their sources from the other chemicals (Appendix Table C4).

In the solvent extracts however, nonanal was found to be positively correlated with DBP, DIBP and DEHP (*p*=0.829, 0.874, and 0.595). DEP was negatively correlated with all the other chemicals, but the negative correlation was only statistically significant with DEHP at p=0.01 (Appendix Table C4).

5.4 Laboratory Investigation of potential sources of Chemicals in the Indoors of Homes

Activities in the indoor environment together with the infiltration of outdoor pollutants may result in increased concentrations of pollutants in the indoor air, leading to increased exposure risk. Airborne samples were collected by standardised pumped and diffusive methods as described in chapter 3 and the presence of chemical contaminants was investigated. The possibility of chemical emissions from other potential sources was investigated by measurement of emissions during different household activities and from pesticides and incenses.

5.4.1 Measurement of VOCs/SVOCs in the air of Homes

Airborne samples collected from various locations (as described in chapter 3) were investigated for the presence of organic chemicals as described in section 3.4.8.

5.4.1.1 Airborne samples

Collection of the airborne samples was carried out diffusively by exposing Tenax tubes for 2 weeks in the living rooms and kitchens of Nigerian homes as well as UK homes. The tubes were then taken to the laboratory and spiked with an internal standard d-toluene prior to TD/GC/MS analysis and the quantified chemicals are shown in section 5.4.2.1. While active (pumped) sampling of the airborne samples was done on Q-Tenax tubes as described in 3.4 during various domestic activities; cooking with kerosene, gas, and firewood; electricity generation with fossil fuels (petrol and diesel) and natural weather (dusty events). The tubes were analysed by TD/GC/MS and the results are shown in section 5.5.2.2.

5.4.1.2 Incenses and Pesticides

The emissions from pesticides and different brands of incenses collected (as described in section 3.4) were also analysed. The chemicals quantified are as shown in 5.5.2.3.

5.4.2 Results of Chemical Analysis of air Samples

The presence of an array of organic chemicals was observed and the chemicals of interest were quantified as in the settled dusts analysis but with addition of limonene due to its frequency in the air samples. The chromatograms showed a wide range of chemicals with different retention times in both diffusive and pumped samples. Examples of chromatograms showing chemical concentrations in diffusively and actively collected samples are shown in Figures 5.19 and 5.20. The target chemical concentrations in ng l^{-1} showed high concentrations of chemical emissions especially during cooking with firewood and kerosene; and during diesel electricity generation. Total volatile organic chemicals (TVOC) values, the sum of all VOCs found with volatilities between those of n-hexane and n-hexadecane quantified using the calibration factor for toluene, were determined for all the samples.

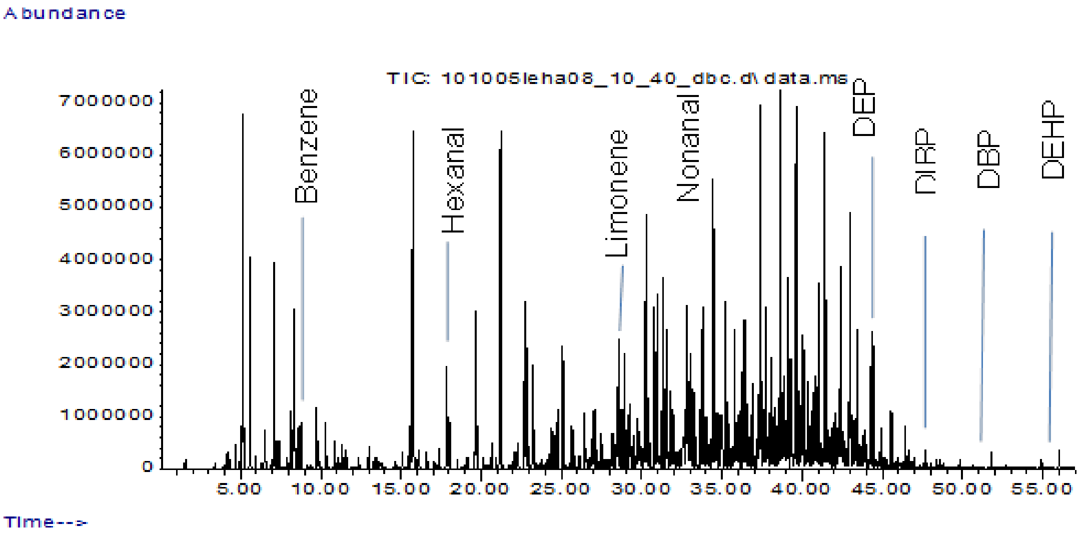


Figure 5.19 Chromatogram of diffusive indoor air sample (FH) during Harmattan

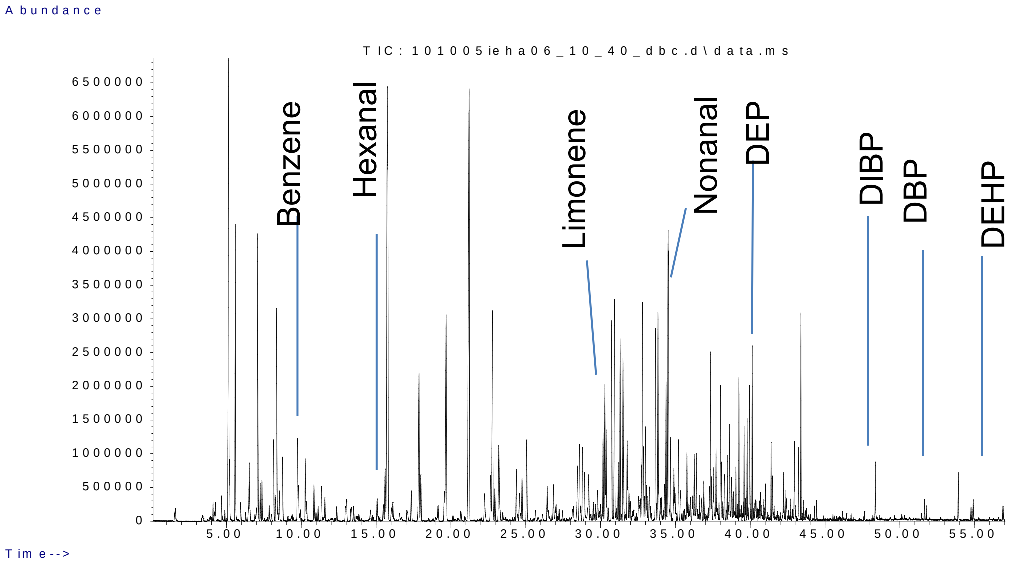


Figure 5.20 Chromatogram of active outdoor sample during Harmattan haze

5.4.2.1 Chemical Concentrations in Diffusive samples

The two diffusive samples collected from the living rooms and kitchens of Nigerian homes during Harmattan and Storm contain similar ranges of compounds, with higher amounts of the aldehydes (hexanal, nonanal) and limonene than the phthalates. Higher amounts of hexanal and nonanal emissions were observed in the living rooms during Harmattan compared with during storm (Table 5.27). The dust storm samples had lower amounts of chemicals than the Harmattan samples (Table 5.28). Chemical emissions were observed in all the samples analysed and the total volatile organic compounds (TVOCs) calculated gave an indication of presence of a host of chemicals in the samples in addition to the target compounds. The TVOCs calculated ranged between 1400 ng l^{-1} to 5000 ng l^{-1} in the Harmattan samples and 22 to 562 ng l^{-1} in the storm samples (Tables 5.27 and 5.28).

Table 5-27 Chemical concentrations in air and TVOC values during Harmattan sampling period

Compound	Chemical concentrations ng l^{-1}								
	FK	FLR	LK	LLR	MK	MLR	YK	YLR	Harmattan haze
Benzene	6	6	3	2	9	6	11	18	55
Hexanal	76	64	65	55	75	78	63	66	1
Limonene	16	20	15	22	11	14	14	23	1
Nonanal	73	48	68	8	73	72	71	45	2
DEP	3	19	3	3	3	5	4	2	5
DIBP	<1	2	<1	2	1	3	<1	2	1
DBP	<1	1	0.5	2	6	1	<1	3	1
DEHP	2	6	2	7	6	3	2	5	2
TVOCs	2500	5000	3500	4140	3500	3300	3930	3700	1400

Table 5-28 Chemical concentrations in air and TVOCs values during Dust Storm sampling period

Compound	Chemical concentrations on tubes in ng l^{-1}				
	FLR	LLR	MLR	YLR	ALR
Benzene	5	3	6	2	4
Hexanal	13	1	1	30	2
Limonene	16	3	8	91	3
Nonanal	57	15	11	30	18
DEP	2	10	<1	1	3
DIBP	0.5	0.5	<1	<1	0.5
DBP	<1	<1	<1	1	0.5
DEHP	1	0.5	0.5	1	1
TVOCs	244	382	562	165	22

5.4.2.2 Chemicals in Active (pumped) Samples

Individual chemical concentrations and TVOCs (ng l^{-1}) of airborne samples collected actively (pumped) showed higher concentrations during household activities especially during burning/use of fossil fuels for cooking and electricity generation (Table 5.29). The diesel generator had the highest TVOC concentration followed by the petrol generator and kerosene stove cooking, while the sample taken during Harmattan haze outdoors had the lowest TVOC concentration. The active sample taken during the Storm contains a number of different compounds in low concentrations. The problem of indoor/outdoor pollution from the use of domestic cooking stoves has attained greater importance in developing countries owing to poor ventilation and the extensive use of low-efficiency stoves and biofuels (Ezzati, 2005). The health effects of indoor pollution from cooking and burning of fossil fuels have been reported in earlier studies (Fullerton *et al.*, 2009; Fullerton *et al.*, 2008).

Table 5-29 Chemical concentrations and TVOCs in air during household activities

Compound	Chemical concentrations ng l^{-1}						
	Kerosene cooking	Gas cooking	Firewood cooking	Diesel generator	Petrol generator	Harmattan haze	Storm episode
Benzene	29	8	212	4	250	1	7
Hexanal	2	6	5	2	2	0.5	30
Limonene	10	5	3	3	10	1	17
Nonanal	11	3	7	8	4	5	41
DEP	2	1	6	2	1613	0.5	8
DIBP	1	11	56	<1	36	0.5	<1
DBP	1	21	4	3	2	0.5	<1
DEHP	0.5	2	6	5	1	0.5	<1
TVOCs	2395	417	1530	18060	6331	152	380

5.4.2.3 Analysis of Diffusively (passive) samples in UK Homes

Concentrations of eight chemicals and the TVOC values for all the diffusively sampled tubes in the UK homes were analysed in the same manner as for the Nigerian samples. Individual chemical concentrations and TVOC values are shown in Table 5.30. The concentrations of chemicals in UK samples were found to be lower than in the Nigerian samples. The nonanal concentration was highest in sample AKB with <1 ng l^{-1} of benzene and DEHP in all the samples.

Table 5-30 Chemical and TVOC concentrations (ng l^{-1}) in samples collected diffusively from UK Homes

Compound	Mean of duplicates amount of chemicals in ng l^{-1}			
	AKB	**AKK**	**FLR-UK**	**FBR-UK**
Benzene	<1	<1	<1	<1
Hexanal	19	25	7	10
Limonene	7	5	4	6
Nonanal	30	29	26	23
DEP	5	1	4	6
DIBP	3	7	<1	2
DBP	1	1	<1	6
DEHP	<1	<1	<1	<1
TVOCs	90	132	184	108

The TVOCs are calculated based on the presence of many compounds observed in the chromatograms. The identification and quantification of all individual VOCs occurring in indoor air samples is difficult if not impossible. The TVOC values were used as a simplified way of expressing the results of VOCs measurements as this has been adopted by many researchers as an indicator of air quality, and as a predictor of the probability of health and comfort effects (Brown *et al.*, 1994). A measure of the TVOCs quantity is defined as all VOCs in the boiling point range of 50–260°C (WHO, 1989; 2005).

Individual VOCs have been reported to be generally below 50 µg m^{-3} and mostly below 5 µg m^{-3} in established buildings, with concentrations much higher in new buildings, where TVOCs concentrations of up to 20,000–40,000 µg m^{-3} occur in extreme cases (Brown, 2002). In Australia, the National Health & Medical Research Council in 1992 recommended the following indoor air goals: TVOCs not to exceed 500 µg m^{-3} (1-hour average); and any individual VOCs not to exceed 250 µg m^{-3} (1-hour average) (Brown, 2007). In this study, total

VOCs (TVOCs) values have been determined for all the tubes and found to be higher in the diffusive and some of the pumped samples in Nigerian homes than that reported in Australia by Brown, (2007).

5.4.2.4 Chemical Concentrations in Pesticides and Incense

Sampling for SVOCs/VOCS emissions using the bag sampling procedure was carried out as described in chapter 3.4 where the emissions were collected from four types of assorted and local incenses and two pesticides (1 powdered and 1 liquid). The chemical emissions collected on duplicate Q-Tenax tubes were analysed by TD/GC/MS under the same condition as with the dusts analysis. The types of incenses used for the analysis are normally burnt in homes in Nigeria. The headspace samples did not release substantial amounts of chemicals. Benzene was present in all the samples at concentrations, with highest emission from liquid pesticide (Table 5.31). Benzaldehyde-3 phenoxy and Permethrin were seen in the liquid pesticide which was also indicated by the manufacturer as active ingredients in the product, but these were not quantified due to the limitations of the method used (the instrument was not calibrated with the chemicals).

The smoke from the burnt incenses collected on sampling tubes and analysed showed emissions of more compounds than the not-burnt headspace samples of the same products. The emissions were then matched with the NIST chemical library. An example of the chromatograms of one of the incenses analysed is shown in Figure 5.20. Incense burning has been reported to be a source of emission of hundreds of chemicals (pollutants) by researchers from different parts of the world indicating incense burning as a source of indoor pollution (Tran and Marriott, 2007; Wang *et al.*, 2007b).

Table 5-31 Chemicals released from different incenses and pesticides using bag tests

	Amount of chemicals on tubes (ng)						
Compound	Morrisons incense (200 ml)	Assorted incense (100 ml)	Oudh incense (200 ml)	Local incense (100 ml)	Local incense (200 ml)	Powdered Pesticide (200 ml)	Liquid pesticide (100 ml)
Benzene	1.5	<1	2.7	14.1	1	3	339
Hexanal	ND	ND	ND	ND	ND	ND	ND
Limonene	ND	205.7	ND	46.3	ND	ND	ND
Nonanal	ND	ND	ND	2.2	123	<1	ND
DEP	7.7	2	24.2	4.5	17.5	<1	ND
DIBP	5	ND	3	<1	ND	4	ND
DBP	<1	<1	<1	<1	ND	<1	ND
DEHP	<1	26.2	<1	<1	<1	ND	ND

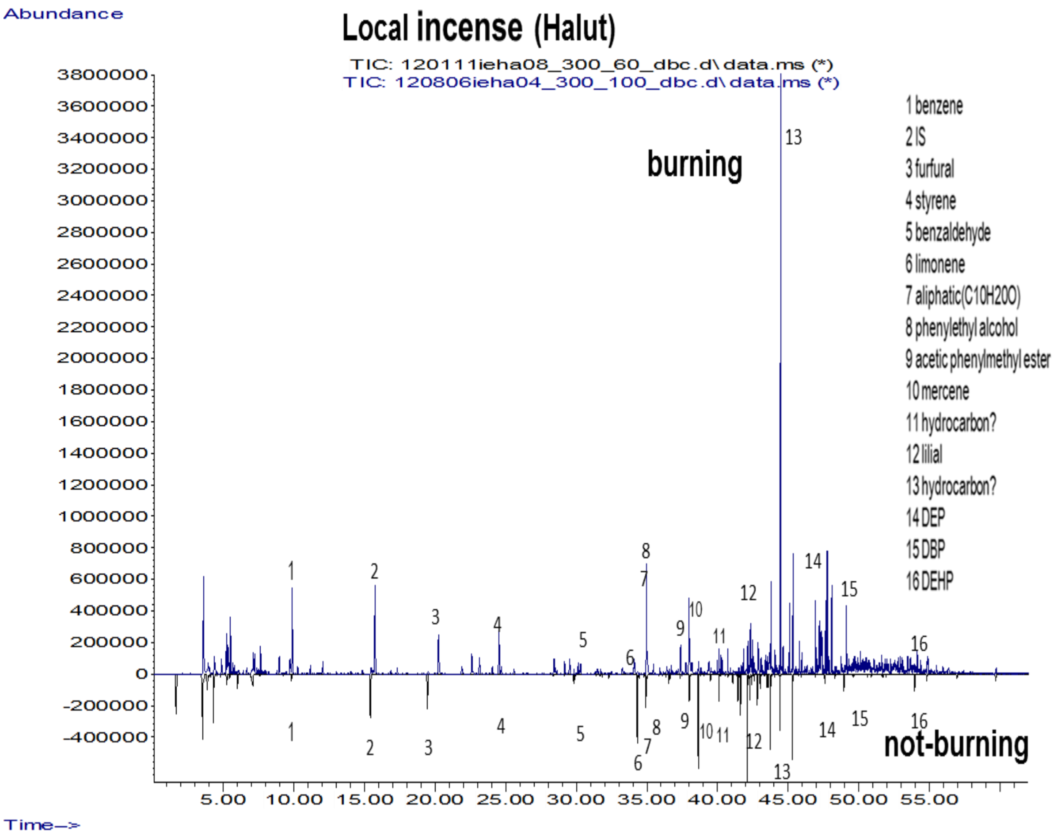


Figure 5.21 Chemical emissions in burnt and not-burnt incense

5.5 Chapter Summary

The µ-CTE thermal extraction offers a relatively rapid and repeatable method to compare the most available fractions of analytes and has been found to be a good method of investigating chemicals in matrices such as dust and other products like incenses, and building materials. Thermal extraction can release more analyte if heated for a longer time.

The higher concentration of the chemicals observed in the solvent extracts compared with the thermal extracts was expected due to the aggressive removal of the chemicals by the organic solvent whereas in the case of thermal extraction only the readily available chemicals (loosely bound to the matrix) that can easily be released to air by increases in temperature were removed.

The pumped and diffusively collected airborne samples during the various indoor/outdoor activities analysed demonstrated the activities were contributory sources of chemical contaminants to house dust. This means that should the behaviour of people differ between homes or change over the seasons then the strength of the contribution of these sources of chemicals to the dust will change and at least account in part for observed differences in chemical concentrations in dusts.

The mean chemical concentrations observed were in higher amounts in the indoor than in the outdoor samples, and DEHP was more than the other compounds. The high DEHP emissions may be due to the fact that it is the most common plasticizer found in almost all plastic and most household products. The organic chemical concentrations were also higher in the modern buildings than the traditional buildings and this can be attributed to the contribution from the indoor sources such as cosmetics, furniture, carpets, paints, and other consumer products which are absent in most of the traditional buildings.

6 METAL ANALYSIS

6.1 Introduction

In most natural environments, metals occur in low concentrations, however in contaminated environments they occur at high concentrations, which may pose risks to public health. The elements that are of particular concern include lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), zinc (Zn), nickel (Ni), and copper (Cu). The natural sources include soil, rocks, and plants, and among the anthropogenic sources are; incomplete combustion of fossil fuels, industrial processes, and some released from sources in the household (Fergusson and Kim, 1991). Metal pollutants have the potential for poisoning humans through inhalation, ingestion, and skin absorption. Acute and chronic exposure to metal contaminants can lead to health effects such as nausea, anorexia, vomiting, headaches, gastrointestinal abnormalities, and dermatitis as discussed in section 2.4.3.1 and Table 2.2.

This chapter reports investigations of elemental (metal) pollutants in household dusts by extraction of the metals through microwave assisted acid digestion of the dust samples followed by inductively coupled plasma-mass spectrometric (ICP-MS) analysis. The microwave digestion method was employed to extract the metal content of dusts in preference to the traditional Soxhlet extraction method, which is much more time consuming and involves greater solvent usage. The settled dust samples collected using a vacuum cleaner in Nigerian homes were analysed along with the sample of surface soil (sand) collected at a distance from the homes and the standard reference dust (SRM 2585).

6.2 Sample Preparation and Instrumentation

6.2.1 Microwave assisted Digestion

Microwave digestion is a technique for the digestion of a wide range of samples such as soils, proteomics, urine, and blood for metals analysis by ICP-MS and other analytical techniques such as graphite furnace-atomic absorption spectrometry (GFAAS) and inductively couple plasma-optical emission spectrometry (ICP-OES). The method produces a clear digestion (near complete extraction of analytes) in most sample types in almost every case because it operates at higher temperature and pressure than the traditional hot plate. The process involved extraction of metal elements in concentrated nitric acid in which the samples were placed in Teflon lined microwave vessels and then heated in the microwave unit. At the end of the process, the vessels were removed and after cooling, the contents filtered, allowed to settle and then diluted to volume (usually 50 ml) and analysed by the appropriate determinative method such as ICP-MS. During the digestion process, the samples are enclosed, so cross contamination and loss of volatiles is prevented.

The microwave digester (Multiwave 3000 - PerkinElmer): consists of the vessel module with a 24 vessel capacity. Vessel number 1 is the control vessel (must contain a test solution) with its cover connected to the temperature and pressure device of the instrument. A rotating turntable was set for centrifugation at 2,000 – 3,000 rpm (Plate 6.1).

Instrument conditions: The start temperature was 50^{o}C, raised to 175^{o}C in 10 minutes, and then held at 16 bars pressure for 20 minutes; then the temperature was reduced to 50^{o}C and held for 20 minutes. It was then cooled to 25^{o}C with pressures of between 2-5 bars. The run takes 60 minutes.

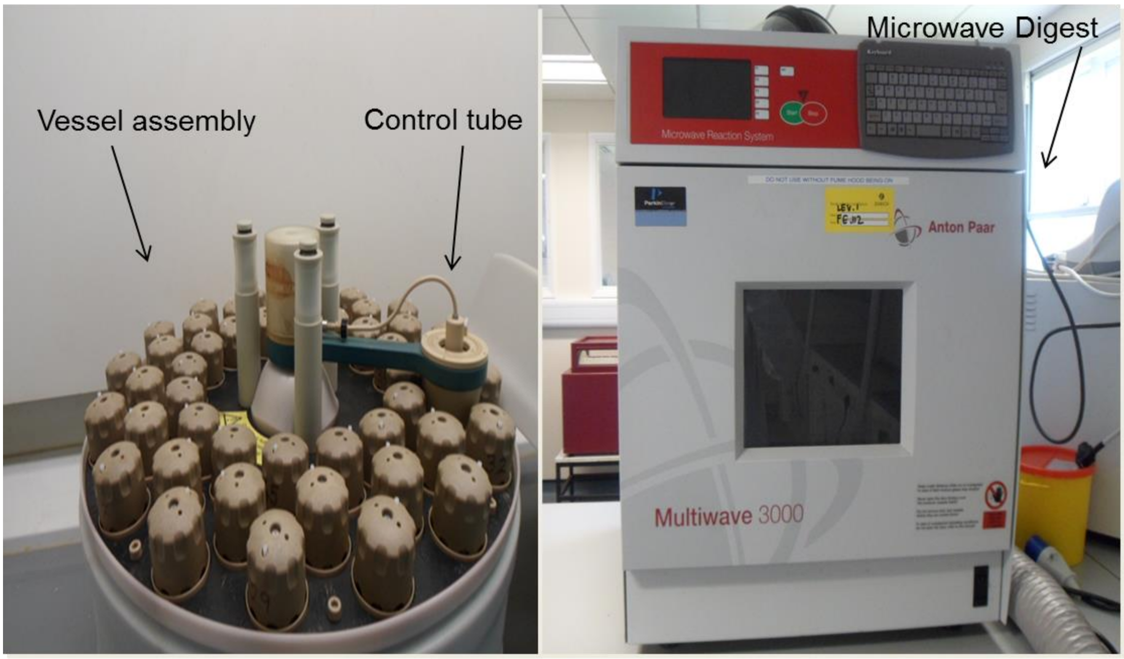


Plate 6-1 The Microwave digest and vessel assembly unit

6.2.2 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

The ICP-MS instrument can be used for the quantitative and semi-quantitative measurement of most of the elements in the periodic table with detection limits at or below the ppb range. The ICP-MS is a type of mass spectrometry which is capable of detecting metals and several non-metals at concentrations as low as one part in 10^{12} (part per trillion). This is achieved by ionizing the sample with inductively coupled (argon) plasma and then using a mass spectrometer to separate and quantify the ions. Unknown samples are analyzed providing semi-quantitative data that is typically within ±30 % of the quantitative values. The ICP-MS assembly used has an S-10 Autosampler (PerkinElmer) with dynamic reaction cell technology (DRC-e Quadrupole) to minimize interference effects during analysis. The instrument consists of the following components:

Sample introduction system: composed of a nebulizer and spray chamber and it provides the means of getting samples into the instrument.

The ICP torch and RF coil: generate the argon plasma, which serves as the ion source in the vacuum system that provides a high vacuum for ion optics, and the quadrupole.

The interface: that links the atmospheric pressure ICP ion source to the high vacuum mass spectrometer and detector.

Collision/reaction cell: that is used to remove interferences that can degrade the detection limits achieved.

Ion optics: that guides the desired ions into the quadrupole while assuring that neutral species and photons are discarded from the ion beam.

Mass spectrometer: this acts as a mass filter to sort ions by their mass-to-charge ratio *(m/z)* and the individual ions exiting the quadrupole are counted by the detector and the information is sent to the data handling compartment (computer system).

The operating conditions are;

Nebulizer gas flow rates at 0.86 l min^{-1},

Auxiliary gas flow of 1.2 l min^{-1}, and

Plasma gas flow of 15 l min^{-1}.

The ICP-MS instrument assembly used in this study is located in the School of Applied Sciences (SAS), Cranfield University. A typical ICP-MS is shown in Plate 6.2.

The ICP-MS process: Acid extracts of dusts samples are first introduced into the ICP-MS instrument by way of a nebulizer (which aspirates the samples with high velocity argon) that form fine mists/aerosols that pass into a spray chamber where larger droplets are removed (typically, only 2% of the original mist passes through the spray chamber). This produces smaller droplets that are then vaporized in a plasma torch. The aerosol moves into the torch body and is mixed with more argon gas. A coupling coil is used to transmit radio frequency (energy) waves to the heated argon gas, producing an argon plasma "flame" located at the torch. The hot plasma removes any remaining solvent and causes sample atomization followed by ionization. Ions are then removed from the plasma by a pumped extraction system and subjected to mass discrimination and detection by MS (Figure 6.1).

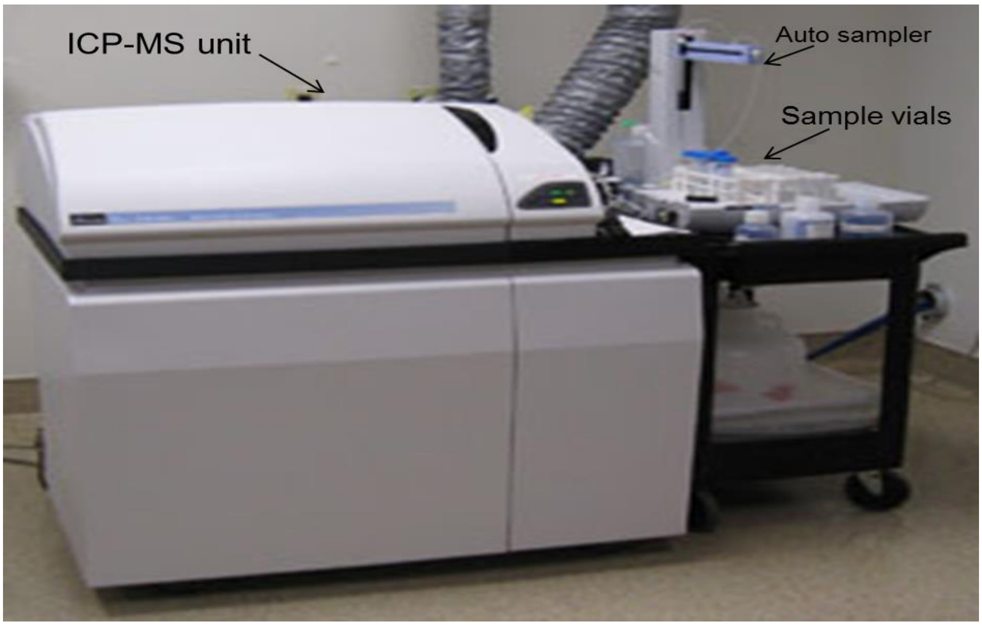


Plate 6-2 The ICP-MS assembly (web image)

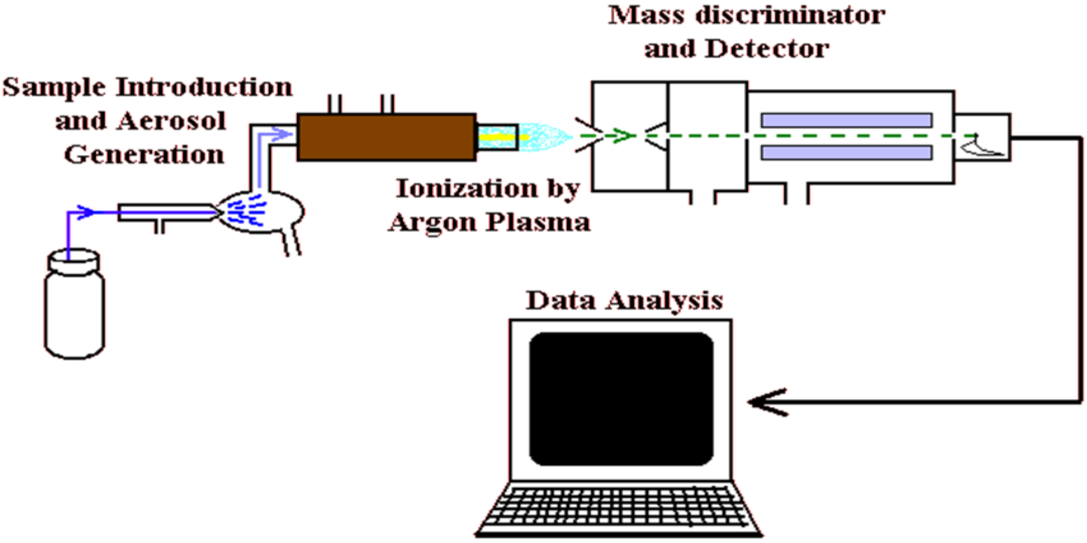


Figure 6.1 Schematic Diagram of ICP-MS main processes

6.2.3 Acid Digestion of Dust Samples

Sample Preparation: The <150 µm fractions of vacuum cleaner dusts (as described in chapter 3) are used for the metal analysis. 5g of each of the dust samples were weighed into crucibles and oven dried at 103^{o}C for 24 hours in accordance with an international standard for determining the dry matter and water content of soil (British Standards Institution, 1994) prior to digestion. The microwave digestion procedure was adopted from EPA method 3051A-*Microwave assisted acid digestion of sediments, sludge, soils, and oils* (US EPA, 2007). The procedure involved adding a strong acid (HNO_3) to the dust sample in a closed vessel, and raising the pressure and temperature through microwave irradiation. The increased temperature and pressure of the system and low pH of the sample medium result in rapid thermal decomposition of the sample, and high solubility of heavy metals in solution.

Procedure: Pre-digestion was done by weighing 0.5 g (<150 µm fraction) of each of the dusts in triplicate and these were transferred into labelled Teflon lined vessels. 10 ml of analytical grade (90%) nitric acid was added to each vessel containing the dust samples and kept overnight in a fume cupboard (samples were completely covered). Three vessels containing only nitric acid were kept as blanks. The vessels were carefully prepared for microwave digestion by inserting each vessel into brown plastic tubes and threading over the vessel covers and tightening in the vessel module. The assembled disk was then loaded (with circular depressions facing up) onto the apparatus carousel in the microwave digester (Multiwave 3000 - PerkinElmer). The instrument was turned on and the sample extraction carried out. At the end of the run, the instrument door was opened and each of the pressured vessels removed (in turn) from the micro digest port (Plate 6.1). The acid digested samples were filtered into 100 ml volumetric flasks through 150 mm Whatman-542 filter papers. The filtrates were allowed to drain, rinsed, and made up to 100 ml with deionised water. The filtered acid extracts were then then poured into clean-labelled digest vials and stored at 4^{o}C, before ICP-MS analysis.

6.2.4 Investigation of Metal in Dusts by ICP-MS analysis

The procedure was adopted from US EPA method-3051A and the work of Ahmed et al., (1992) with modifications. 20 mL of each of the acid extracts (in triplicates) of the various dust samples were placed in labelled wide mouthed polypropylene vessels and these vessels were arranged on the ICP-MS auto sampler for analysis. The use of an auto sampler reduced cross contamination during sample handling. A blank sample containing only nitric acid was used.

The extracts were analysed for the presence of individual metal analytes by ICP-MS (multi element analysis), first using the Total quant method (semi-quantitative method) followed by the quantitative method for selected metals and the concentration of the metals were blank corrected. The acid extracts of various settled dust samples collected from the vacuum cleaner bags of Nigerian homes, samples of sand collected at a distance from the homes as well as the standard reference material SRM2585 were analysed.

6.2.4.1 Total Quant Method (TQM)

A working standard for the TQM which is a general metal standards solution (produced by diluting 2.5 ml of a TQ stock solution) containing the metal standards (Table 6.1) was used and run with the 5 Nigerian house dusts (collected during method development phase) and the sand sample.

6.2.4.2 ICP-MS Analysis of Target Metals

After the analyses by the TQM run, all the other dust samples (i.e. those subject to organics analysis described in chapter 5) were treated as in 6.2.3 and the investigation of elemental pollutants was carried out by the quantitative method for specific metals. This was carried out after the ICP-MS instrument was calibrated with standards of the six target metals; cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), and zinc (Zn). The selection of the 6 target metals was done based on the available reports from other studies on their presence in dust, the possible health effects on human exposure and the appropriateness of the method (Table 6.2).

Table 6-1 Calibration solutions used in total quant method of ICP-MS

Element	**Stock (ppm)**	**ml of stock diluted to 100 ml**	**TQ stock (ppm)**	**TQ working standard (ppb)**
Aluminium (Al)	1000	0.1	1	50
Arsenic (As)	1000	0.1	1	50
Cadmium (Cd)	1000	0.1	1	50
Calcium (Ca)	1000	1.0	10	500
Chromium (Cr)	1000	0.1	1	50
Cobalt (Co)	1000	0.1	1	50
Copper (Cu)	1000	0.1	1	50
Iron (Fe)	1000	0.1	1	50
Lead (Pb)	1000	0.1	1	50
Lithium (Li)	1000	0.1	1	50
Magnesium (Mg)	1000	1.0	10	500
Manganese (Mn)	1000	0.1	1	50
Mercury (Hg)	1000	0.01	0.1	5
Nickel (Ni)	1000	0.1	1	50
Phosphorus (P)	1000	1.0	10	500
Potassium (K)	1000	1.0	10	500
Silicon (Si)	1000	0.1	1	50
Silver (Ag)	1000	0.01	0.1	5
Sodium (Na)	1000	1.0	10	500
Thallium (Tl)	1000	0.1	1	50
Tin (Sn)	1000	0.1	1	50
Titanium (Ti)	1000	0.1	1	50
Uranium (U)	1000	0.1	1	50
Zinc (Zn)	1000	0.1	1	50

Table 6-2 Summary information about the target metal pollutants quantified (from various sources)

Metal	Characteristics	Sources/Uses	Health effect
Zn	Zinc in pure elemental or metallic form is a bluish-white, shiny metal. Powdered zinc is explosive and may burst into flames if stored in damp places.	Zinc is found in the air, soil, water and is present in all foods. Zinc is an essential element needed by the body in small amounts. Metallic zinc is used to galvanize steel and iron, form alloys as in brass and bronze, and in dry cell batteries.	Inhaling large amounts of zinc dust or fumes can cause specific short-term effects. Ingesting high levels of zinc for several months may cause anemia, and damage the pancreas.
Pb	Lead is a bluish or silvery-grey soft metal.	Lead is mostly deposited in soils and crops. It is also present in exhausts of fossil fuel combustion.	Inhalation and/or ingestion of lead may cause decreased intelligence in children, especially when exposed to lead within the first two to three years of life.
Cu	Copper is a reddish metal. It is an essential element for all known living organisms including humans and other animals at low levels of intake.	Copper is common in the environment; air, water, food, soil, and plants. Most copper compounds found in the air, water, sediment, soil and rock are strongly attached to dust and dirt or imbedded in minerals.	Copper is essential for good health. However, exposure to higher doses can be harmful. Long-term exposure to copper dust can cause irritation to the nose, mouth, and eyes, headaches, dizziness, nausea, and diarrhea.
Ni	Nickel is a silvery white, soft metal that is highly resistant to atmospheric corrosion and retains a high polish. Evidence suggests that some forms of nickel may be essential in the human diet.	Natural sources of ambient nickel are windblown dusts and volcanic activity. The anthropogenic sources include fossil fuel combustion, asbestos mining and milling, refuse and sewage sludge incineration.	Acute health effects include irritation and allergic sensitization. Chronic non-cancer effects from exposure to nickel include asthma and other respiratory effects.

Cr	Chromium is a grey, hard metal most commonly found in the trivalent state in nature.	Cr is associated with particles emitted when burning fossil fuels, metal smelting and foundries, cement production, pulp and paper mills, chrome plating, timber treatment using copper/chrome/arsenic preservatives, cooling towers and leather tanning.	Chromium VI compounds are more toxic than chromium III. High levels cause coughing and wheezing and gastrointestinal and neurological effects; chronic inhalation causes effects on the respiratory tract, such as bronchitis, pneumonia, asthma and nasal itching; and potentially effects on the liver, kidney, and gastrointestinal and immune systems.
Cd	Pure cadmium is a soft, silver-white metal. One of the most toxic elements which can be exposed to at work or in the environment.	Sources include leafy vegetables such as lettuce and spinach, potatoes and grains, peanuts, soybeans, and sunflower seeds contain high levels of cadmium. Used to plate metal and additive for plastic.	High cadmium levels can irritate the stomach, causes vomiting and diarrhoea, and sometimes death. Acute levels can cause kidney disease, lung damage, bones fragility, and death.

Summary information about the target metal pollutants quantified- *cont.*

6.3 Results of Metal Analysis of the Acid Extracts of Dusts

The dusts analysed were the five indoor/outdoor dusts in Nigerian homes, the sand samples, the SRM 2585, Harmattan and Storm Dust samples, outdoor dust sample, and the dust samples collected from indoors and outdoors of modern and traditional homes in Damaturu Nigeria as described in chapter 3. All the acid extracts were analysed using the quantitative method based on the method described in section 6.2.4.

6.3.1 Metals Concentrations in Total Quant method (TQM)

The total quant (semi-quantitative) method was carried out to investigate the general profile of the elemental pollutants present in the acid extracts of the various dusts. The acid extracts of five indoor, one outdoor Nigerian dusts and sand samples were analysed, and the presence of an array of more than 50 elements revealed. The concentration of the elements had the general ranking (high to low) of Al>Li>Fe>As>Na>Mg>Ca>K>P>Mn>Si>Ti. The mean concentrations of some of the metals present in the indoor and outdoor dust samples and the sand are shown in Table 6.3. The concentrations of Al in the 4 dust samples AH, LH, MH and YH were more than the quantification limit. The lighter metals were in higher concentrations than the heavy metals in all the samples with the sand sample showing the least amount of elements. The mean concentrations of some of the lighter and heavy metals as analysed by the total quant method are shown in Figures 6.2 and 6.3. The results indicated that house dust contains a host of metal contaminants, which include both the lighter and the heavy metals, some of which could potentially cause health effects on exposure of humans to the house dust. The abundance of such elements as Br, Cu, Cl, Pb, Zn, Cr, Ca, Co, As and Sb in house dust, and Zn, Cr, Cu and Pb in street dust have been reported in a previous study (Fergusson *et al.*, 1986).

Table 6-3 Mean metal concentrations (mg kg^{-1}) in dusts and sand

	AH DUST	FH DUST	LH DUST	MH DUST	YH DUST	FHO	SAND
Li	10,011	19,636	29,392	21,174	40,607	17,744	6368
Na	2137	3041	1455	2303	1592	3632	2509
Mg	1337	2087	1438	3023	5034	5034	3644
Al	>dl	9501	>dl	>dl	>dl	9092	2283
Si	2501	1117	1515	1235	1107	1151	1131
P	1120	1491	323	854	394	1776	1008
K	1125	2775	1612	2639	2134	4373	3049
Ca	1121	3078	1964	2124	2222	3562	1178
Sc	127	1.3	2.0	43	2.7	1.3	0.3
Ti	23	108	176	146	171	92	53
V	25	11	19	12	24	12	14
Cr*	182	15	22	14	32	15	182
Mn	1091	194	259	187	335	182	118
Fe	6.0	5904	8628	6126	11760	7195	5241
Co	13	2.9	6.0	4.9	10	2.7	1.8
Ni*	25	7.6	13	9.1	19	6.0	3.2
Cu*	141	11	81	19	91	14	2.7
Zn*	105	102	197	246	162	241	240
As	0.0	1435	3189	1645	3183	1380	941
Se	5.3	0.1	0.0	16	0.1	0.3	0.5
Br	0.0	3.2	7.4	4.8	19	5.2	1.5
Rb	52	4.7	6.9	5.7	11	5.1	0.9
Sr	5.5	33	64	68	101	26	2.8
Y	8.8	3.5	5.5	3.3	6.4	4.0	2.2
Zr	0.1	6.0	12	9.9	17	7.0	3.5
Mo	0.0	0.2	0.2	0.2	0.3	0.2	0.1
Pd	8.5	0.1	0.1	0.0	0.1	0.1	0.1
Ag	0.3	4.3	8.0	6.0	19	4.6	0.5
Cd*	11	19	7	8	8	4	8
Sn	0.0	0.4	0.8	0.7	2.7	0.5	0.1
Ba	0.6	70	97	100	155	45	17
Ce	2.6	32	39	27	49	48	42
Pr	8.9	2.3	14	2.0	3.3	3.2	3.0
Nd	1.4	7.3	7.7	6.7	10	9.9	8.7
Au	0.0	0.0	0.2	0.0	0.0	0.0	0.0
Hg	0.0	0.0	0.2	0.1	1.0	0.1	0.0
Tl	31	0.0	0.0	0.1	0.0	0.0	0.1
Pb*	10	17	88	83	56	21	16
Bi	0.0	0.1	13	0.0	0.2	0.2	0.0
U	0.0	0.5	0.6	0.5	0.8	0.7	0.6

* = target metals >ql= above upper quantification limit

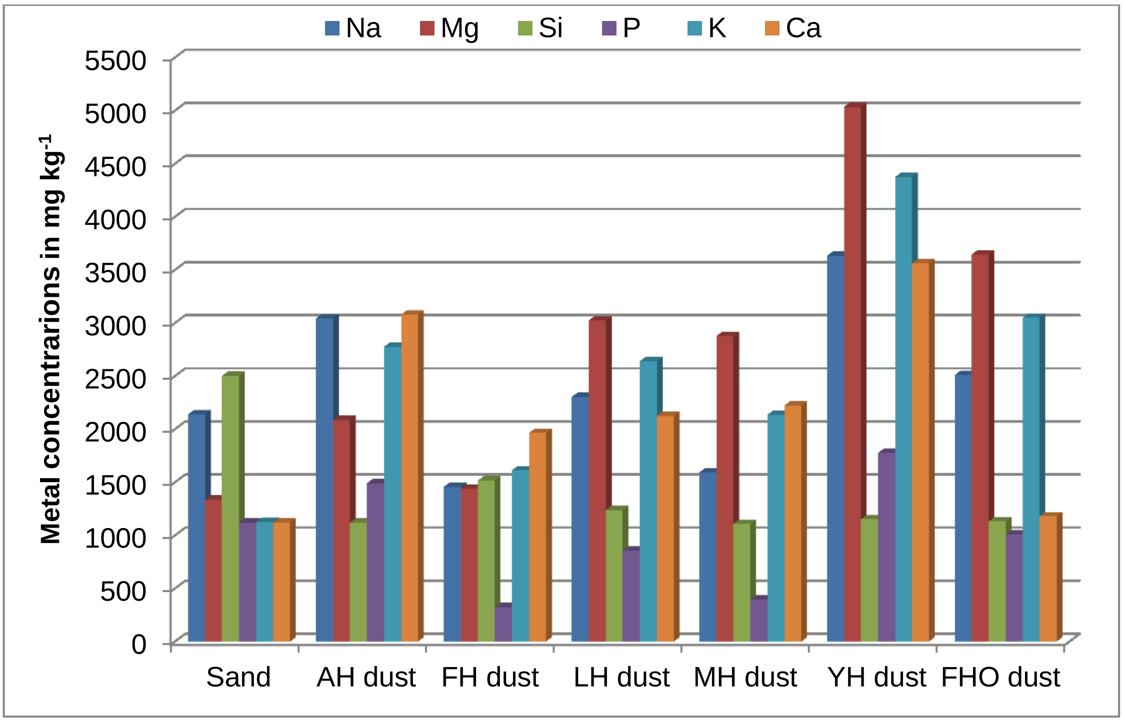


Figure 6.2 Mean concentrations of metals (lighter) in indoor/outdoor Dusts

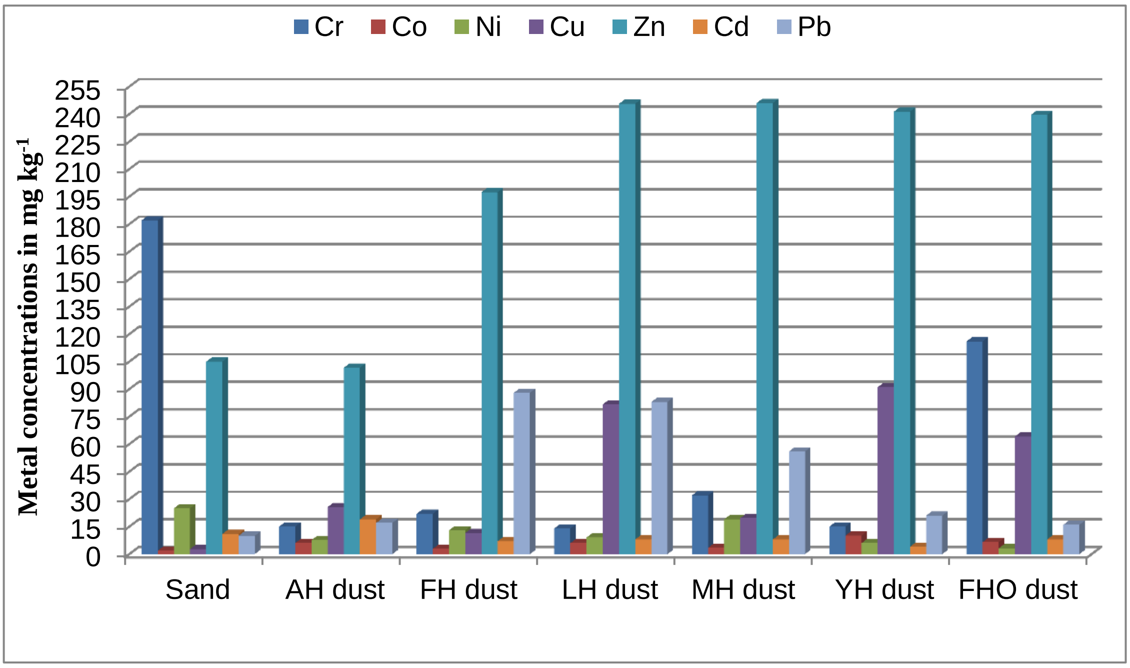


Figure 6.3 Mean concentrations of heavy metals in the indoor/outdoor Dusts

6.3.2 Metal Concentrations in Indoor/Outdoor Dusts analysed by the Quantitative method

The results showed the presence of all the six target metals in all indoors/outdoors dust samples analysed. The mean concentrations showed that the metals present were in higher concentrations in the indoor dusts than the outdoor dusts. In the indoors, Pb was highest and Cd had the least mean concentration (Table 6.4). The arithmetic mean concentrations of the metals in the indoor dusts were in the order Pb>Cu>Zn>Cr>Ni>Cd and the RSD were all <50% indicating low variations in the concentrations and the possibility of common indoor sources of the metal contaminants (Table 6.5). In the outdoor dusts, Zn had the highest concentration while Cr was the least. The AM of the metal concentrations were in the order Zn>Pb>Cr>Cu>Cd>Ni with the RSD of <40% for the five metals except Zn which had the RSD >100%. There may be common outdoor sources of the other metals with different or additional sources in the case of Zn. The mean concentrations of Zn, Pb, Cu and Ni were found to be higher in the indoors than outdoors whereas Cd and Cr were higher in the outdoor than in the indoor dusts (Table 6.4).

Table 6-4 Summary statistics of metals in indoor/outdoor house dusts

Metal concentrations in mg kg^{-1} in Dust samples							
Dust Source		**Zn**	**Cu**	**Pb**	**Ni**	**Cd**	**Cr**
Indoors (n=15)	**AM**	36.6	57.9	60.6	9.5	5.5	10.2
	GM	36.3	57.5	60.5	8.9	5.4	10.1
	Max	42.8	68.4	65.4	15.0	7.7	11.8
	Min	30.8	48.9	56.5	5.7	4.2	7.6
	SD	5.2	7.3	3.3	3.8	1.5	1.6
	RSD%	14.1	12.5	5.4	40.1	26.4	15.8
	Median	37.1	58.2	59.8	10.4	5.2	9.3
Outdoors (n=12)	**AM**	60.9	10.2	14.8	4.3	6.2	12.6
	GM	57.0	10.1	14.7	4.2	1.0	12.6
	Max	78.3	11.0	18.0	5.6	19.2	13.8
	Min	29.5	8.6	13.5	3.3	0.1	11.4
	SD	22.1	1.1	2.2	1.0	9.0	1.2
	RSD%	36.3	10.7	14.8	23.2	146.0	9.2
	Median	68.0	10.5	13.8	4.2	2.7	12.7

6.3.3 Metal Concentrations in different Dusts analysed by Quantitative method

The results of the quantitative analysis of metals in different types of dusts: Dust Storm, Harmattan, airborne dust, sand samples and the standard reference dust revealed the presence of all the six target metals in all the samples. The samples were analysed in replicates for repeatability testing and the arithmetic mean (AM), geometric mean (GM), standard deviations (SD) and relative standard deviation (RSD) were calculated. The RSDs between the replicates of each of the dusts were found to be <10% with the exception of the SRM 2585 which was <30%. These results indicated good repeatability of the methods used in the metal analysis of dust (Table 6.5). The mean concentration of Zn was higher in outdoor airborne dust but the rest of the metals were more in the Dust Storm than in the other dust types, and sand had the lowest mean concentrations of all the metals (Table 6.5). The distribution of and variations in the chemical concentrations during the different weather events are shown in box plots in Appendix C-4.

The comparison between the mean concentrations of the dusts indicated the similarity in amount of the metals quantified in all the various dust samples analysed (Figure 6.4). The similarities may be due to the influence of the strong winds blowing during storm and Harmattan resulting in infiltration of the outdoor dust indoors. The results found were not in line with the earlier reported studies that metals had higher concentrations in the outdoor than the indoor dusts (Ahmed *et al.*, 1993; Akhter and Madany, 1993; Madany *et al.*, 1994). The metals in the indoor/outdoor settled and airborne samples were derived possibly from soil (e.g. Cu and Zn) as they are naturally present as well as from products such as paints and plastic materials, particularly those of poor quality. The use of fossil fuels (kerosene) in cooking and emissions from combustion of petrol/diesel and corrosion or improper disposals of batteries are other possible important sources of the metal pollutants (e.g. Pb and Cd).

Table 6-5 Summary statistics of metals (mg kg^{-1}) in different dust samples

Dust Source		Zn	Cu	Pb	Ni	Cd	Cr
Storm Dust (n=9)	**AM**	65.1	37.9	14.4	6.9	10.0	17.4
	GM	65.0	37.8	14.3	6.8	9.9	17.2
	Max	68.6	41.8	16.5	8.5	11.9	19.8
	Min	59.1	34.3	12.9	5.3	8.5	13.7
	SD	5.2	3.7	1.9	1.6	1.7	3.3
	RSD%	8.1	9.9	13.2	23.2	17.2	18.8
	Median	67.7	37.6	13.7	6.9	9.7	18.8
Harmattan Dust (n=9)	**AM**	39.1	18.4	9.6	5.9	4.2	12.9
	GM	39.0	18.3	9.6	5.5	4.1	12.9
	Max	41.7	21.0	10.2	8.4	5.2	14.0
	Min	36.3	16.9	8.8	3.7	2.9	11.8
	SD	2.7	2.2	0.7	2.4	1.2	1.1
	RSD%	6.9	12.1	7.5	40.4	28.2	8.5
	Median	39.2	17.4	9.8	5.5	4.6	13.0
Sand (n=9)	**AM**	18.0	1.8	2.7	2.4	1.4	5.5
	GM	18.0	1.7	2.7	2.3	1.3	5.5
	Max	19.0	2.0	3.0	3.0	1.8	6.5
	Min	16.6	1.4	2.5	1.7	1.0	4.8
	SD	1.3	0.3	0.3	0.6	0.4	0.9
	RSD%	7.0	18.4	9.9	27.0	28.1	16.2
	Median	18.4	1.9	2.7	2.5	1.3	5.2
Airborne dust (n=9)	**AM**	111.8	10.3	13.5	5.6	0.1	13.4
	GM	110.6	10.2	12.6	5.3	0.1	12.7
	Max	125.5	11.6	18.3	7.0	0.2	19.7
	Min	7.2	3.1	0.1	0.1	0.1	9.0
	SD	19.1	1.5	5.7	2.2	0.0	5.5
	RSD%	17.1	14.7	42.4	39.3	33.5	41.2
	Median	120	11	15	7	0	12
SRM2585 Dust (n=9)	**AM**	43.7	7.6	7.4	6.3	1.9	6.8
	GM	43.5	7.6	7.3	6.1	1.9	6.7
	Max	47.8	8.4	8.3	8.1	2.1	8.9
	Min	39.5	6.8	5.9	4.5	1.8	5.3
	SD	4.2	0.8	1.3	1.8	0.2	1.9
	RSD%	9.5	10.5	17.5	28.7	7.9	27.2
	Median	43.7	7.6	7.9	6.2	1.9	6.3

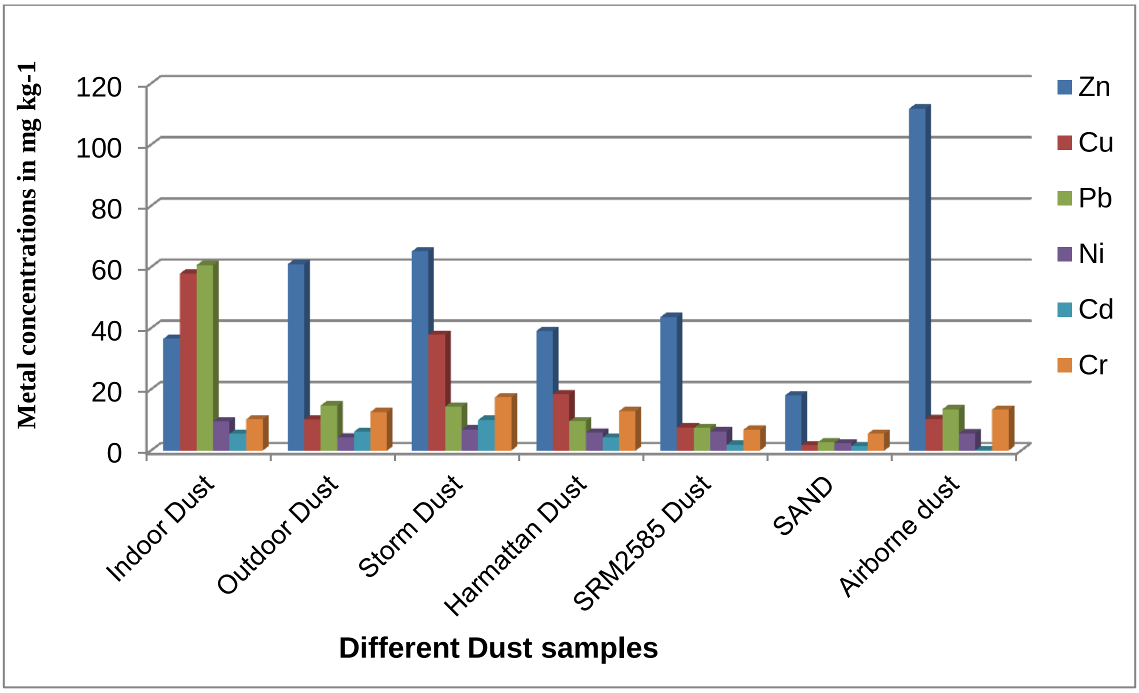


Figure 6.4 Mean concentrations of metals in different dusts

6.3.4 Metal concentrations in Dusts from Modern and Traditional Homes

The result of the quantitative method of ICP-MS analysis for specific metals carried out in 52 samples from the indoors and outdoors of modern and traditional types of buildings also indicated the presence of the 6 target metals in all the samples analysed in varying concentrations. In the indoors of the modern type of buildings the mean concentration of Zn was highest at 567.6 with the range of 402.3 mg kg^{-1} to 696.1 mg kg^{-1} in the individual samples. The means for the rest of the metals were 21.5-Pb, 15.0-Cr, 14.2-Cu, 6.8-Ni, and 3.4-Cd mg kg^{-1} (Table 6.6). This may indicate the variability in sources of the metals especially Zn in the indoors of the buildings. The sources of indoor metals may include household items such as cooking utensils, which are usually alloys of aluminium with other metals (tin, copper, iron). In the outdoors, the sources that contribute to metals in dust include utility fittings (pipes and cables), also metals can be in soil and transported_by the strong winds.

In the outdoor samples the metal concentrations were lower than the indoors with a similar concentration of the metals, but still a higher concentration of Zn was observed (Table 6.6). In the traditional buildings, the mean concentration of Zn was 614.8 mg kg^{-1} with the individual mean concentrations in the range of 217.8 to 902.1 mg kg^{-1} and Cd had the lowest mean concentrations with the range 0.2 -1.1 mg kg^{-1}. The outdoors of the traditional homes had mean concentrations of Zn-325, Pb-18.2, Ni-8.4, Cu-3.0, Cr-2.1 and Cd-1.1 mg kg^{-1} (Table 6.6). The trend was that some of the metals were higher in the indoors while others higher outdoors among all the indoors/outdoors dusts in both types of buildings (Figure 6.5) with Zn concentrations being more than x10 the concentrations of the other metals (Figure 6.6). The results were in agreement with the reported previous study in Ottawa, Canada, that house (indoor) dust had higher concentrations of elements, including lead, cadmium, antimony and mercury, than street dust and garden soil samples and that, indoor/outdoor concentration ratios varied widely for different elements, and from one residence to another within the community (Rasmussen *et al.*, 2001).

The high metal contents in the indoor dusts may be attributed to the possibility of their potential release from the indoor sources such as newly painted rooms, new furniture, and utensils and then deposited on the carpets in the case of the modern buildings, which are the most airtight and are between 19 to 20 years old. In the traditional buildings, with the exception of Zn there was not much difference in the indoor/outdoor metal contents. This may be because most of the homes did not have carpets that can release/trap more dust particles and there is not much distinction between the indoors and the outdoors, and they have similar functions. Another reason may be the presence of sources such as old decayed paints, and enamel utensils mostly used by the occupants in both the indoors and the outdoors. The occupants of the traditional type of buildings are frequently exposed to the metal contaminants outdoors as well as those indoors. The distribution of and variations in the metal concentrations in the modern and traditional homes are shown in box plots in Appendix C-4.

Table 6-6 Summary statistics of metal concentrations in mg kg^{-1} of dusts in Modern and Traditional Homes

Metal concentrations (mg kg^{-1}) of dusts in modern and traditional homes							
Source		**Zn**	**Cu**	**Pb**	**Ni**	**Cd**	**Cr**
Modern Indoor	**AM**	567.6	14.2	21.5	6.8	3.4	15.0
	Max	696.1	25.7	58.5	17.2	26.2	19.2
	Min	402.3	6.8	10.9	2.3	0.7	10.5
	SD	97.5	7.0	13.0	4.6	6.9	3.3
	RSD%	17.2	49.5	60.5	67.1	203	22.0
	Median	576.3	12.3	17.7	5.0	1.4	12.0
Modern Outdoor	**AM**	15.1	2.3	3.3	1.1	0.2	1.3
	Max	20.5	6.9	7.3	4.7	1.3	2.5
	Min	9.1	0.3	0.6	0.3	0.0	0.6
	SD	3.6	1.5	1.9	1.3	0.3	0.6
	RSD%	23.8	66.6	55.7	122.6	147	50.0
	Median	15.6	2.0	3.5	0.5	0.2	1.0
Traditional Indoor	**AM**	614.8	18.2	32.5	6.2	1.1	26.7
	Max	902.1	48.6	53.1	14.9	2.0	35.0
	Min	100.0	8.2	16.4	0.4	0.2	19.0
	SD	217.8	11.2	12.5	3.8	0.4	5.5
	RSD%	35.4	61.7	38.7	60.3	40	20.6
	Median	655.5	12.8	28.3	5.3	1.1	25.9
Traditional Outdoor	**AM**	325.1	3.0	18.2	8.4	1.1	2.1
	Max	569.1	7.0	33.9	16.4	3.2	5.9
	Min	224.5	1.1	11.4	1.2	0.1	1.1
	SD	113.4	1.8	6.6	5.2	1.1	1.4
	RSD%	34.9	60.5	36.0	62.6	101	69.2
	Median	251.1	2.9	16.9	9.7	0.8	1.5

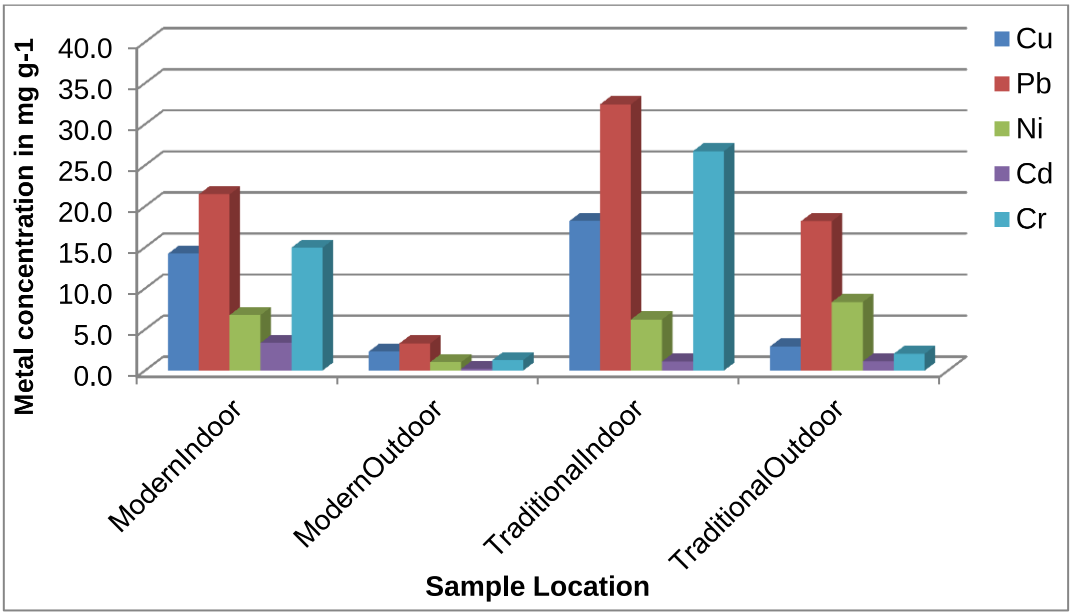


Figure 6.5 Mean metal concentrations (mg kg^{-1}) in modern and traditional homes

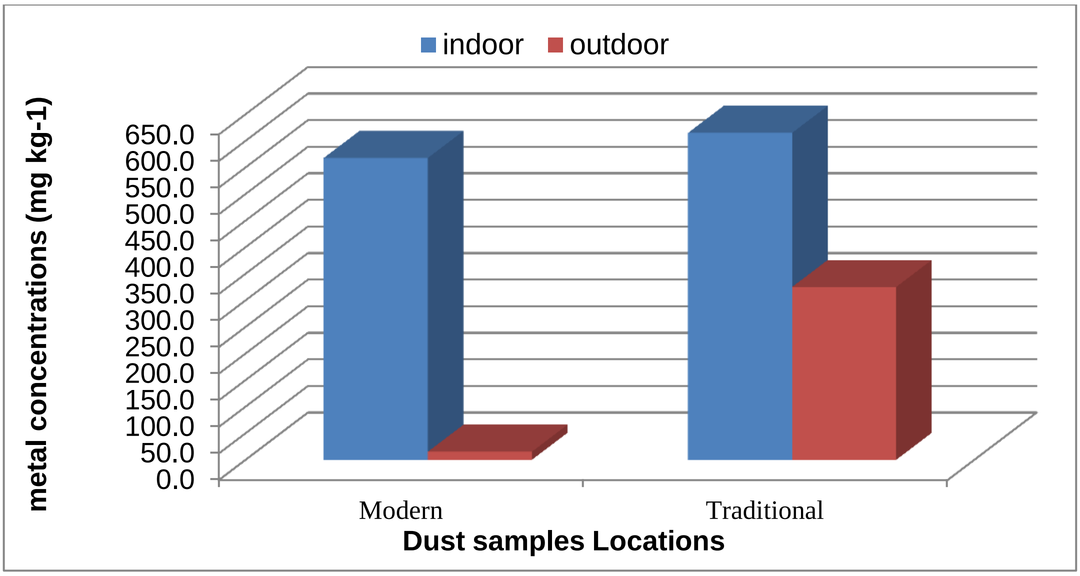


Figure 6.6 Mean Zn concentrations (mg kg^{-1}) in modern and traditional homes

6.3.5 Statistical Analyses

Non-parametric statistical tests were carried out using SPSS (IBM version 20) statistical software because of the non-normal distribution of the data. The Friedman's two-way test (non-parametric test) was also performed in place of the paired sample t-test for the determination of similarities in the concentrations of the metals in the indoor/outdoor dusts. There was indication of statistically significant differences in the mean concentrations of the metals between the indoor/outdoor dusts of the modern homes as well as in the traditional homes (Table 6.7). This indicated that the mean concentrations of all the target metals were different in the indoor/outdoor samples.

Table 6-7 Friedman's 2-way test on mean concentrations of metals

Paired Samples Test between indoor/outdoor of modern and traditional homes					
Metals	**Paired mean Differences (at 95% CI)**		**t-value**	**df**	**Sig. (2-tailed) p value**
	Lower	Upper			
ZnMi -ZnMo	493.38481	611.62288	20.362	12	0.0005
CuMi - CuMo	7.52300	16.32777	5.902	12	0.0005
PbMi - PbMo	20.97841	37.26159	7.793	12	0.0005
NiTi - NiMo	2.55817	7.80644	4.303	12	0001
CdTi - CdMo	0.46278	1.31568	4.543	12	0.001
CrMi - CrMo	8.97876	12.59663	12.993	12	00005
ZnTi - ZnTo	468.47881	730.98581	9.956	12	0.0005
CuTi - CuTo	9.10405	22.70518	5.096	12	0.0005
PbTi - PbTo	20.97841	37.26159	7.793	12	0.0005
NiTi - NiTo	2.55817	7.80644	4.303	12	0.001
CdTi - CdTo	0.46278	1.31568	4.543	12	0.001
CrTi - CrTo	22.00502	28.90729	16.071	12	0.0005

Mi=modern indoor Mo=Modern outdoor Ti=Traditional indoor TO=Traditional outdoor

To determine the correlation between concentrations of the target metals across the dust samples in the modern and traditional buildings the Mann-Whitney U test for independent samples was carried out. The analysis showed a strong correlation between Cu and Cd in the indoors/outdoors of the modern type of buildings as well as in the traditional type of buildings indicating the possibility of common sources of the two metals in the indoors/outdoors of the different buildings. No positive correlations were observed between the rest of the target metals, which may suggest that they were from different sources.

In order to establish any correlation between metal concentrations with the location, Spearman's correlation was performed. The correlation coefficients for metals in the indoor dust samples are shown on the upper right side and the outdoors on the lower left side of Table 6.8. In the indoor samples, there were negative correlations, though not statistically significant, between Zn with Cu, Ni, and Cr, and between Cd and Cr, which showed that the indoor sources of the metals were different. Positive correlations were shown between all the other metals indicating increased concentration of one metal is associated with the increase of the other, but strong correlations of statistical significance existed only between Pb with Cd indicating that the metals are likely to be from the same sources. Cu was positively correlated with all the other metals but strong positive correlations of statistical significance only occurred with Cu and Cr, Pb and Cd (Table 6.8). In the outdoor samples the metal concentrations were all positively correlated with statistically significant values at $p= 0.05$ and 0.01 with the exception of correlations between Pb with Cu, and Ni with Cu (Table 6.8).

Table 6-8 : Nonparametric correlations between metals in indoor/outdoor Dusts

Spearman's correlations between metals in indoor/outdoor Dusts							
Spearman's rho		**Zn**	**Cu**	**Pb**	**Ni**	**Cd**	**Cr**
	N	26	26	26	26	26	26
Zn	Correlation Coefficient		-.208	.351	-.046	.203	-.238
	Sig. (2-tailed)		.307	.079	.823	.320	.242
Cu	Correlation Coefficient	**.446***		.376	.359	.366	**.455***
	Sig. (2-tailed)	.022		.058	.072	.066	.020
Pb	Correlation Coefficient	**.817****	.323		.228	**.529****	.107
	Sig. (2-tailed)	.0005	.108		.263	.005	.604
Ni	Correlation Coefficient	**.704****	.159	**.694****		.336	.371
	Sig. (2-tailed)	.0005	.437	.0005		.093	.062
Cd	Correlation Coefficient	**.692****	**.562****	**.754****	**.441***		-.015
	Sig. (2-tailed)	.0005	.003	.0005	.024		.942
Cr	Correlation Coefficient	**.590****	**.494***	**.492***	**.575****	**.549****	
	Sig. (2-tailed)	.001	.010	.011	.002	.004	
	N	26	26	26	26	26	26

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

6.3.6 Metal concentrations in Dusts from different regions

There are no specific guidelines for metal concentrations in dusts but researchers have used a permissible limit for metals in soil to assess the metal concentrations in dust such as that reported in Egypt (Hassan, 2012) which may have a similar terrain with Nigeria being in the same geographical (Sub-Saharan) region. The metal permissible limits for the Egyptian soil in µg m^{-3} are; Zn-300, Pb-100, Cu-100, Ni-50, Cd-3, and Cr-100: In this study, the mean concentrations of all the 6 target metals were within the Egyptian permissible limits as reported by Hassan (2012).

The mean indoor concentration of Cd found in household dusts in Damaturu was higher than found in UK, Bahrain, and Riyadh and lower than that reported in Cairo and another Bahrain study. The mean concentration of Zn in Damaturu dusts was lower than that obtained in the UK homes, but higher than the other dusts reported. All the remaining metals were lower in the indoor dusts of Damaturu than in those from the other cities. For the outdoor dusts, the results obtained in this study showed lower concentrations than in the other cities (Madany *et al.*, 1994; Akhter and Madany, 1993; Turner and Simmonds, 2006). The mean concentrations of the metals in the indoors/outdoors dusts as reported in other studies are shown in Table 6.9.

Table 6-9 Mean metal concentrations in indoor/outdoor dusts from different Geographical regions

Metal	**Cd**		**Cu**		**Cr**		**Ni**		**Pb**		**Zn**		
Source/city	**in**	**out**	**in**	**out**	**in**	**out**	**in**	**out**	**in**	**out**	**in**	**out**	**Reference**
Bahrain (n=106) μg g^{-1}	72.0	NA	NA	NA	144.7		125.6	NA	697.2	NA	151.8	NA	Madany et al., 1994
UK (n=32) μg g^{-1}	1.2	NA	301	NA	NA	NA	53.1	NA	150	NA	622	NA	Turner and Simmonds, 2006
Bahrain (n=79)) μg g^{-1}	1.9	1.5	NA	NA	11	9.6	10	12	517	742	202	67	Akther,1994
Cairo (n=16) μg g^{-1}	2.71	2.86	122.0	168.2	83.17	85.99	46.66	49.6	254.5	268	103.3	209.3	Hassan, 2012
Damaturu (n=26) mg kg^{-1}	2.26	0.68	16.23	1.66	19.40	2.64	6.51	4.71	26.97	10.77	591.2	170.1	This study
Riyadh μg g^{-1}	0.24				145				389.3		52.3		Ahmed et al., 1993

in =indoor out =outdoor NA= No available data

6.4 Chapter Summary

The ICP/MS analysis revealed the presence of all the target metals in the collected samples including the top soil sample and the SRM although sold commercially only as an organic chemical reference material.

The high metal contents observed in the indoor dusts may be attributed to the release from indoor sources such as newly painted rooms, new furniture, and utensils in the case of the modern buildings, which are the most airtight and are between 19 to 20 years old. Therefore exposure to metals in dust indoors may be greater than that outdoors for occupants of modern homes.

In the traditional buildings, with the exception of Zn, there was not much difference in the indoor/outdoor metal contents. This may be because most of the homes did not have carpets that can release/trap more dust particles and there is not much distinction between the indoors and the outdoors, and they have similar functions. Another reason may be the presence of sources such as old decayed paints, and enamel utensils mostly used by the occupants in both the indoors and the outdoors. The occupant’s exposure to the metal contaminants could therefore be significant outdoors as well as indoors in the traditional homes.

The metal concentrations were higher in the storm dust than the other weather periods, which may be due to the influence of the strong winds blowing and lifting the soil borne elemental residues during storm.

7 EXPOSURE AND HEALTH EFFECTS OF HOUSE DUST

7.1 Introduction

House dust, which may be regarded as a simple nuisance, can play an important role in the exposure of humans to toxic contaminants. It is a complex and heterogeneous matrix composed of a mixture of materials (including pollutants) of diverse characteristics and in varying concentrations: originating from various natural and anthropogenic indoor and outdoor sources. In this chapter, the possible human health risks associated with exposure to dusts are considered by comparison of the types and levels of pollutants determined in this study with those obtained in other studies. The exposure assessment was done by consideration of the available exposure limits defined by agencies such as EU, WHO, US-EPA and exposure limits calculated based on studies in other countries.

Exposure is defined as the contact over time between a pollutant (toxic or irritant) and an individual, a particular sub-group or population. In a given population the degree of exposure and the distribution of possible exposure levels to a particular pollutant can be determined by the period of occurrence and duration of the exposure; the target population (such as infants or the elderly); the individual exposure patterns (such as lifestyle, occupation, diet); and the natural variability of that population (WHO, 2000).

Exposure assessments are undertaken to obtain exposure information for assessing, monitoring, and managing health risks, which may result in the setting of control enforcement or regulatory standards in the various exposure media by Government departments and agencies. In an appropriate exposure assessment, the aspects considered include the sources and pathways of exposure, the magnitude, duration, and frequency of exposure and population variability. People are exposed to contaminants from a range of different sources (industrial materials, agrochemicals, household products and activities, and environmental pollutants). Exposure assessment thus entails measurement of the magnitude, estimating the duration/frequency, or prediction of exposure to a pollutant for individuals, sub-groups or the general population (WHO, 2000).

The pollutants present in the house dust as presented in the earlier chapters in this study, may enter the human body via ingestion, inhalation, or skin contact causing possible health effects (Figure 7.1). In non-occupational settings such as indoors/outdoors of homes, exposures via inhalation and non-dietary ingestion routes is said to be more significant than by dermal contact (Madany *et al.*, 1994; Maertens *et al.*, 2004). The exposure via ingestion of dust and soil is a function of the combination of the amounts of dust and soil ingested daily, and the concentrations of the contaminants in these media (WHO, 2002).

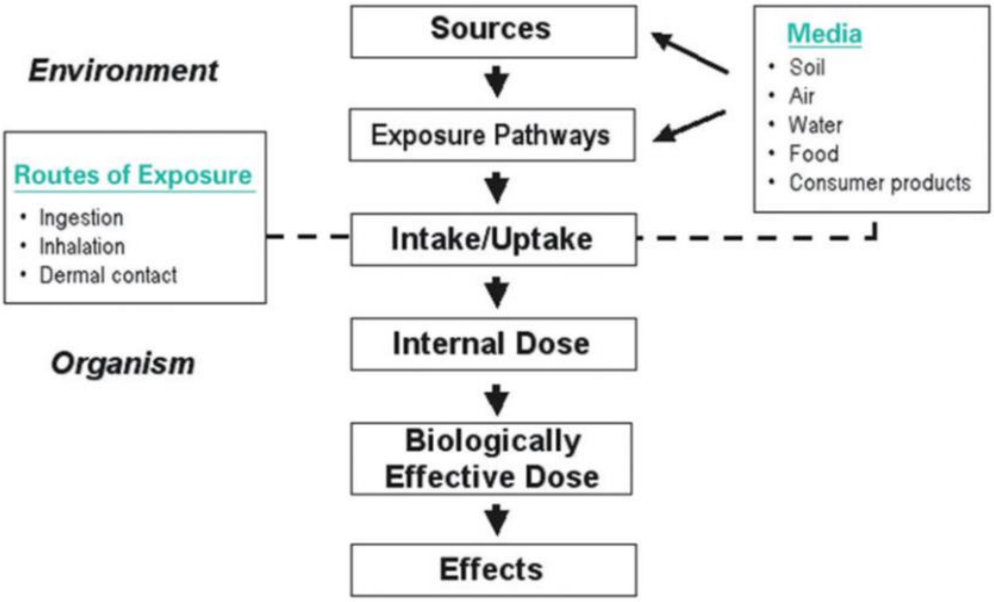


Figure 7.1 Pathways of exposure and effects (Source: WHO-IPCS 2002)

7.2 Health effects of dust constituents

Exposure to the various pollutants in the indoor environment has been associated with numerous adverse health effects including allergenic and immune system effects, respiratory effects, cardiovascular and nervous system effects, irritating effects of the skin and mucous membranes, cancer, and reproductive effects (Hsu *et al*., 2011).

The weather events Harmattan and dust storm are associated with high loadings of dust particles that remain suspended or settled in the environment for long periods. The anthropogenic activities together with the household products also contribute to the increased dust loadings possibly ingested and inhaled. The exposures to the dust particles and the possible pollutants contained in the dust can lead to various health effects such as irritation and allergies especially in children. The results of the physical characterisation of dusts by SEM revealed that house dust is composed of heterogeneous particles of different shapes, sizes, and constituents. The dust particles found contain mixtures of particles including those in the size range considered to be inhalable fractions. These will have originated from different indoor and outdoor sources including; burning of fossil fuel and wood for cooking, personal care products, insecticides, and sand/diatom particles. The PM_{10} and $PM_{2.5}$ are of most concern because they are retained in the airways causing systemic effects to the lungs and the lower respiratory tract. The particles from biomass fuel have been associated with increased respiratory symptoms with the reduction in lung function (Fullerton et al 2008), and the adverse health effects of exposure to the particles based on their sizes have also been reported (Cao *et al.*, 2012).

The spores of several fungal and bacterial species have been observed in varying concentrations in all the settled dust and airborne samples analysed, which indicated their ubiquitous occurrence in the environment. The microbial flora identified in this study are among those reported by other researchers as indoor air pollutants that may cause short term respiratory and inflammatory health effects, which may potentially lead to chronic, long term health impact (Gorny and Dutkiewicz, 2002; Rintala *et al.,* 2010). The bacterial species identified in this study were predominantly gram-positive species with only one gram negative specie identified. The colonies included; rod and long filamentous gram positive *Bacilli*, *Staphylococcus aureus* (gram negative), and unidentified pink and spread colonies.

The majority of substances present in house dusts have not been identified as presenting a potential human health risk. However, some substances in house dust are frequently found to exceed the tolerable daily intake (TDI) values; these include lead, DEHP, arsenic, cadmium, and the sum of PAHs, indicating that they may cause potential health risk with high exposures (Lijzen *et al.*, 2001). The TDI is a toxicological reference value that represents the estimated amount of a substance that humans can ingest daily during their lifetime without a resultant adverse health effect. The intake from dust plus the background exposure (via food and water consumption) is used as a criterion for calculating the potential health risk of pollutants in dust by comparison with the TDI. The mean ingestion of the contaminants (in µg kg^{-1} day^{-1}) was calculated for both adults and children in a study in the Netherlands by using estimated mean ingestion rates of house dust of 50 and 100 mg for adults and children and mean body weights of 70 kg and 15 kg for adults and children respectively (Oomen et al., 2008). The estimates used in the Dutch study were adopted to calculate the mean ingestion rates of the target metals and phthalates investigated in this study.

7.3 Exposure risk assessment

A study in Northeast China reported that ingestion of dust particles by children and adults appears to be the main route of exposure in a study of heavy metals in street dust, followed by dermal contact and that the inhalation of resuspended particles through the mouth and nose is almost negligible (Zheng et. al., 2010). However, absorption through the skin may be of more concern in the case of the organic chemical compounds while the fine particles inhaled may lodge in the lungs, and be absorbed into the bloodstream faster compared to ingestion. Ingestion is particularly important for those exposed repeatedly over a long period (Science communication, 2013).

The exposure to house dust via ingestion occurs most frequently through accidental ingestion of particles that have adhered to food or skin. Children are particularly more prone to this route of exposure due to frequent hand to mouth activities from toys and other objects. It has been reported that some children may ingest up to 10 g of dust per day as against the more commonly applied estimated amounts of 50 to 100 mg of soil and dust ingestion per day and 0.56 mg ingestion by adults (Calabrese and Stanek, 1992).

The people in Damaturu community may ingest particularly high amounts of dust especially during dusty weather events (Harmattan and dust storm) when large amounts of the dust particles are blown indoors by strong winds and may remain suspended (and re-suspended) in the indoor air for days and weeks after the episodes. The dusty events together with household activities such as burning fossil fuels for cooking and electricity generation account for the presence of the dust in the indoors all year round and this settles on internal surfaces, including cooking utensils, food and the body surfaces causing increased human exposure to pollutants present in the dust.

The people living in the modern buildings in Damaturu can have higher exposures indoors than outdoors. They may ingest more than the estimated 100 mg of dust per day by children and 0.56 mg per day by adults because they stay mostly indoors with closed doors and windows open which can allow dust to be blown in by the strong winds which then accumulates indoors. Children might even ingest more than the 10 g of dust per day estimated as the worst-case scenario as suggested by Calabrese and Stanek, (1992). In the traditional buildings in particular children play outdoors near homes or stay indoors and dust loadings in both the indoors/outdoors are always high due to the fact that doors stay open at all times. However, the outdoor soil/dust contaminations are more than in the indoor leading to potentially high exposures especially among children. Further, it is notable that livestock, reptiles (lizards/wall gecko) and rodents move freely around homes where the children play including where they eat in the daytime in the traditional homes in Damaturu.

Exposures to house dust by inhalation mostly occur when dust is suspended or re-suspended by activities such as vacuuming, playing, or walking in the indoors. Dust particles greater than 10 µm are generally trapped by the nose, throat or upper respiratory tract, and the particles less than 2.5 µm may penetrate deep into the respiratory system leading to health effects (Maertens *et al.,* 2004). It has been estimated that young children inhale between 0.15 and 0.34 mg of dust per day, while adults inhale approximately 0.81 mg per day in the USA (Hawley, 1985). In another report, it is estimated that 0.2 mg dust is inhaled by children and 0.8 by adults per day in the Netherlands (Oomen *et al.*, 2008).

The scenarios for inhalation exposure take into account the time spent in various microenvironments; the concentrations of pollutants in the air (including particles available for inhalation), and activity-dependent inhalation volumes. It can be expected that people in Damaturu inhale higher amounts of dust than estimated in the US by Hawley (1985) and in the Netherlands by Oomen et al., (2008) leading to high exposures and health effects. This is as a result of the prolonged presence of dust particles in the air due to the continuous human activities that generate dust particles in addition to the prevailing weather scenarios. However even with the higher concentrations the intake by inhalation is expected to be considerably lower than amounts ingested, noting that the ratio of estimates for intake by ingestion and inhalation in developed countries for young children for example are the order of 1:0.003 (i.e. 100 mg ingested:0.34 mg inhaled).

Exposure to dust may result from dermal absorption due to the skin contact with dust that has settled on furniture, floors, and surfaces of objects as well as peoples' skin. Retained dust particles of ≤ 100–200 µm on contact with the skin may lead to irritation/allergies depending upon the dust constituents. An estimated 28 mg of house dust adsorb to children's hands, while 51 mg adsorb to the hands of adults per day. The various exposure scenarios could lead to a high level of physical contact with dust particles via mouth, eyes, and skin (Hawley, 1985; McDonagh et. al., 2012).

7.4 Exposure and health risk assessment for organic chemicals in house dust

The chemical emissions in both the indoor and outdoor household dusts analysed indicated the presence of organic chemical pollutants in the various samples. The airborne samples collected during household activities also gave an indication of the household activities being major contributing sources to the indoor pollutants that can bring about varying health effects on exposure as was reported in a previous study (Wang *et al.*, 2007b).

There are many organic chemical contaminants reported as being irritants of the eyes and mucous membranes; a mixture of different VOCs at low levels is capable of acting synergistically to elicit neural behaviours (Mølhave et al., 1997; Hirvonen et al., 2004). Hexanal and nonanal are described as dermal and respiratory irritants (Schrapp, K., and Al-Mutairi, N. (2010). An association between phthalates exposure and endocrine disruption and cancer has been reported by several in- vivo studies (Falconer et al., 2006; Rudel and Perovich, 2009; Hwang et al., 2008). In an observational study by Lopez-Carillo et al., (2010), it was reported that indoor biological and chemical agents cause short term respiratory and inflammatory health effects which may be experienced soon after exposure or, possibly, years later and may potentially lead to chronic, long term health impacts (López-Carrillo et al., 2010).

Phthalates have a relatively short half-life in humans and are rapidly cleared (from the human system), but continuous exposures lead to serious health effects due to their toxic effects when present. Exposure to phthalates has been associated with health effects such as obesity, infertility, testicular dysgenesis, asthma and allergies, and breast cancer. Exposure to phthalates and other SVOCs in air and dust over long periods are also attributed to systemic effects such as endocrine disruption and carcinogenesis (Rudel et al., 2010).

The geometric mean concentrations of chemicals obtained in the current study and the estimated values of 100 and 50 mg of dusts ingested by a child and an adult (per day estimated) by Oomen et al. (2008) were used to calculate the estimated mean ingestion of the phthalates. These were 0.011, 0.013, 0.017, and 0.15 μg kg^{-1} d^{-1} for a child and 0.002, 0.003, 0.004 and 0.032 for adults for DEP, DIBP, DBP and DEHP respectively (Table 7.1). Each of the individual chemicals contributes less than 1 % of the TDI values given in Table 7.1. The phthalates ingestion calculated using the maximum concentrations of the phthalates obtained showed the ingestion of the chemicals as 0.02, 0.04, 0.06, and 0.64, μg kg^{-1} d^{-1} for DEP, DIBP, DBP, and DEHP respectively and this also contributed less than 1% of the TDI (Table 7.1). This indicated that ingestion of 100 mg of Damaturu house dust by a child per day or 50 mg by an adult would result in the ingestion of the organic contaminants in amounts below the tolerable daily intake regarded as a safe level that can be ingested daily through a lifetime without causing any health effects.

However, in Damaturu because of the dusty nature of the environment people are likely to ingest more dust per day. For instance, with 1 g of dust ingested per day the percentage of chemical contaminants ingested may reach 6.8 % of the TDI and the worst-case scenario of ingesting 10 g of dust per day may result in the ingestion of phthalates of up to 68 % of the TDI (Table 7.1). Since the TDI refers to intake from all sources, assessment of intake from other sources i.e. food and water are required for a full risk assessment.

Table 7-1 Ingestion rates of phthalates by a child and an adult based on mean and the maximum concentrations of the compounds in house dust compared with TDI

Compound	TDI µg kg^{-1} d^{-1}	Geomean mg kg^{-1}	Ingestion rate µg kg^{-1} d^{-1}	%TDI 100 mg	%TDI 1g	%TDI 10g	Maximum mg kg^{-1}	Ingestion rate µg kg^{-1} d^{-1}	%TDI 100 mg	%TDI 1g	%TDI 10g
Child (15 kg bw)											
DEP	200	1.7	0.011	0.01	0.06	0.6	4	0.02	0.01	0.12	1
DIBP	NA	1.9	0.013	NA	NA	NA	6	0.04	NA	NA	NA
DBP	52	2.5	0.017	0.03	0.33	3	9	0.06	0.11	1.13	11
DEHP	50	22	0.149	0.30	2.97	30	51	0.34	0.68	6.84	68
Adult (70 kg bw)											
DEP	200	1.7	0.002	0.001	0.01	0.1	4	0.01	0.001	0.03	0.26
DIBP	NA	1.9	0.003	NA	NA	NA	6	0.01	NA	NA	NA
DBP	52	2.5	0.004	0.007	0.1	0.7	9	0.01	0.02	0.24	2
DEHP	50	22	0.032	0.064	0.6	6.4	51	0.07	0.15	1.5	15

(Adopted values from Oomen et al., 2008) TDI= is for ingestion of 100 mg dust day^{-1} NA= Not available

7.4.1 Exposure and Health risk assessment for Metals in House Dust

Using the Dutch estimated values by Oomen et al (2008), the calculated ingestion of metal contaminants per 100 mg of dust per day by a child was calculated as 0.020, 0.007, 0.040, 0.087, 0.020, and 0.129, µg kg^{-1} d^{-1} for Cd, Cr, Cu, Pb, Ni, and Zn respectively for the geomean of the metal concentrations obtained in Damataru. Calculated mean ingestion of the metals using the maximum concentrations are 0.05-Cd, 0.17-Cr, 0.33-Cu, 0.37-Pb, 0.11-Ni, and 6.01 µg kg^{-1} d^{-1} of Zn, representing 9.3 %, 3.5, 0.4, 10.3, 1.13 and 1.2 % of the TDI of the quantified metals (Table 7.2).

Using the geomean concentration, in the event that 1 g of house dust is ingested by a child Cd intake will be 40%, Pb 24% and the others are <3% of the TDI. The ingestion of Cd of up to 400% and Pb 240% could result if 10 g of dust per day is ingested. Using the maximum concentration in the dust and an assumed ingestion of 1 g can amount to 93 % for Cd and 104 % for Pb of the TDI, reaching the high amounts of 933 and 1037 % in the worst-case scenario of 10 g dust ingestion (Table 7.2).

In an adult the mean ingestion rates (for geomean and maximum concentrations) for the target metals were 0.004, 0.001, 0.009, 0.019, 0.004, 0.28 µg kg^{-1} d^{-1} and 0.01, 0.04, 0.07, 0.08, 0.02, and 1.29 µg kg^{-1} d^{-1} respectively contributing to 0.5 - 0.8 % and 0.08 - 2.2 % of the TDI. The ingestion of 1 g of dust per day by an adult increases the metals ingestion to between 0.1 - 8.6% (geomean) and 0.84 - 22% (maximum) which rises to 1.0 - 86% and 8.4 - 222% when 10 g of dust is ingested (Table 7.2). Ingestion of dust in large quantities is expected to occur in Damaturu due to the continuous presence of the dust in the atmosphere as well as settling of the dusts on foods and drinks and household utensils. This can result in possible exposures to high amounts of the metal contaminants present in the dust that have the potential to cause various health effects.

The concentrations of the metal pollutants were found to be higher in the indoor samples than the outdoor dusts which may pose a higher risk of exposures due to the longer times people stay indoors, especially children and women.

Acute exposures to metal contaminants can lead to health effects such as nausea, anorexia, vomiting, gastrointestinal abnormalities and dermatitis; chronic exposures can cause systemic poisoning and cancer (Goyer *et al.,* 2004; Silvera and Rohan, 2007). Acute high exposure to Cd can cause acute bronchitis or even chronic disease, such as emphysema or pulmonary fibrosis and lung cancer while chronic exposure over several years to low doses of cadmium may result to kidney tubular dysfunction, osteoporosis, and even cancer. Chromium (III) has no known health effects and no TDI value, but the most serious known health effect is associated with Cr (VI) which is lung cancer (Goyer and Clarkson, 2001; (Bernard, 2008).

One of the causes of contact dermatitis is multiple skin contact with nickel compounds in dust/soil with inhalation exposure leading to possible nickel-induced toxicity in the respiratory tract and immune system (Cempel and Nikel, 2006). The health effects from exposure to Pb include; impairment of motor function and cognitive development and anemia in children. Chronic high levels of exposure to older children may in addition result in seizures, coma and death (Florea and Büsselberg, 2006). Long term treatment or high doses of Zn may provoke a Zn accumulation with subsequent damage to immune efficiency causing toxic effects (Mocchegiani et al. 2001). Copper is essential for good health, however, long-term exposure to copper dust can irritate the nose, mouth, and eyes, and cause headaches, dizziness, nausea, and diarrhoea. When ingested at high levels it causes nausea, vomiting, stomach cramps, or diarrhoea. Intentionally high intakes of copper can cause liver and kidney damage and even death.

Table 7-2 Ingestion rates of metals in a child and an adult based on mean and the maximum concentration of the compounds in house dust compared with the TDI

Compound	TDI µg kg^{-1} d^{-1}	Geomean mg kg^{-1} N=52	Ingestion rate µg kg^{-1} d^{-1}	%TDI 100 mg	%TDI (1g)	%TDI (10g)	Maximum mg kg^{-1}	Ingestion rate µg kg^{-1} d^{-1}	%TDI 100 mg	%TDI (1g)	%TDI (10g)
Child (15 kg bw)											
Cadmium	0.5	3	0.020	4	40	400	7	0.05	9.33	93	933
Chromium (III)	5	1	0.007	0.13	1.33	13	26	0.17	3.47	35	347
Copper	83	6	0.040	0.05	0.48	5	49	0.33	0.39	3.9	39
Lead	3.6	13	0.087	2.41	24	241	56	0.37	10.37	104	1037
Nickel	10	3	0.020	0.20	2	20	17	0.11	1.13	11	113
Zinc	500	194	1.293	0.26	2.6	26	902	6.01	1.20	12	120
Adult (70 kg bw)											
Cadmium	0.5	3	0.004	0.857	8.6	85.7	26	0.04	2.00	20	200
Chromium	5	1	0.001	0.029	0.3	2.9	49	0.07	0.74	7.43	74
Copper	83	6	0.009	0.010	0.1	1.0	56	0.08	0.08	0.84	8.43
Lead	3.6	13	0.019	0.516	5.2	51.6	17	0.02	2.22	22	222
Nickel	10	3	0.004	0.043	0.4	4.3	902	1.29	0.24	2.43	24
Zinc	500	194	0.277	0.055	0.6	5.5	902	1.29	0.26	2.58	26

7.5 REMARKS

The various pollutants investigated in the indoor/outdoor dusts in Damaturu were present in all the samples analysed. The physical characterisation revealed that the house dusts are composed of particles of varying shapes and sizes including the PM_{10}, $PM_{2.5}$ as well as microbial spores known to cause various health effects ranging from irritation and allergies to systemic effects when inhaled.

Generally the metals and the organic chemicals were detected in varying concentrations in all the samples analysed with no distinctive pattern as high concentrations of some of the chemicals were found in the indoors over the outdoors and vice versa. Although the mean calculated intakes were below the TDI using the estimated dust ingestion per day used for risk assessment in the Netherlands, the people in Damaturu have higher amounts of exposure to dusts than the Dutch population because of the geographical and socio-economic factors resulting in higher ingestion of dust. With higher plausible amounts of dust ingestion used for the risk assessment, some of the pollutants exceeded their TDI values. In addition, when other routes of exposure are considered the population may be exposed to the pollutants in considerably higher amounts than the TDI leading to possible health effects. The estimated exposures to metal contaminants in particular indicated potential health risks associated with dust ingestion in Damaturu community. Thus there is an important need for more work to determine the background intakes of the pollutants from other sources such as: food and water, as well as obtain data on the actual amounts of ingestion of dust and inhalation of airborne particulates (PM_{10} and $PM_{2.5}$) by people in Damataru.

8 GENERAL CONCLUSIONS, RECOMMENDATIONS FOR FURTHER WORK

This chapter presents a summary of the methods developed and applied and the results obtained. The strengths and weaknesses of the work are also highlighted along with concluding remarks on the findings and implications of the research. It also presents recommendations for further work.

8.1 Methods for the study of dusts

The selection, development, and application of methods in this study was undertaken in five main stages:

i. The selection and development of methods of dust sampling and analysis was carried out because there is no widely accepted standard method of sampling indoor dusts. Thus, several dust-sampling methods were investigated; collection of settled dusts on spectro-tabs with pin stubs, collection on ceiling boards, and by vacuuming with collection of the settled dust in vacuum cleaner bags. Collection by vacuum cleaner was deemed the most suitable because substantial quantities of the samples were obtained which were then used for the investigation of the dust constituents by different analytical techniques. Further, its previous use in some other studies provided a basis for some comparisons between the Nigerian dusts and those in other countries.

ii. Airborne particles/vapours were sampled to provide some initial data on inhalation exposure to indoor pollutants and to investigate some possible sources of pollutants present in the dust.

iii. A novel method of extracting organic chemical emissions from dust was developed that involved heating of the dusts directly in a micro chamber (µ-CTE^{TM}) and collection of emissions on sampling tubes. The sampled tubes were analysed by TD/GC/MS. This provided a relatively quick analysis to characterise the dust and provide a measure of the amounts of chemicals in the dust that are quite readily available for release.

iv. An initial survey study using the 150 µm fractions of the vacuum cleaner bag dusts from Nigerian homes was conducted involving the application of TD/GC/MS analysis for organic compound analysis, scanning electron microscopy (SEM), inductively coupled plasma-mass spectrometry (ICP-MS) for analysis of metals, and microbiological analysis. Airborne and settled dust samples were collected from UK homes and analysed for comparison. The survey results revealed the presence of a wide range of pollutants in the settled house dusts.

v. The study compared a number of selected constituents (metals, VOCs and SVOCs) in the settled house dusts collected from Damaturu at different periods. The samples investigated include dusts deposited in the indoors/outdoors of homes; during two notable dusty-weather events (Harmattan and Storm) as well as when there was no notable dust event; during domestic activities; and dusts from different types of buildings (modern and traditional homes) as well as inside and outside homes. The standard reference material for house dust (SRM 2585) obtained from the National Institute of Standards (NISTS) USA, as well as topsoil (sand) collected far away from built areas in Damaturu were also analysed. The investigation included the use of a solvent extraction procedure to determine VOCs and SVOCs present in dust that are more strongly bound than the fraction released by thermal extraction and this facilitated comparison with other published work.

8.2 Strengths and limitations of the research work

- The study was successfully undertaken and all the study objectives were addressed, although further work is identified in order to achieve a comprehensive health risk assessment.
- There are no standardized methods of dust sampling and application of the various methods reviewed in reports from previous studies found some to be of limited use in the present study, for example because too little mass was collected for the physical and chemical analysis.

However, some techniques, and notably the use of a vacuum cleaner to collect settled dust, were found appropriate for the study objectives.

- All laboratory analyses were carried out by the researcher and the study provides the first data on the composition of dust and exposure to indoor pollutants in this area of Nigeria.
- The development of thermal extraction of chemicals from dust was found to provide a method to examine weakly bound organics and have some practical advantages over the traditional solvent extraction method (no use of solvent; time saving and reduced possibility of contamination).

However, challenges encountered during the course of the research study limited the scope and depth of the study:

- Lack of data from previous research in the study area (a developing country) limited the comparisons that could be made with other work.
- Exposure assessment primarily adopted the exposure models and acceptable human intake limits developed for the European/USA context as there is no similar data obtained for the developing countries and Africa in particular.
- The study focus was on Damaturu, Nigeria and it involved several trips for sampling (field work). A number of difficulties were encountered such as loss or damage of samples in transit. Microbial airborne samples were cultured at the study area to avoid transport of microbes and problems of maintaining appropriate sample storage conditions.
- The resources of a single researcher as in the present study are a key determiner of the extent of fieldwork, laboratory investigation and data analysis achieved.
- The civic unrest that escalated in the study area during the course of the study (still ongoing) hampered the possibility of collection of more samples.

8.3 Research findings on dust composition and risk to Health

i. The scanning electron micrographs of the UK and Nigerian dust samples revealed that the constituents of all the samples included PM_{10} and sub-PM_{10} particles, which are within the inhalable and respirable size fractions with potential health effects. The elemental spectra of the particles also showed the presence of numerous elements indicating differences in the nature and sources of the particles. Images of Harmattan dust particles for example included those closely resembling crushed diatoms from dried lakes.

ii. The spores of several fungal and bacterial species were found in varying concentrations in all the settled dust and airborne samples that were subjected to microbial analysis. The microbial flora identified are among those reported by other researchers as indoor air pollutants that cause short term respiratory and inflammatory health effects, which may potentially lead to chronic, long term health impact.

iii. The results of the quantified target organic chemicals in weather events samples showed nonanal to have the highest mean concentration in dusts collected during Harmattan and Dust storm periods with DEP and DEHP having the least concentrations during Harmattan and Dust storm. Generally, all the chemicals have higher mean concentrations in the dust collected during the Harmattan period than the other periods. However, the differences were only statistically significant for nonanal and DIBP in Harmattan versus No-event and Harmattan versus Storm dusts.

iv. The results of the chemical analysis of the µ-CTE extracts of dusts from modern and traditional homes showed nonanal as having the highest mean concentration followed by DEHP in the indoors of modern houses. The lowest mean concentration of the investigated chemicals was found to be for DEP in traditional outdoor houses.

v. The chemical concentrations in the solvent extracts of dusts from modern and traditional homes showed DEHP to have the highest concentration followed by DEP in the modern indoor dusts and the chemical with least concentration was DIBP in the traditional homes outdoor dusts.

vi. The mean chemical emissions were higher in the solvent extracts than the thermal extracts while hexanal and limonene were detected only in the thermal extracts. The ratios of the concentrations from the solvent and thermal extracts were in the range of 3 to 15 fold.

vii. Mean chemical concentrations and TVOCs (ng l^{-1}) of airborne samples collected actively (pumped) during household activities showed highest concentrations especially during burning/use of fossil fuels in cooking and electricity generation.

viii. The results of the metal analysis showed that the mean concentration of Zn was higher than the rest of the metals quantified in the indoors of both the modern and traditional homes followed by Pb, Cu, Cd, Ni, and then Cr.

ix. Similar metal concentrations in the indoor and outdoor dusts of the traditional homes indicated the possibility of the metals coming from the same sources. The concentrations in the modern homes were however higher in the indoors indicating more exposure risks indoors than outdoors.

x. The estimated mean concentrations of the metals and phthalates ingested in 100 mg of dust per day were within reported tolerable daily limits. In the event of higher exposures of 1 g to 10 g of dust ingestion per day as may be the case of Damaturu, the mean exposures to some pollutants from the dust ingestion would exceed the TDI. These indicate that high exposures to pollutants in dust are associated with potential health effects. Thus, combined with other sources of pollution intake may lead to high exposures.

xi. Results obtained in this study established that house dusts as well as the airborne particulates in Damaturu contain a host of pollutants, which can cause various health effects ranging from irritation to systemic effects on exposure.

8.4 Concluding Remarks

- The development and application of the µ-CTE method of thermal extraction of VOCs and SVOCs from dusts followed by TD/GC/MS analysis offered a relatively rapid and repeatable method to compare the most available fractions of these compounds.
- The investigations of the constituents of household dusts in Damaturu revealed the presence of microbial, chemical, and metal pollutants that are capable of causing health effects such as irritation, allergic reactions like asthma, systemic effects, endocrine disruption, and cancer on exposure to dusts in the indoor/outdoor environments.
- The calculated estimate of daily ingestion rate indicated possible high exposures to pollutants in dust above the TDI because the people live in a continuous dusty environment during both day and night. Along with other sources (especially food and water) this may lead to high exposures to the various pollutants, notably some phthalates and heavy metals.
- This is the first ever report of its kind undertaken in the Damaturu community and all comments and or suggestions are the researcher’s personal opinions/experiences.

8.5 Recommendations for Further Work

- Communication with the local communities about the high dust loads, potential exposure routes and possible health effects through local media and production of leaflets. Informing and educating the communities about dust and the associated pollutants, including potential exposure via drinking water and the amounts ingested.
- Informing the communities of simple tips for reducing dust exposure by adopting such habits as covering their cooking utensils and foods, and cooking in roofed areas to reduce dust deposition on food items.
- Introduction of the benefits of regular hand washing, sweeping of hard surfaces, as well as wiping/mopping of surfaces and utensils in order to reduce exposure to dust and contaminants.

- There is a need for pollution mapping of the north-eastern region involving dust sampling, taking note of the possible variations such as seasonal, socio-economic, and environmental factors in order to obtain enough data for a comprehensive region-specific exposure and health risk assessment. This should involve the setting up of a network of continuous PM monitors in strategic positions within the community.
- There is need to refine the exposure risk assessment by determining the amount of dust ingested daily by direct ingestion and from the background sources by quantitatively analysing the dust content in food, water and the amount of dust that may be present on the hands especially of children. In addition, to determine the average body weight of children and adults living in the region as well as confirm appropriate TDI values.
- There is need for work on a broad constituent analysis of other pollutants in the house dusts such as Polyaromatic hydrocarbons (PAHs), brominated flame-retardants, and pesticides.
- More work needs to be carried on the strong sources of air pollutants, notably generators and cooking by biofuels, as well as investigation of time spent indoors by adults and children.
- There is the need for development of dust extraction methods pertaining to biologically available fractions of total organics/metal in blood, urine etc.
- Need for better health services: so that relevant data for the whole population can be obtained and with proper record keeping for determining the prevalence of health effects and enable further comparison between the incidence of diseases and weather events.
- Need for an extensive collection of socio-demographic data through questionnaires and interviews that can be used to inform development of policies/actions for controlling the exposures to pollutants in dust and reducing the health hazards posed.

- Need for questionnaire study to examine the incidence of perceived ailments during different seasons using a validated questionnaire and applied in a study designed on a statistical basis.
- Need for standard methods for sampling and analysis of dust. There is a lot of research work going on and several studies have reported on the characteristics of house dust. However, given the range of strategies and methods used it is difficult to compare results from different studies. Further there are no internationally accepted guidelines/standards for dust exposure limits perhaps in part because of the variations in the house dust constituents in the indoors environment in different countries and geo-political regions. Therefore, the focus should be on establishing an agreed international method for the sampling and analysis of dust applied by researchers in their own countries / regions to provide comparative data for exposure risk assessment.
- An international survey on household dust exposures and health risk assessment taking into consideration the socio-economic, demographic, national, geographic, and climatic factors conducted in order to collect enough baseline data that may enable standard setting in different regions.

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APPENDICES

APPENDIX A

Appendix A **Various Sampling Techniques**

Plate A-1 Dust collection on petri dishes

Plate A-2 Collection of settled dust on a ceiling board placed on a shelf in a local kitchen

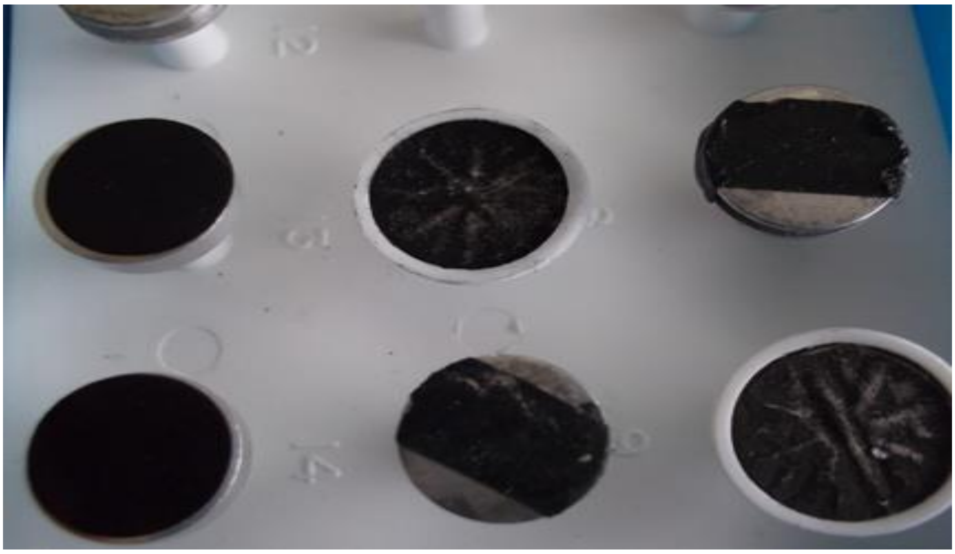


Plate A-3 Collected settled dust on Carbon spectrotabs mounted on pin stubs

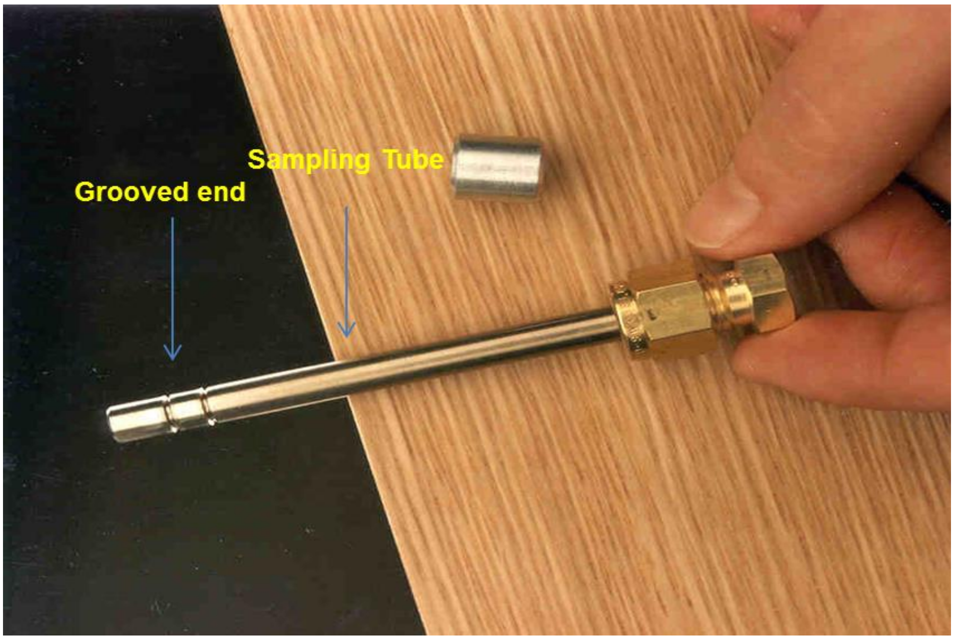


Plate A-4 Collection of airborne vapours/emissions with sorbent tube

Plate A-5 Counting ultrafine particles during cooking with fire wood

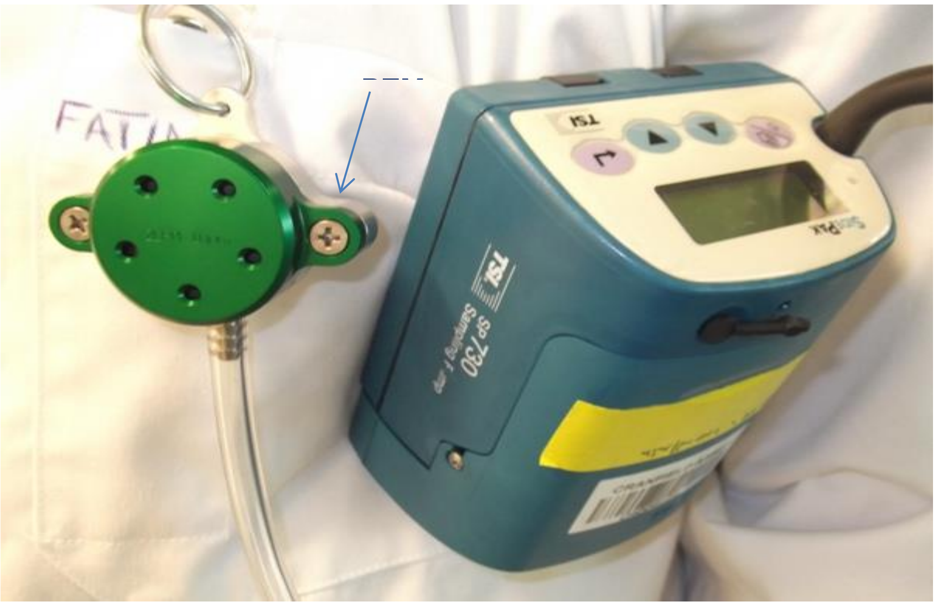


Plate A-6 Collection of airborne particles with PEM with using sidepak pump

Plate A-7 Collection of airborne microbial spores with Burkard biological sampler

Plate A-8 Dust sampling with vacuum cleaner

Plate A-9 Dust collection using Frisbee dust deposit gauge

Plate A-10 Bucket gauge device

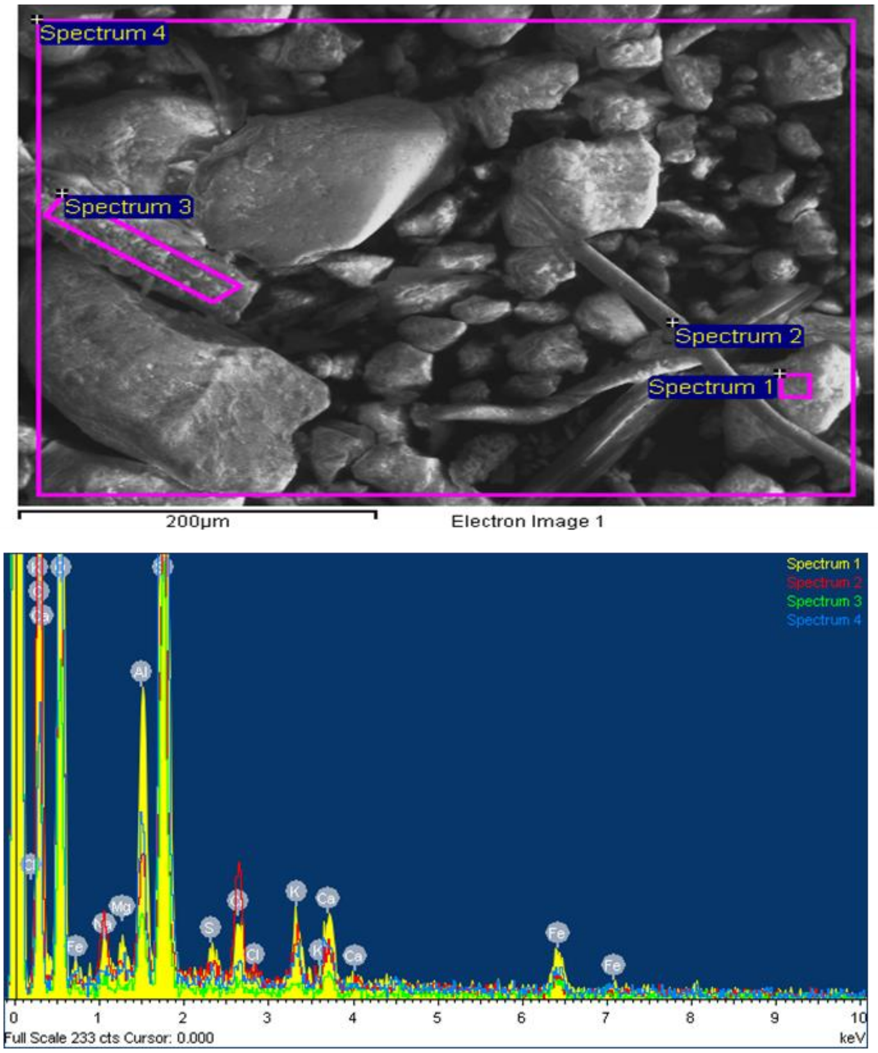
Appendix B **Scanning Electron microscopy of settled dust samples of Nigerian and UK homes**

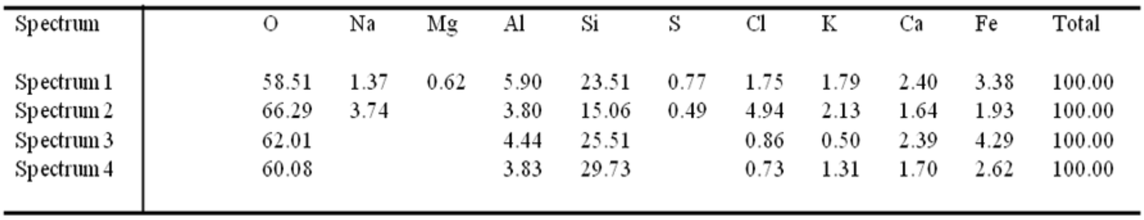
The scanning electron micrograms of both the Nigerian and UK dust samples revealed that the particle sizes include the respirable fractions which have the potential of passing through the respiratory tract and potentially cause health problems. The element spectra also showed the presence of numerous elements of various origins. The constituents of all the samples included PM_{10} and sub-PM_{10} particles considered as the respirable fractions thus, can potentially cause health hazards as described by Horwell et al., (2003).

B.1 SEM results of Nigerian Dusts

B.1.1 SEM of AH dust

The Nigerian dusts AH showed finer (respirable) particles than the other samples. Filamentous parcels were seen in samples AH, FHO and YH. A filament particle in MH dust is shown as segmented. LH dust contains a spongy (mass) shape. Rectangular, sharp edged particles (Plate B1) were more conspicuous containing mainly oxygen, aluminium, and silicon (spectrum 1).





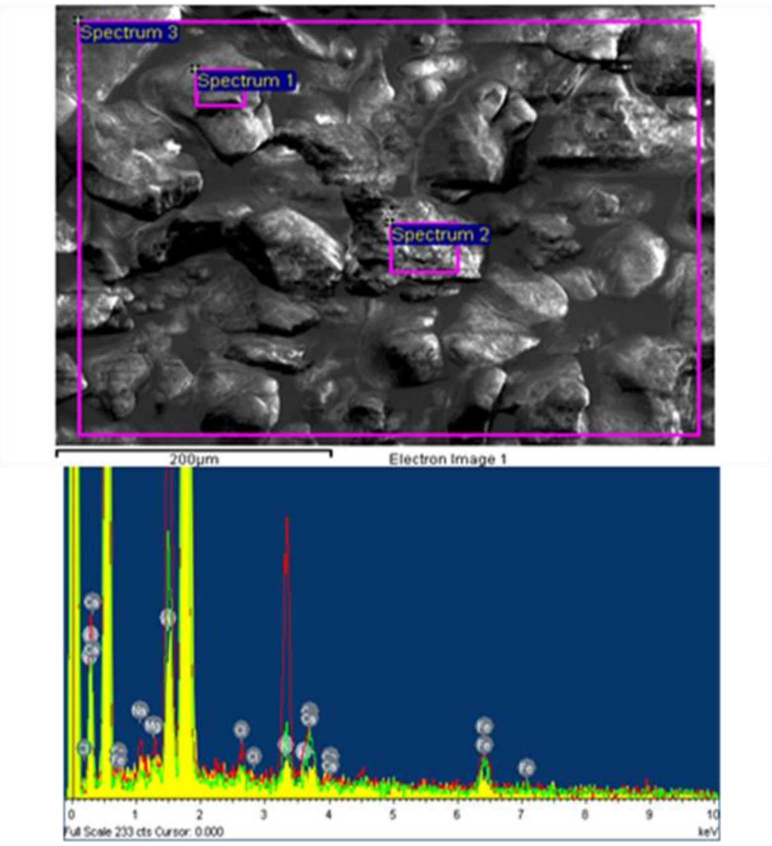
Spectrum	O	Na	Mg	Al	Si	S	Cl	K	Ca	Fe	Total
Spectrum 1	58.51	1.37	0.62	5.90	23.51	0.77	1.75	1.79	2.40	3.38	100.00
Spectrum 2	66.29	3.74		3.80	15.06	0.49	4.94	2.13	1.64	1.93	100.00
Spectrum 3	62.01			4.44	25.51		0.86	0.50	2.39	4.29	100.00
Spectrum 4	60.08			3.83	29.73		0.73	1.31	1.70	2.62	100.00

Plate B-1 Micrograph and elemental spectra of AH dust

B.1.2 SEM Result of FH dust

The elemental content of spectrum 1 (Plate B.2) showed a similarity between the particles; as did their shapes. The long cylindrical particle (Spectrum 2) composed of 9 elements resembles a human hair strand. The rectangular multifaceted particle (Spectrum 3) dominated the FH dust sample resembling sand particles.

Plate 4- SEM picture and elemental constituents of particles in FH dust-indoor



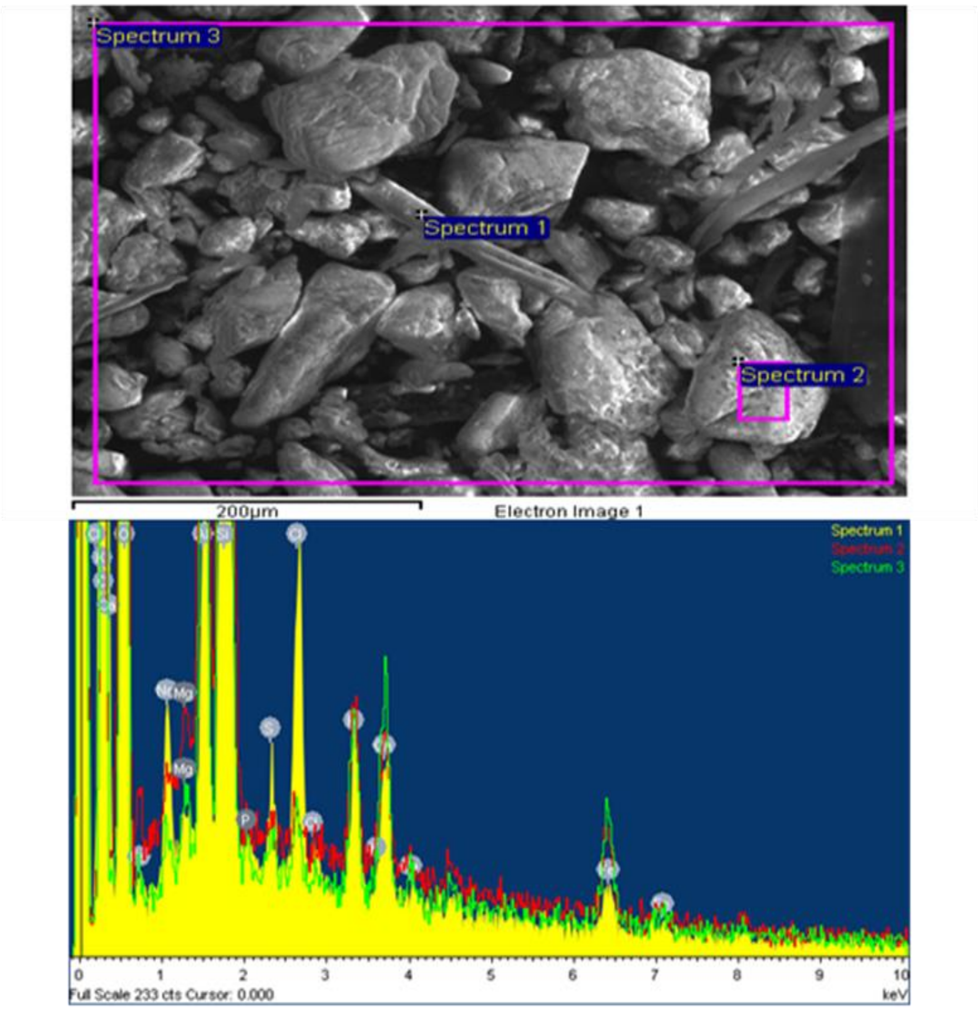
Spectrum	O	Na	Mg	Al	Si	Cl	K	Ca	Fe	Total
Spectrum 1	62.96			1.29	35.34		0.40			100.00
Spectrum 2	55.18	0.95	0.47	9.29	23.45	0.55	5.81	1.10	3.20	100.00
Spectrum 3	58.12			4.69	31.27		1.73	1.78	2.41	100.00

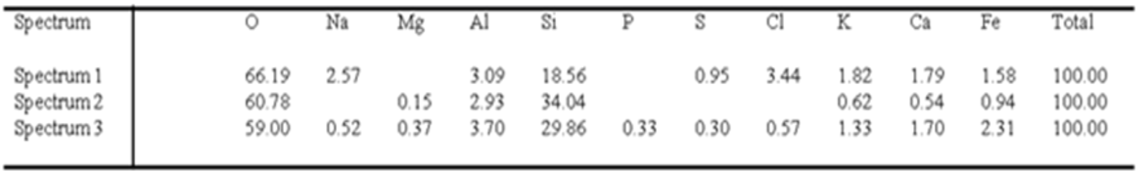
Plate B-2 Micrograph and elemental spectra of FH dust

B.1.3 SEM Result of LH dust

The long cylindrical particle in spectrum 1 of Plate B.3 and the one in AH dust (Plate B.2) have similar composition. The amorphous particle in spectrum 2 has similar composition with spectrum 1 in FH dust (plate B.1) but contains lower silicon than the former.

Plate 6- SEM picture and elemental constituents of particles in LH dust-indoor





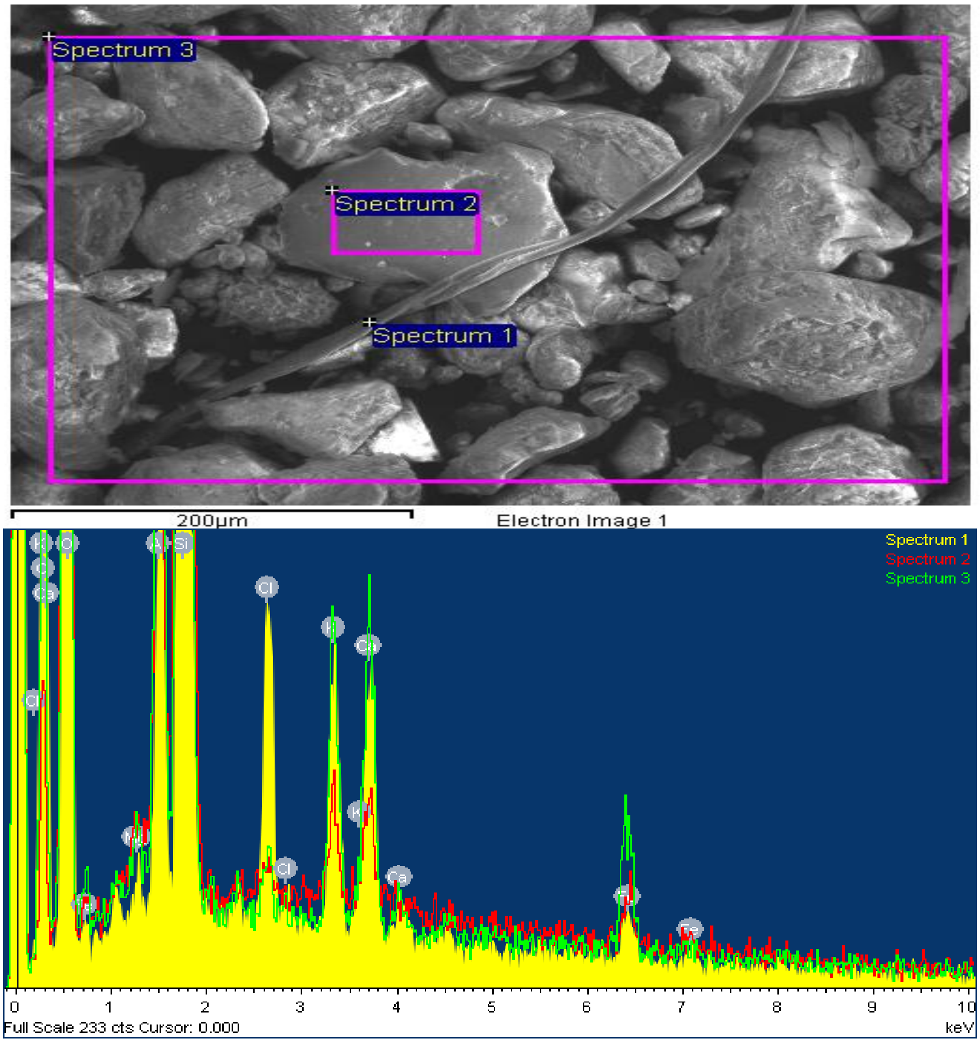
Spectrum	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Total
Spectrum 1	66.19	2.57		3.09	18.56		0.95	3.44	1.82	1.79	1.58	100.00
Spectrum 2	60.78		0.15	2.93	34.04				0.62	0.54	0.94	100.00
Spectrum 3	59.00	0.52	0.37	3.70	29.86	0.33	0.30	0.57	1.33	1.70	2.31	100.00

Plate B-3 Micrograph and elemental spectra of LH dust

B.1.4 SEM Result of MH dust

In YH dust there was the presence of a long segmented fibre in spectrum 1 (plate B.4). All the 3 spectra were found to be composed of similar elements.

The particles in LH dust sample contain more titanium, calcium, and iron than in the other dust samples (Plate B.4).

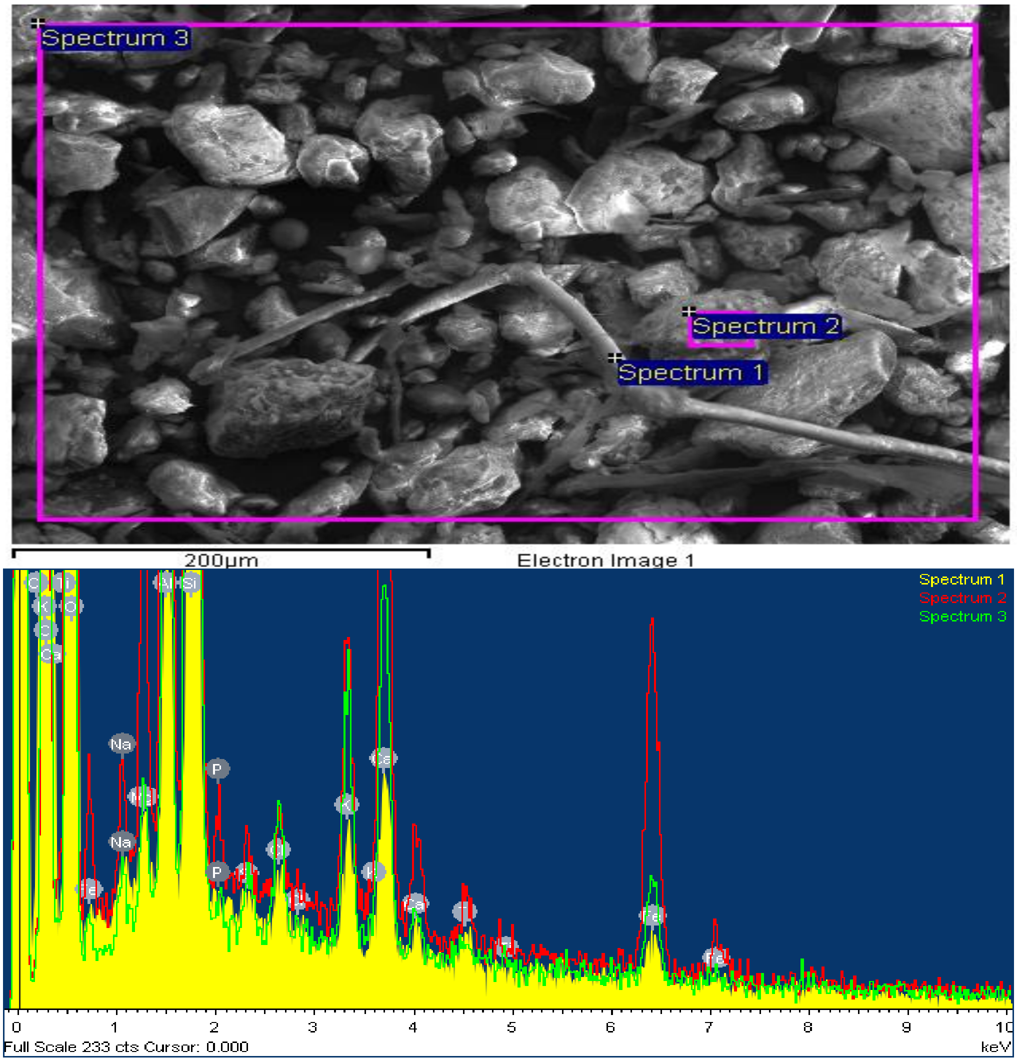


Spectrum	O	Mg	Al	Si	Cl	K	Ca	Fe	Total
Spectrum 1	61.21	0.38	3.45	23.63	3.43	3.10	3.19	1.60	100.00
Spectrum 2	53.40		1.39	43.55		0.50	0.53	0.63	100.00
Spectrum 3	57.54	0.26	4.26	31.02	0.39	1.91	2.15	2.47	100.00

Plate B-4 Micrograph and elemental spectra of MH dust

B.1.5 SEM Result of YH dust

The long fibre-like particle in spectrum 1 (Plate B.5) has similar shape and composition with the others seen in the other dust samples. The particle in Spectrum 3 resembles that in Spectrum 3 in YH dust.

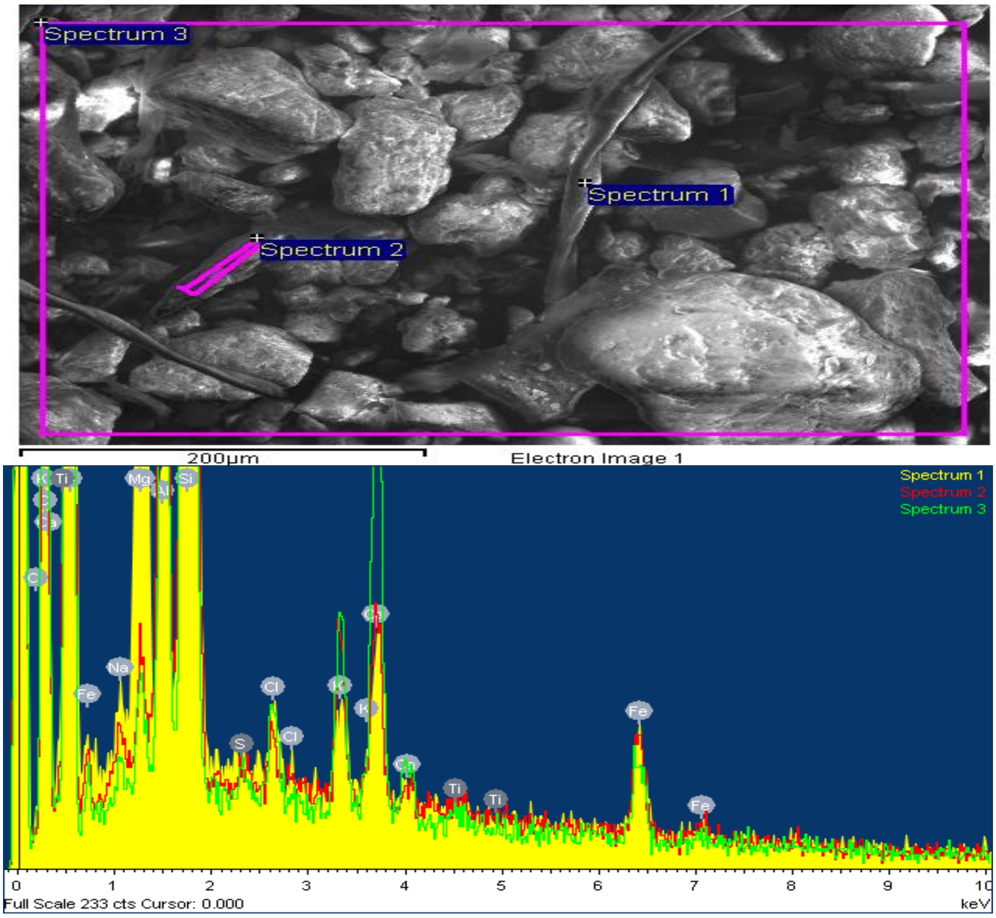


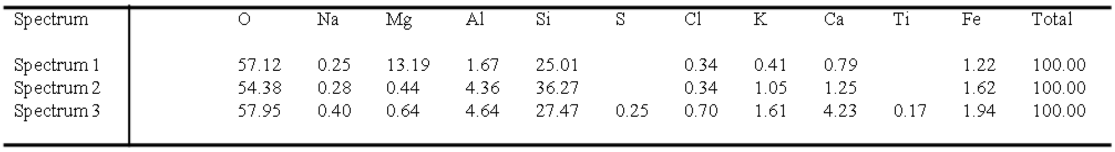
Spectrum	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Total
Spectrum 1	76.18		0.81	3.36	12.71		0.26	0.66	1.44	2.37	0.65	1.57	100.00
Spectrum 2	60.19	0.68	1.37	8.38	18.10	0.35	0.21	0.32	1.24	4.26	0.37	4.52	100.00
Spectrum 3	59.70	0.67	0.81	4.79	24.09	0.26	0.42	1.02	2.24	3.36	0.14	2.49	100.00

Plate B. 5 SEM Micrograph and elemental spectra of YH dust

B.1.6 SEM Result of FH-outdoor dust

The outdoor dust sampled from the frontage of home FH with the spectra dominated by oxygen, aluminium, and silicon (Plate B.5). Rectangular particulates with sharp edge and of sizes <200 µm particles were seen in Spectrum 1 (Plate B.6).





Spectrum	O	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe	Total
Spectrum 1	57.12	0.25	13.19	1.67	25.01		0.34	0.41	0.79		1.22	100.00
Spectrum 2	54.38	0.28	0.44	4.36	36.27		0.34	1.05	1.25		1.62	100.00
Spectrum 3	57.95	0.40	0.64	4.64	27.47	0.25	0.70	1.61	4.23	0.17	1.94	100.00

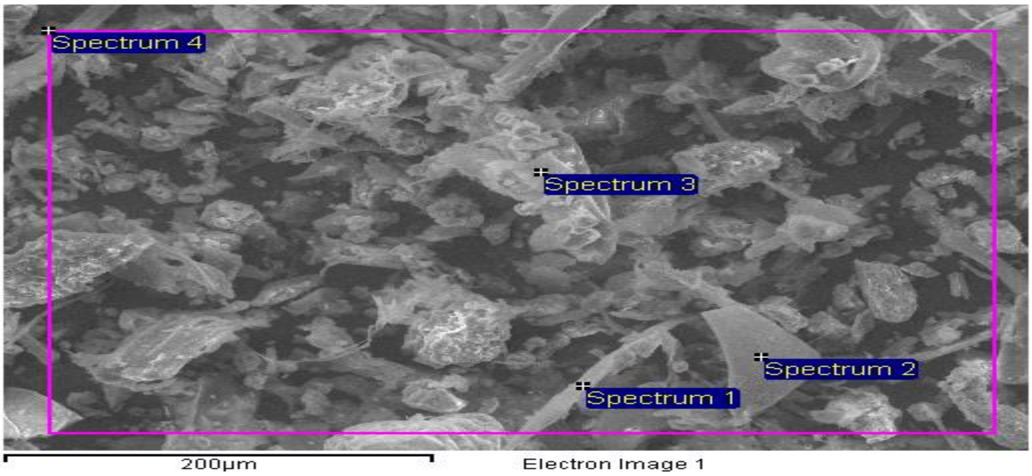
Plate B-6 Micrograph and elemental spectra of FH -outdoor dust

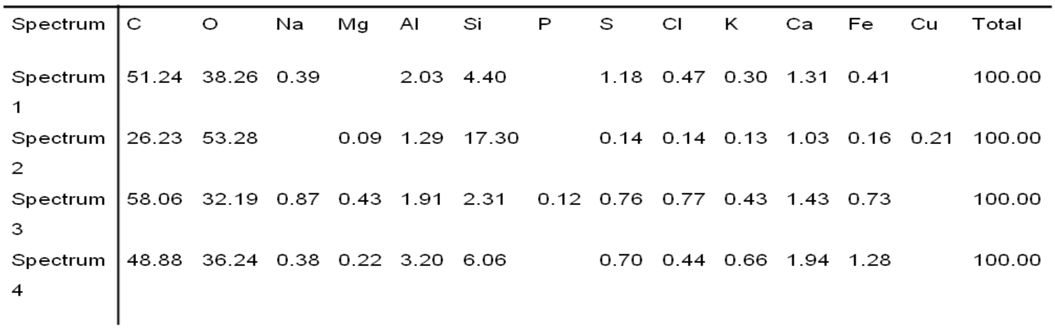
B.2 SEM Results of UK Indoor/outdoor settled Dusts

The images of UK samples are mostly amorphous, puffy, sheet-like and clustered.

B.2.1 SEM Result of DH dust

The particles in DH dust contain elements that were absent in Nigerian dusts, indicating the difference in nature and sources of the particles. The UK dust DH particles contain carbon and potassium in all the dominant spectra, phosphorus in Spectrum 3, and copper in Spectrum 2 (Plate B.7). These elements were not present in significant amounts in the Nigerian dusts.



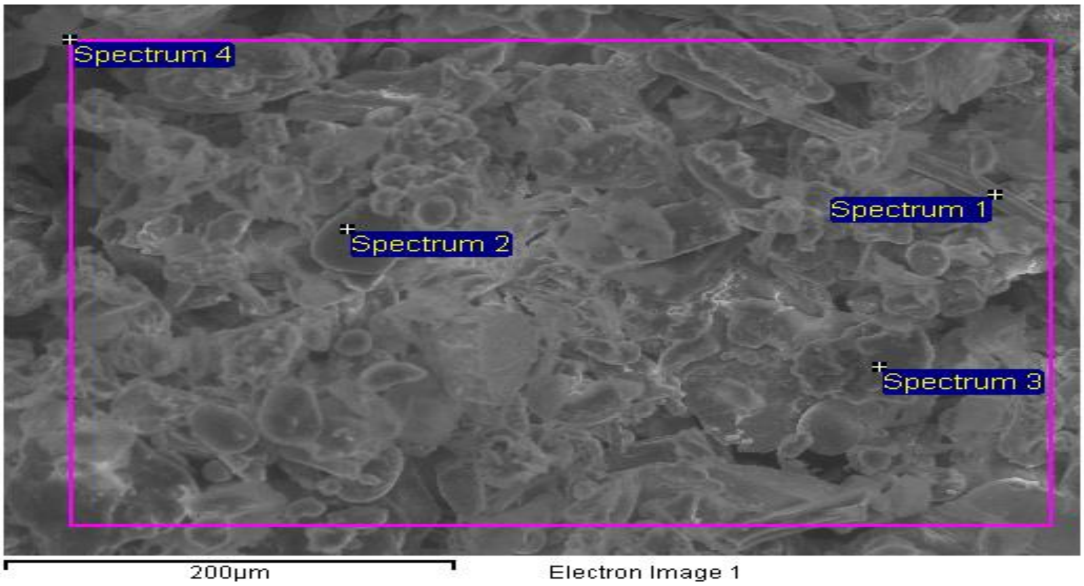


Spectrum	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Cu	Total
Spectrum 1	51.24	38.26	0.39		2.03	4.40		1.18	0.47	0.30	1.31	0.41		100.00
Spectrum 2	26.23	53.28		0.09	1.29	17.30		0.14	0.14	0.13	1.03	0.16	0.21	100.00
Spectrum 3	58.06	32.19	0.87	0.43	1.91	2.31	0.12	0.76	0.77	0.43	1.43	0.73		100.00
Spectrum 4	48.88	36.24	0.38	0.22	3.20	6.06		0.70	0.44	0.66	1.94	1.28		100.00

Plate B-7 Micrograph and elemental spectra of DH dust

B.2.2 SEM Result of AKH Dust

AKH dust has a sheet-like appearance with particles clustered together (plate B.8). Particles in Spectrum 1 and 2 contain nitrogen that is absent in the other particles.

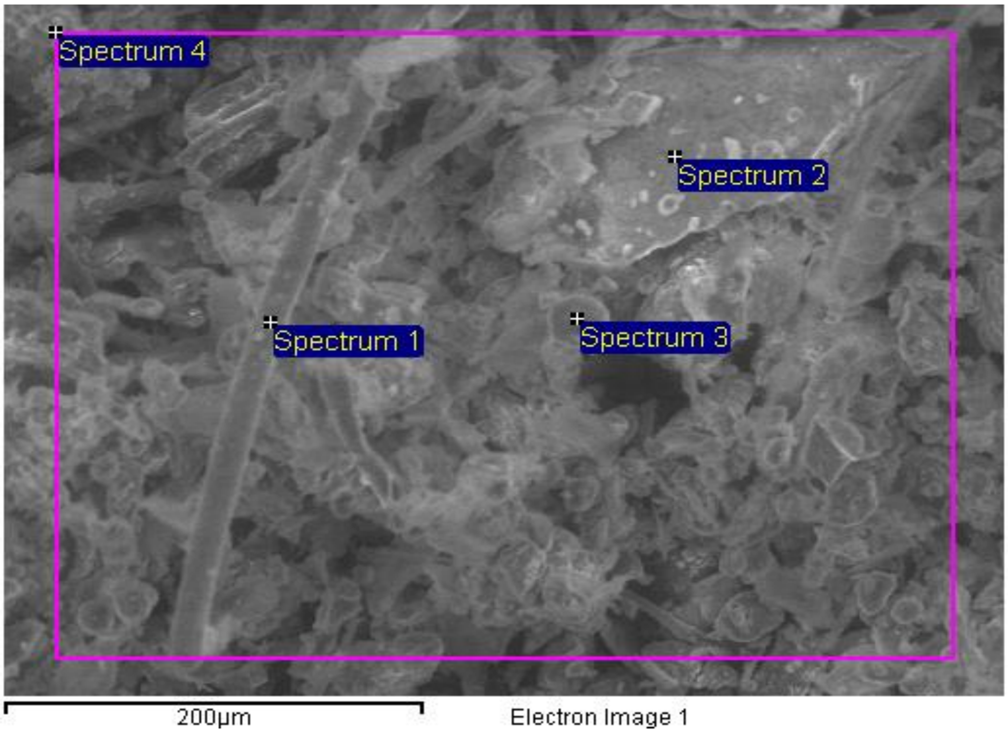


Spectrum	C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe
1	41.30	9.22	35.33	1.20	0.16	0.76	2.41	0.34	0.85	2.13	0.78	4.82	0.72
2	53.01		38.50	2.34	0.05	0.25	0.74		0.44	1.97	0.53	2.17	
3	52.03		37.62	3.00		0.23	0.79		0.42	2.19	0.71	2.78	0.24
4	37.39	7.06	40.95	0.88	0.15	0.60	2.92		0.53	1.19	0.51	7.34	0.47

Plate B-8 Micrograph and elemental spectra of AKH dust

B.2.3 SEM Result of VH Dust

The particle in spectrum 3 is composed of 13 elements, having a larger amount of carbon (Plate B.9). The long filamentous particle may be a hair strand.

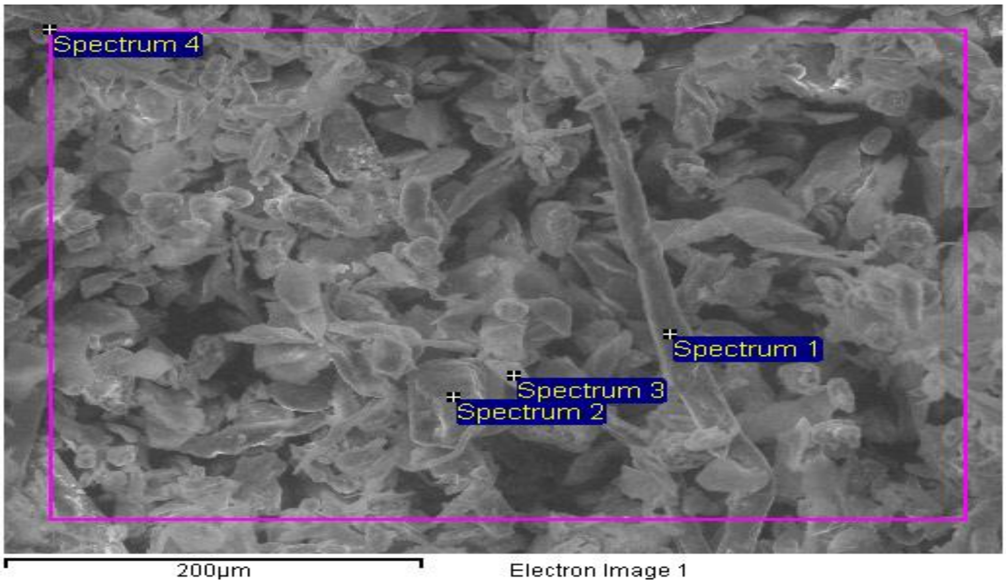


Spectrum	C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Total
Spectrum 1	45.53	16.59	31.11		0.36	0.41	1.59		2.91	0.19	0.14	0.81	0.36	100.00
Spectrum 2	23.20		45.44		0.41	0.52	28.36		0.24	0.18	0.14	0.79	0.72	100.00
Spectrum 3	42.38	7.27	40.37	0.72	0.82	0.99	3.59	0.14	0.64	0.70	0.39	1.30	0.69	100.00
Spectrum 4	37.71	7.74	38.18	0.33	1.01	1.20	7.81		0.93	0.97	0.41	2.15	1.56	100.00

Plate B-9 Micrograph and elemental spectra of VH dust

B.2.4 SEM Result of FH-UK Dust

The particles in FH-UK dust are mainly composed of carbon and oxygen with little amount of silica compared with the other UK dust samples as shown in Plate B.10.

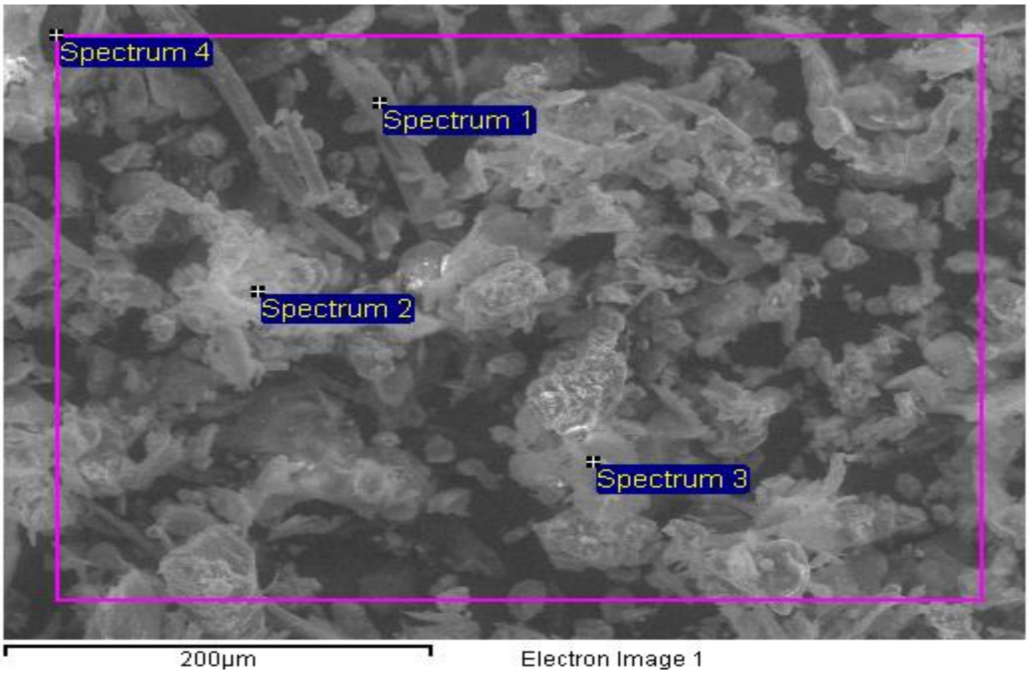


Spectrum	C	N	O	Na	Mg	Al	Si	S	Cl	K	Ca	Fe	Total
Spectrum 1	58.53		37.74	0.29		0.38	0.77	0.23	0.65	0.31	1.10		100.00
Spectrum 2	69.99		22.59	0.36		1.62	2.40	0.35	0.59	0.82	1.28		100.00
Spectrum 3	47.90	7.33	36.72	1.40	0.18	0.58	1.17	0.57	1.48	1.04	1.63		100.00
Spectrum 4	43.91	9.09	35.69	1.04	0.21	0.88	2.14	0.72	1.51	0.94	3.35	0.51	100.00

Plate B-10 Micrograph and elemental spectra of FH-UK dust

B.2.5 SEM Result of SH Dust

The element constituents obtained from the various spectra in SH dust indicated that it is composed of particles clustered together as shown in the other UK samples (Plate B.11).

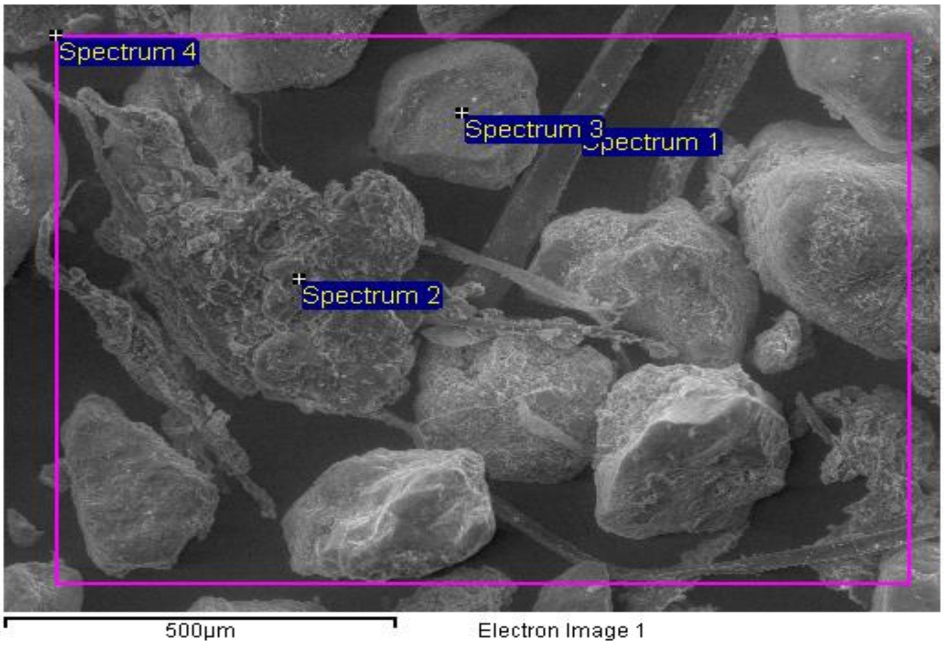


Spectrum	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Total
Spectrum 1	44.78	42.54	0.68	0.11	0.40	1.98	3.46	0.27	0.28	0.40	4.56	0.24	0.29	100.00
Spectrum 2	46.20	40.47	0.41	0.21	1.22	5.94	0.15	0.56	0.65	0.66	1.49	0.31	1.74	100.00
Spectrum 3	48.15	37.90	0.68	0.21	2.06	4.63	0.13	0.64	0.81	0.79	2.22	0.19	1.59	100.00
Spectrum 4	51.19	37.80	0.46	0.14	1.06	4.34	0.16	0.68	0.57	0.53	1.97	0.30	0.80	100.00

Plate B-11 Micrograph and elemental spectra of SH Dust

B.2.6 SEM Result of UK outdoor Dust

The outdoor sample contains mainly sand and fragments of dead leaves showing a very large carbon content (Plate B.12). Spectrum 1 has an elemental composition similar to that of hair strand.

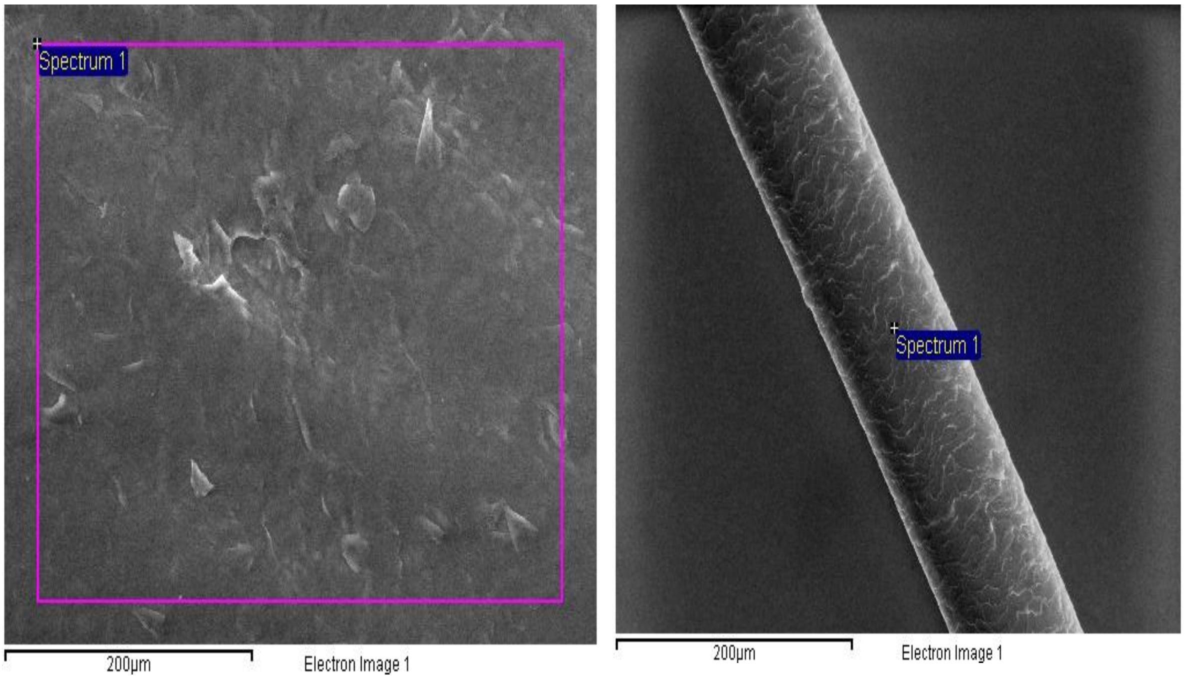


Spectrum	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Total
Spectrum 1	57.95	36.05			0.46	4.65				0.12	0.31		0.46	100.00
Spectrum 2	45.77	37.56	2.35	0.39	1.15	6.91	0.32	0.72	0.39	1.07	1.61	0.40	1.36	100.00
Spectrum 3	18.02	48.17			0.90	30.25				0.21	0.39		2.06	100.00
Spectrum 4	35.62	44.30	0.45		1.31	14.29		0.24		0.38	1.79		1.63	100.00

Plate B-12 Micrograph and elemental spectra of UK-outdoor Dust

B.3 SEM Result of Skin and Hair Strand

The human skin flakes and a hair strand analysed as known samples for a comparison with the particle fractions of the indoor and outdoor dusts. Carbon is the dominant element in both samples (Plate B13).The flake of human skin is composed of mainly carbon followed by oxygen and nitrogen with less than 1% each of sodium, silicon, sulphur, chlorine, and potassium. Human hair also had carbon as the main constituent followed by oxygen, then nitrogen and sulphur, with trace amounts of aluminium and calcium as shown in Plate B.13.



Spectrum	C	N	O	Na	Si	S	Cl	K	Total
Spectrum 1	58.7	9.7	29.2	0.3	0.1	0.8	0.4	0.5	100.

Spectrum	C	N	O	Al	S	Ca	Total
Spectrum 1	67.64	5.69	20.82	0.16	5.18	0.50	100.0

Plate B. 13 Micrograph and elemental spectra of skin flake (left) and human hair strand (right).

Appendix C

C.1 Main Peaks in chromatograms of analyses of household Dusts

Table C 1 high peak-chemicals present in dust samples other than the target chemicals

high peak-chemicals present in dust samples other than the target chemicals and their retention time																				
Compound	Ret.Time (min^{-1})	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D11	D12	D13	D14	D15	D16	D17	D18	D19
Heptanal	25.4	+	+	-	-	+	+	+	-	+	+	+	+	-	+	+	-	-	+	+
Hexanoic acid	28.6	-	-	-	-	+	-	-	-	-	+	-	-	-	-	+	+	-	-	-
α-methyl styrene	29.4	+	+	+	-	-	+	+	+	+	+	+	-	-	+	-	+	-	+	-
Octanal	30. 5	-	-	-	+	-	-	+	+	+	+	-	-	-	+	+	+	+	-	-
Furan	31	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-	+	+
Cyclopentasiloxane	36.4	+										+	-	-	-	-	-	-	-	-
Octanoic acid	37	-	-	-	+	+	+	-	-	+	+	-	-	-	+	-	+	+	_	+
Naphthalene	37.4	+	+	+	+	+	+	+	+	+	-	+	+	-	+	-	+	-	+	+
Nonanoic acid	39	-	+	-	+	+	+	-	-	-	-	-	-	+	-	+	-	-	-	-
2-undecene	44.2	-	-	-	+	-	+	+	-	+	-	-	+	-	+	+	-	-	+	-
2-m,3-e,heptane	43						-	-	-	-	-	-	-	-	-	-	-	-	+	-
Benzoic acid	46.9						+		+								-	+	-	+
Heptadecane	49.5	-	-	-	+	+	-	-	-	-	-	+				+	-	-	+	+
Phenenthrene	50.8	-	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-
Heincosane	51	-	-	-	+	+	+	-	-	-	-	-	-	+	+	+	-	-	-	+
S-tetra-acyl-ester	52.3	-	-	-	-	+						-	-	-	-	+	-	-	-	-

+ = present in dust sample - =Not present in dust sample D1-D26 = indoor dusts D27-D=outdoor dusts

		Other high peak-chemicals present in dust samples																	
Compound	Ret.Time (min^{-1})	D20	D21	D22	D23	D24	D25	D26	D27	D28	D29	D30	D31	D32	D33	D34	D35	D36	D37
Heptanal	25.4	+	+	+	-	+	+	+	-	+	-	+	-	+	-	-	+	+	+
Hexanoic acid	28.6	-	-	-	-	-	-	-	-	-	-	-	+	+	-	-	+	-	-
α-methyl styrene	29.4	-	-	-	+	-	-	-	-	-	-	-	+	-	+	+	+	-	-
Octanal	30. 5	-	-	-	-	-	+	+	-	-	-	-	-	+	+	-	+	+	-
Furan	31	-	-	-	-	+	+	-	-	-	-	-	-	-	-	+	-	-	-
Cyclopentasiloxane	36.46	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Octanoic acid	37	+	+	+	+	+	+	+	-	-	+	+	-	+	-	-	-	+	-
Naphthalene	37.43	+	+	-	+	-	-	+	-	+	+	-	-	+	-	-	-	+	-
Nonanoic acid	39	-	-	-	-	-	-	-	-	-	-	-	-	+	+	-	-	-	-
2-undecenal	44.2	-	-	-	-	-	+	-	-	+	-	-	-	-	-	-	+	+	+
Benzoic acid	46.98	-	-	-	+	-	+	-	-	-	-	-	-	-	-	-	-	+	-
Heptadecane	49.5	+	+	-	+	+	-	-	-	+	+	+	-	+	-	-	+	-	+
Phenenthrene	50.87	+	+	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-
Heincosane	51	-		-	+	-	-	-	+	+	-	+	-	-	-	+	+	-	-
S-tetra-acyl-ester	52.3	-	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

+ = present in dust sample - =Not present in dust sample D1-D26 = indoor dusts D27-D=outdoor dusts

Other high peak-chemicals present in dust samples																		
Compound	RT(min^{-1})	D38	D39	D40	D41	D42	D43	D44	D45	D46	D47	D48	D49	D50	D51	D52	HD	DS
Heptanal	25.4 min	-	-	+	+	-	+	+	+	+	-	-	-	+	+	+	-	-
Hexanoic acid	28.6min	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-
α-methyl styrene	29.4 min	-	+	+	+	-	-	+	-	-	-	+	+	-	-	-	-	-
Octanal	30. 5min	+	+	+	-	-	-	-	+	+	-	-	-	+	-	-	+	-
Furan	31 min	-	+	-	-	-	-	-	-	-	-	-	-	+	-	-	-	-
Cyclopentasiloxane	36.6 min	-	-	-	-	-	-	-	-	-	-	+	+	-	-	-	-	+
Octanoic acid	37 min	-	-	-	-	-	-	-	+	-	-	-	-	-	+	+	-	-
Naphthalene	37.43min	-	-	+	-	-	+	-	-	-	+	-	-	-	-	-	-	-
Nonanoic acid	39 min	-	+	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-
2-undecenal	44.2 min	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-	+	-
Benzoic acid	46.9 min	-	-	-	-	-	-	-	-	+	+	-	-	+	-	+	+	-
Heptadecane	49.5 min	-	-	-	+	-	+	+	-	-	-	+	+	+	-	+	+	-
Phenenthrene	50.87 min	-	-	-	-	-	-	-	-	-	+	+	-	-	-	-	+	-
Heincosane	51 min	-	+	+	-	+	-	-	+	-	-	-	-	-	-	-	-	+
S-tetra-acyl-ester	52.3 min	-	+	-	+	-	-	-	-	-	-	-	-	-	-	-	-	-

RT= retention time + = present in dust sample - =Not present in dust sample D1-D26 = indoor dusts D27-D=outdoor dusts HD-Harmattan dust DS-Storm dust

C.2 Independent paired t-test

The independent 2-tailed paired t test was conducted to determine if there are significant differences between the means of chemical emissions in the μ-CTE extracts and solvent extracts of dust in Modern and traditional homes. There were significant differences in all the chemical emissions in the two extracts with the exception of DEP, with p=0.718 showing similarity of DEP emissions in the two extracts of the modern indoor dust sample.

Table C 2 Comparison of chemicals in dusts from modern and traditional homes analysed by solvent and thermal extraction

Compounds	df	**Paired sample t test (2-tailed) significance**			
		Modern indoor	**Modern outdoor**	**Traditional indoor**	**Traditional outdoor**
NONt - NONs	12	.000	.0005	.0005	.0005
DEPt - DEPs	12	.718	.001	.002	.002
DIBPt - DIBPs	12	.000	.0005	.001	.0005
DBPt - DBPs	12	.000	.0005	.050	.006
DEHPt - DEHPs	12	.000	.0005	.0005	.0005

NON= nonanal t= thermal extract s= solvent extract

Table C 3 Paired Samples Correlations of chemicals in indoor and outdoor dusts from modern and traditional homes

Non parametric correlations (Mann whitney test)			
Compounds	**N**	**Correlation**	**Sig.**
NONt & NONs	52	.427	.002
DEPt & DEPs	52	.449	.001
DIBPt & DIBPs	52	.544	.000
DBPt & DIBPs	52	.538	.000
DEHPt & DEHPs	52	-.087	.541

NON= nonanal t= thermal extract s= solvent extract

C.3 Spearman’s correlation

The Spearman's rank-order correlation coefficient-ρ is a non-parametric alternative to the Pearson’s correlation, which is a measure of the strength and direction of the association/relationship between two continuous or ordinal variables. It answers the question with a null hypothesis:

H_0: There is no association between the variables in question, P=0

And the alternative hypothesis is:

H_A: $\rho \neq 0$, the correlation coefficient is not equal to zero, when there is association between the variables

The computed outcome indicates whether to reject, or fail to reject, the null hypothesis.

To determine any possible association between the chemical concentrations in the solvent as well as the thermal extracts of the indoor/outdoor dusts from modern and traditional type of buildings, Spearman’s correlation coefficients were calculated and the results are shown in Tables C4 and C5.

Table C-4 Spearman's Correlations for thermal verses solvent extracts of indoor dusts in modern and traditional homes

Spearman's rho		**HEXt**	**LIMt**	**NONt**	**DEPt**	**DIBPt**	**DBPt**	**DEHPt**	**NONs**	**DEPs**	**DBPs**	**DIBPs**	**DEHPs**
	N	26	26	26	26	26	26	26	26	26	26	26	26
Hext	Correlation Coefficient		**.711****	-.312	-.079	**.535****	**.552****	**.602****	**.602****	**-.266**	**.560****	**.646****	.318
	Sig. (2-tailed)		.0005	.121	.700	.005	.003	.001	.001	.189	.003	.000	.114
LIMt	Correlation Coefficient	**.711****		-.076	-.082	**.725****	**.630****	**.779****	**.779****	-.309	**.809****	**.814****	**.516****
	Sig. (2-tailed)	.0005		.711	.690	.000	.001	.000	.000	.125	.0005	.0005	.007
NONt	Correlation Coefficient	-.312	-.076		**.555****	-.093	-.041	.006	.006	-.130	.107	.015	.197
	Sig. (2-tailed)	.121	.711		.003	.651	.842	.975	.975	.526	.603	.941	.335
DEPt	Correlation Coefficient	-.079	-.082	.555**		.213	-.029	.030	.030	-.249	.069	.016	.227
	Sig. (2-tailed)	.700	.690	.003		.296	.888	.884	.884	.221	.739	.939	.264
DIBPt	Correlation Coefficient	**.535****	**.725****	-.093	.213		**.569****	**.750****	**.750****	-.249	**.707****	**.766****	**.619****
	Sig. (2-tailed)	.005	.0005	.651	.296		.002	.0005	.0005	.221	.0005	.0005	.001
DBPt	Correlation Coefficient	**.552****	**.630****	-.041	-.029	**.569****		**.558****	**.558****	-.186	**.565****	**.623****	.213
	Sig. (2-tailed)	.003	.001	.842	.888	.002		.003	.003	.364	.003	.001	.296

DEHPt	Correlation Coefficient	**.602****	**.779****	.006	.030	**.750****	**.558****		**1.000****	-.298	**.829****	**.874****	**.595****
	Sig. (2-tailed)	.001	.0005	.975	.884	.0005	.003			.139	.0005	.0005	.001
NONs	Correlation Coefficient	**.602****	**.779****	.006	.030	**.750****	**.558****	**1.000****		-.298	**.829****	**.874****	**.595****
	Sig. (2-tailed)	.001	.0005	.975	.884	.0005	.003	.		.139	.0005	.0005	.001
DEPs	Correlation Coefficient	-.266	-.309	-.130	-.249	-.249	-.186	-.298	-.298		-.348	-.338	**-.421***
	Sig. (2-tailed)	.189	.125	.526	.221	.221	.364	.139	.139		.082	.091	.032
DBPs	Correlation Coefficient	**.560****	**.809****	.107	.069	**.707****	**.565****	**.829****	**.829****	-.348		**.889****	.584**
	Sig. (2-tailed)	.003	.0005	.603	.739	.000	.003	.0005	.0005	.082		.0005	.002
DIBPs	Correlation Coefficient	**.646****	**.814****	.015	.016	**.766****	**.623****	**.874****	**.874****	-.338	**.889****		**.630****
	Sig. (2-tailed)	.0005	.0005	.941	.939	.0005	.001	.0005	.0005	.091	.0005		.001
DEHPs	Correlation Coefficient	.318	**.516****	.197	.227	**.619****	**.213**	**.595****	**.595****	**-.421***	**.584****	**.630****	
	Sig. (2-tailed)	.114	.007	.335	.264	.001	.296	.001	.001	.032	.002	.001	.

******. Correlation is significant at the 0.01 level (2-tailed). ***.** Correlation is significant at the 0.05 level (2-tailed).

Table C-5 Spearman’s Correlations for thermal vs solvent extracts in outdoor dusts of modern and traditional buildings

Spearman's rho		**HEXt**	**LIMt**	**NONt**	**DEPt**	**DIBPt**	**DBPt**	**DEHPt**	**NONs**	**DEPs**	**DBPs**	**DIBPs**	**DEHPs**
	N	26	26	26	26	26	26	26	26	26	26	26	26
HEXt	Correlation Coefficient		.295	**.440***	**.453***	.256	.082	.220	.220	.250	.206	.128	-.082
	Sig.(2-tailed)		.143	.025	.020	.207	.690	.280	.280	.218	.312	.533	.690
LIMt	Correlation Coefficient	.295		**.537****	**.422***	.227	.369	**.757****	**.757****	**.503****	**.659****	**.612****	-.017
	Sig.(2-tailed)	.143		.005	.032	.265	.063	.0005	.0005	.009	.0005	.001	.935
NONt	Correlation Coefficient	**.440***	**.537****		**.803****	**.793****	**.595****	**.591****	**.591****	**.507****	**.559****	**.487***	.016
	Sig.(2-tailed)	.025	.005		.0005	.0005	.001	.001	.001	.008	.003	.012	.938
DEPt	Correlation Coefficient	**.453***	**.422***	**.803****		**.708****	**.512****	**.487***	**.487***	**.621****	**.572****	**.472***	.234
	Sig.(2-tailed)	.020	.032	.0005		.0005	.007	.012	.012	.001	.002	.015	.249
DIBPt	Correlation Coefficient	.256	.227	**.793****	**.708****		.395*	.286	.286	.250	.238	.300	.087
	Sig.(2-tailed)	.207	.265	.000	.000		.046	.156	.156	.218	.242	.136	.673
DBPt	Correlation Coefficient	.082	.369	**.595****	**.512****	**.395***		.400*	.400*	.361	.455*	.365	.312
	Sig.(2-tailed)	.690	.063	.001	.007	.046		.043	.043	.070	.019	.067	.121
DEHPt	Correlation Coefficient	.220	**.757****	**.591****	**.487***	.286	**.400***		**1.000****	**.685****	**.763****	**.803****	-.040

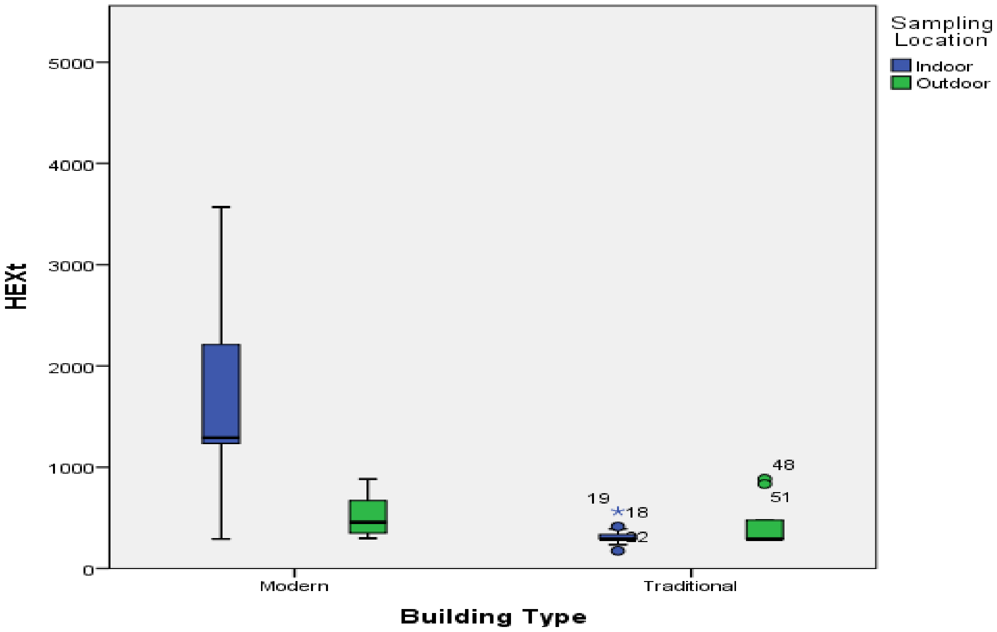
	Sig.(2-tailed)	.280	.000	.001	.012	.156	.043		.	.000	.000	.000	.846
NONs	Correlation Coefficient	.220	**.757****	**.591****	**.487***	.286	**.400***	**1.000****		**.685****	**.763****	**.803****	-.040
	Sig. (2-tailed)	.280	.000	.001	.012	.156	.043	.		.0005	.0005	.0005	.846
DEPs	Correlation Coefficient	.250	**.503****	**.507****	**.621****	.250	.361	**.685****	**.685****		**.758****	**.776****	.225
	Sig. (2-tailed)	.218	.009	.008	.001	.218	.070	.000	.000		.000	.0005	.270
DBPs	Correlation Coefficient	.206	**.659****	**.559****	**.572****	.238	**.455***	**.763****	**.763****	**.758****		**.866****	.156
	Sig.(2-tailed)	.312	.000	.003	.002	.242	.019	.000	.000	.000		.0005	.448
DIBPs	Correlation Coefficient	.128	**.612****	**.487***	**.472***	.300	.365	**.803****	**.803****	**.776****	**.866****		.115
	Sig.(2-tailed)	.533	.001	.012	.015	.136	.067	.000	.000	.000	.000		.577
DEHPs	Correlation Coefficient	-.082	-.017	.016	.234	.087	.312	-.040	-.040	.225	.156	.115	
	Sig.(2-tailed)	.690	.935	.938	.249	.673	.121	.846	.846	.270	.448	.577	

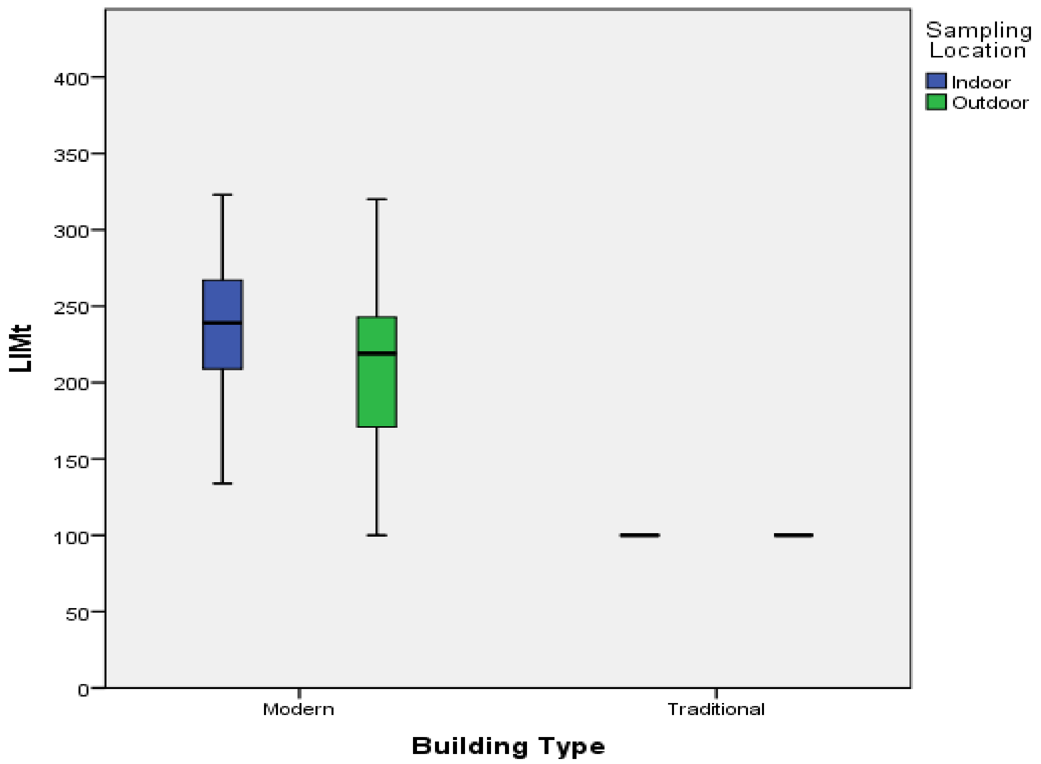
*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

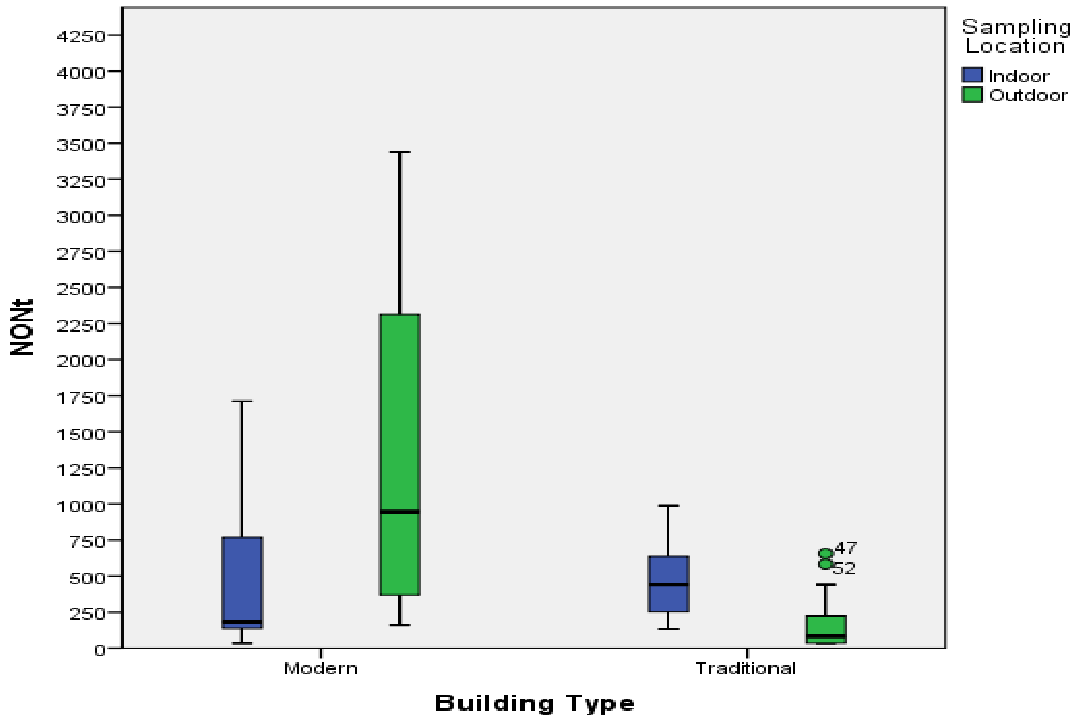
C.4 Box Plots

Box plots are used to show overall patterns of response for a group of data. They provide a useful way to visualise the range and how the data is spread around the median of data set.

C.4.1 Box plots for chemicals in dusts from building types (thermal extracts)




LIMt
0
50
100
150
200
250
300
350
400
Modern
Traditional
Building Type
Sampling Location
Indoor
Outdoor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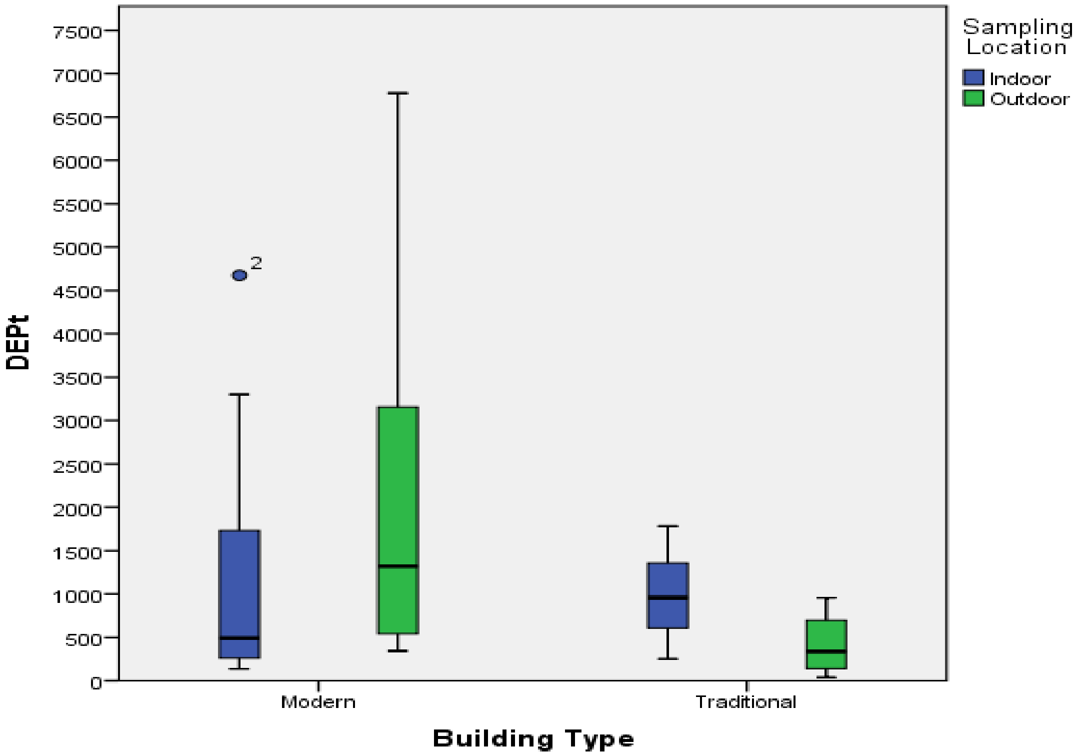
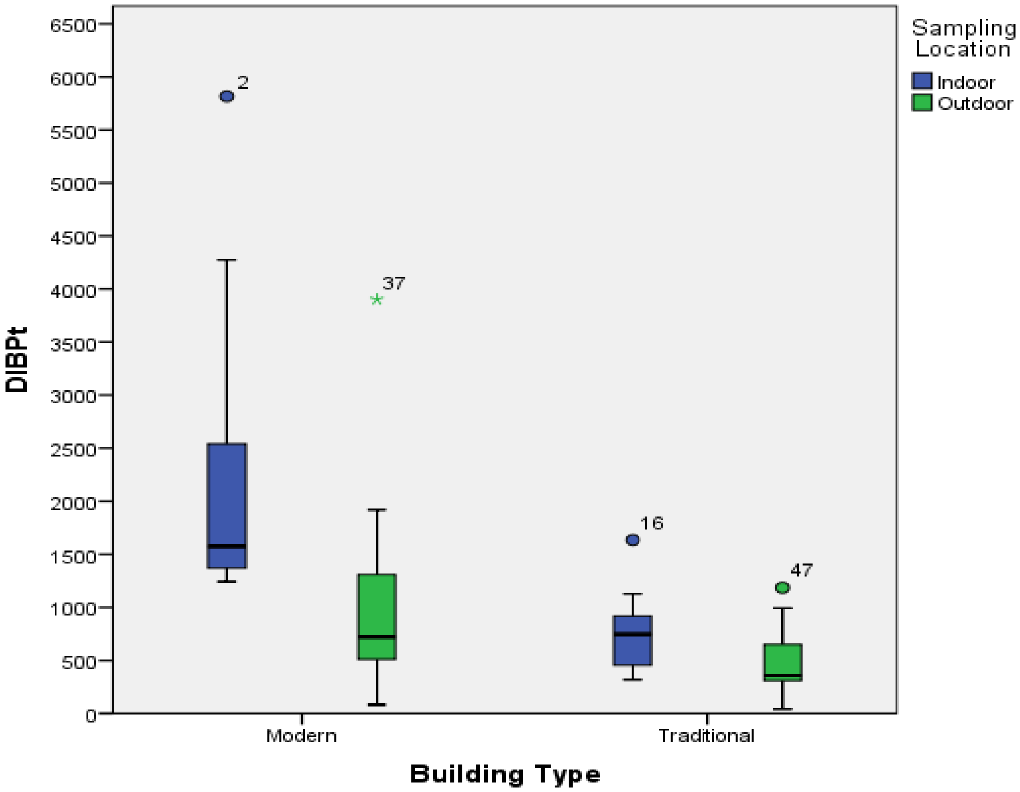
0
250
500
750
1000
1250
1500
1750
2000
2250
2500
2750
3000
3250
3500
3750
4000
4250
47
52
Modern
Traditional
Building Type
Sampling Location
Indoor
Outdoor


DEPt
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
2
Modern
Traditional
Building Type
Sampling Location
Indoor
Outdoor


DIBPt
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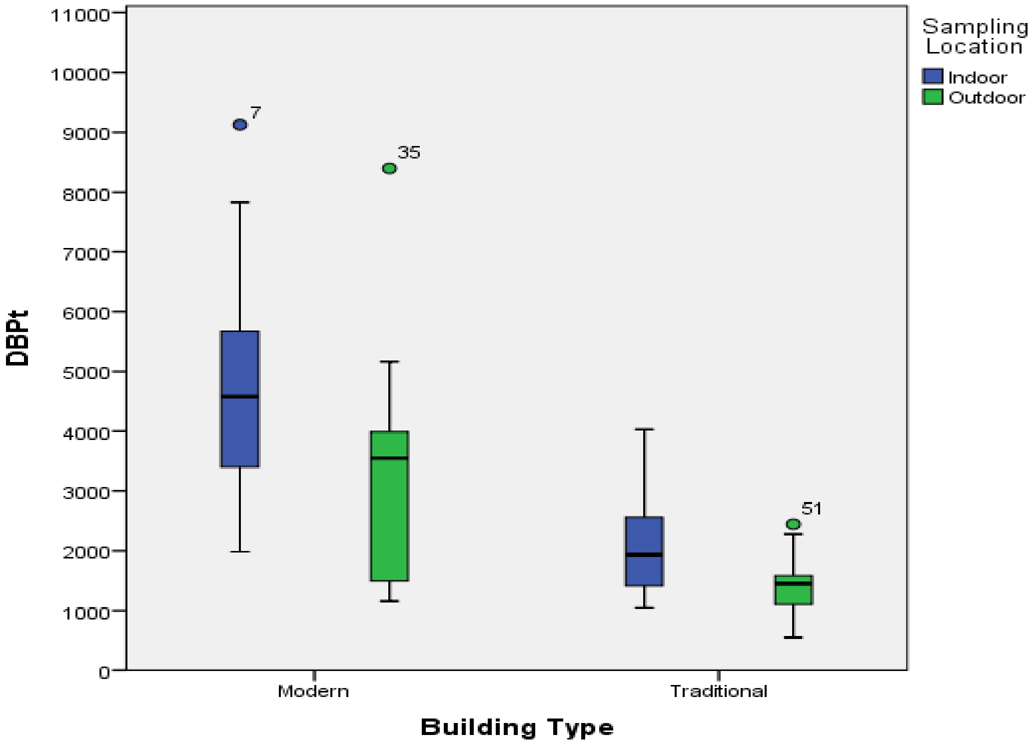
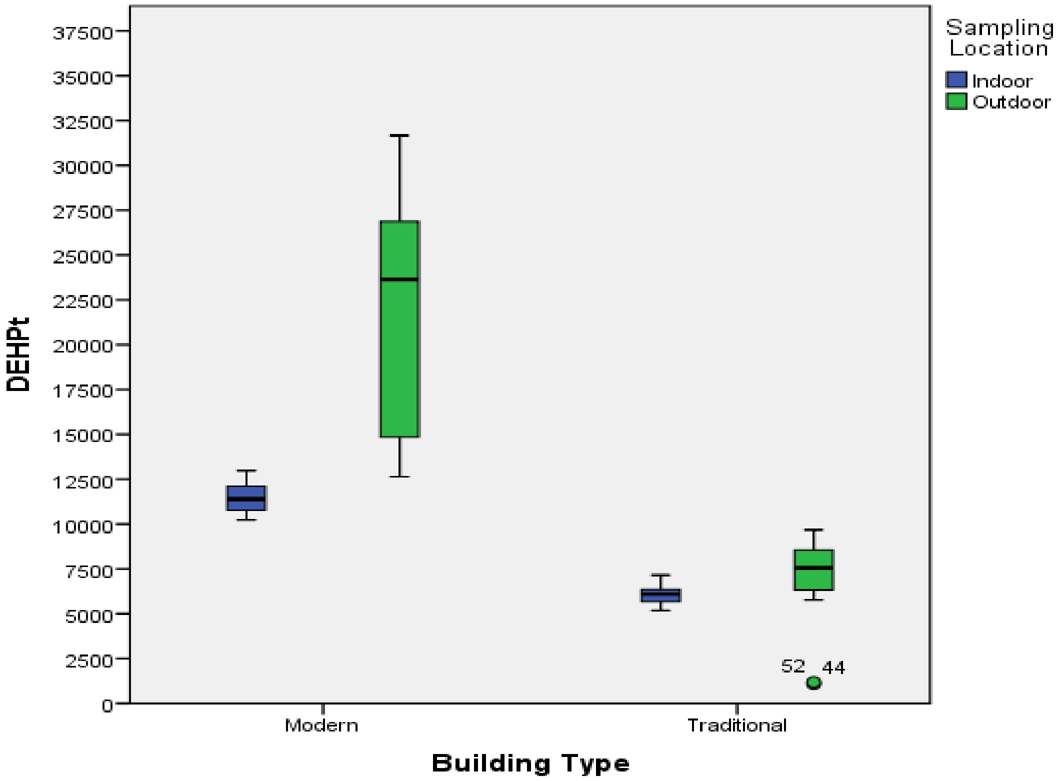
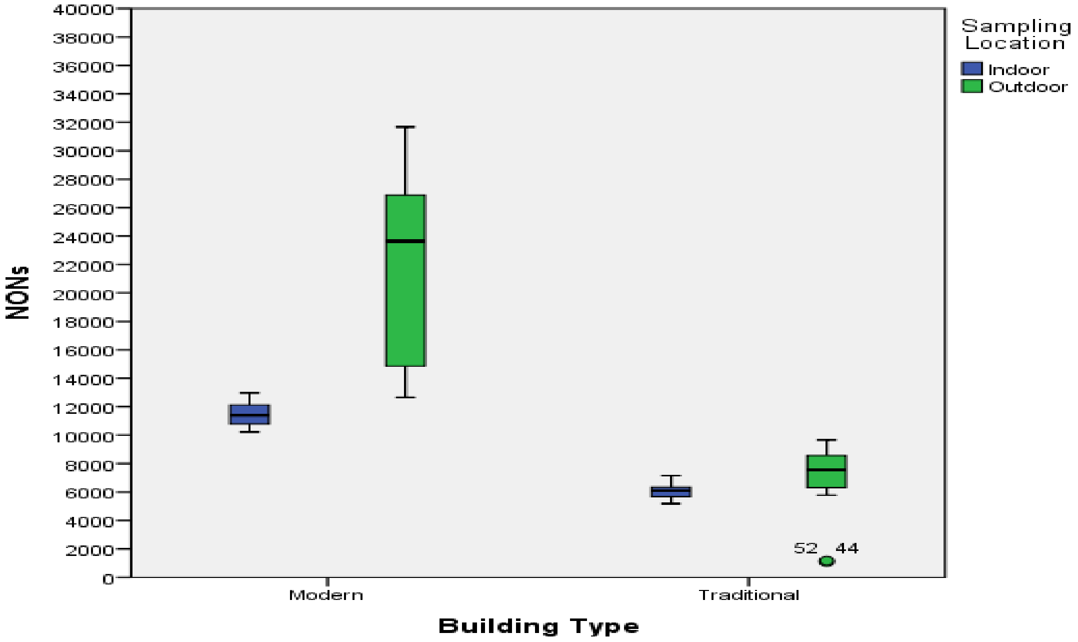
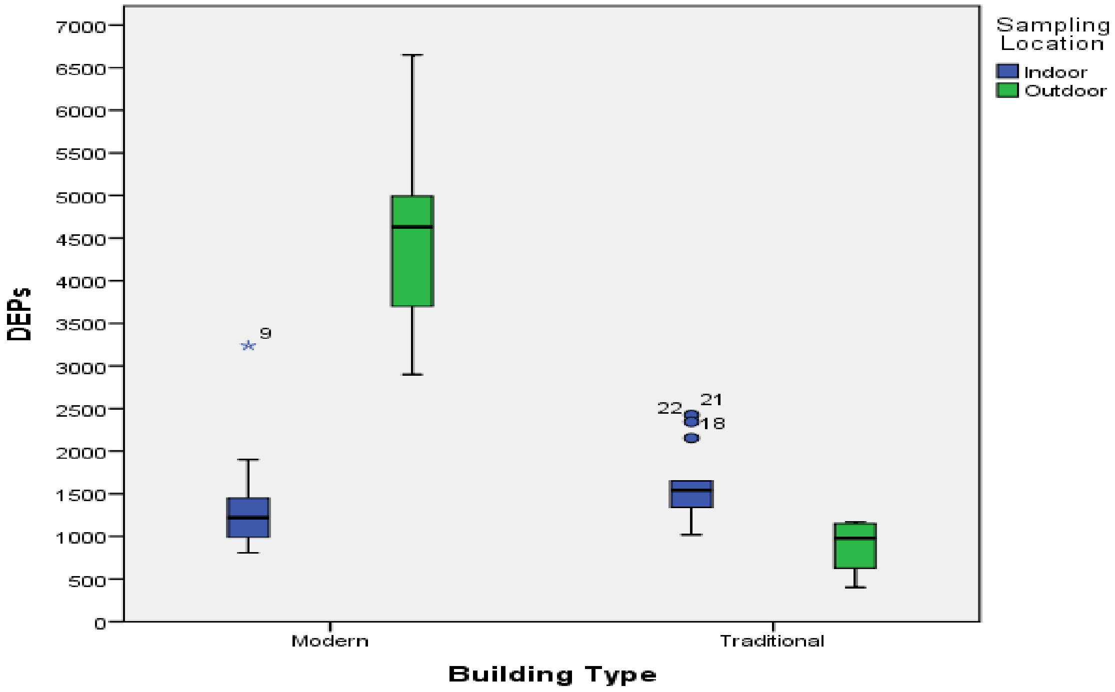
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
2
37
16
47
Modern
Traditional
Building Type
Sampling Location
Indoor
Outdoor

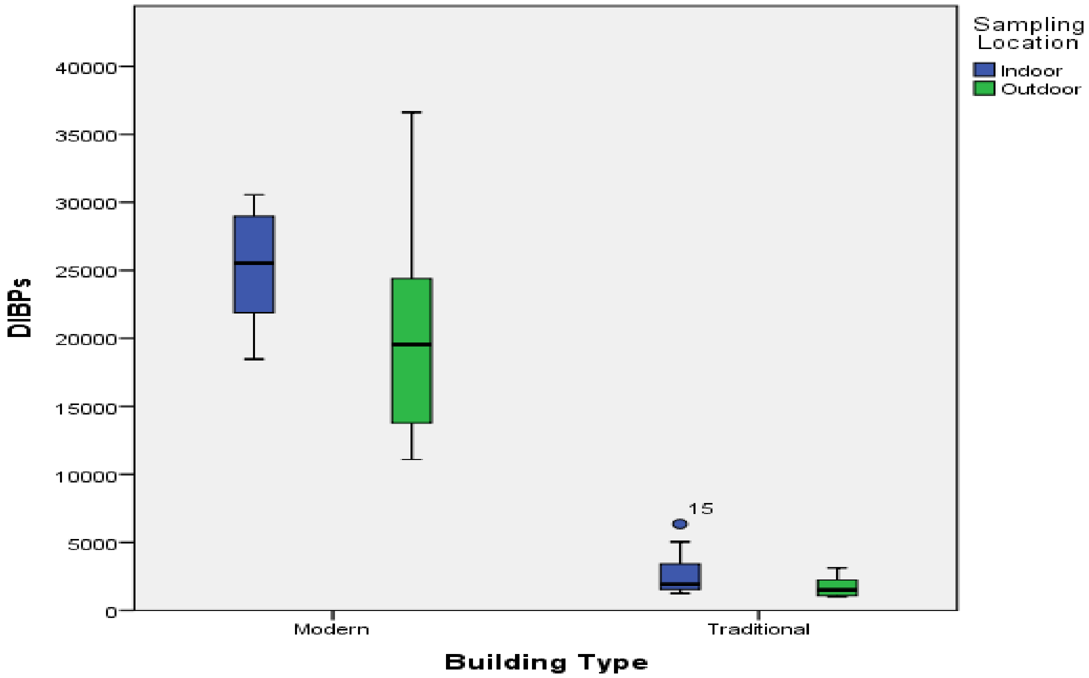

DBPt
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
7
35
51
Modern
Traditional
Building Type
Sampling Location
Indoor
Outdoor


37500
35000
32500
30000
27500
25000
22500
20000
17500
15000
12500
10000
7500
5000
2500
0
DEHPt
Modern
Traditional
Building Type
52
44
Sampling Location
Indoor
Outdoor

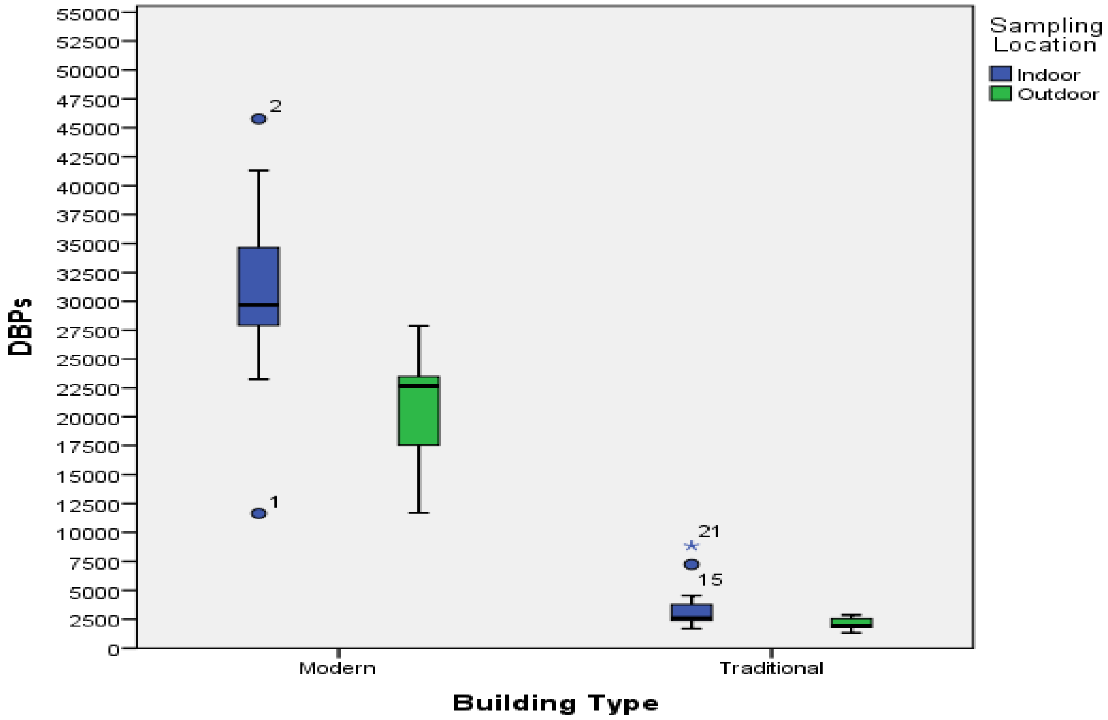
C.4.2 Box plots for chemicals in dusts from building types (solvent extracts)







DIBPs
40000
35000
30000
25000
20000
15000
10000
5000
0
15
Modern
Traditional
Building Type
Sampling Location
Indoor
Outdoor



DBPs
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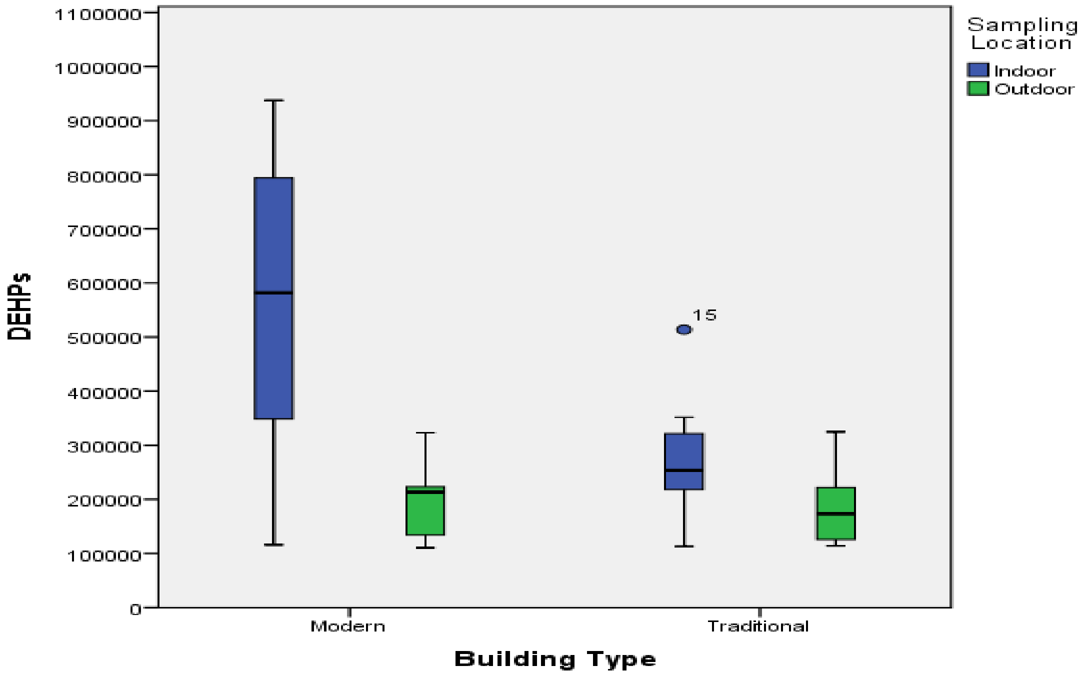
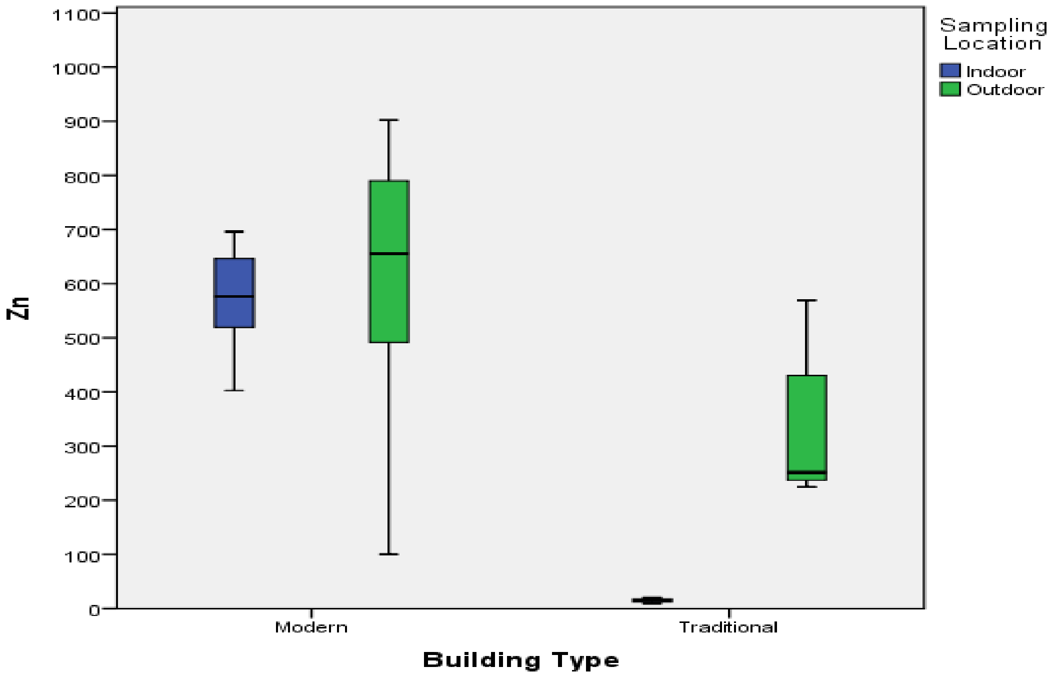
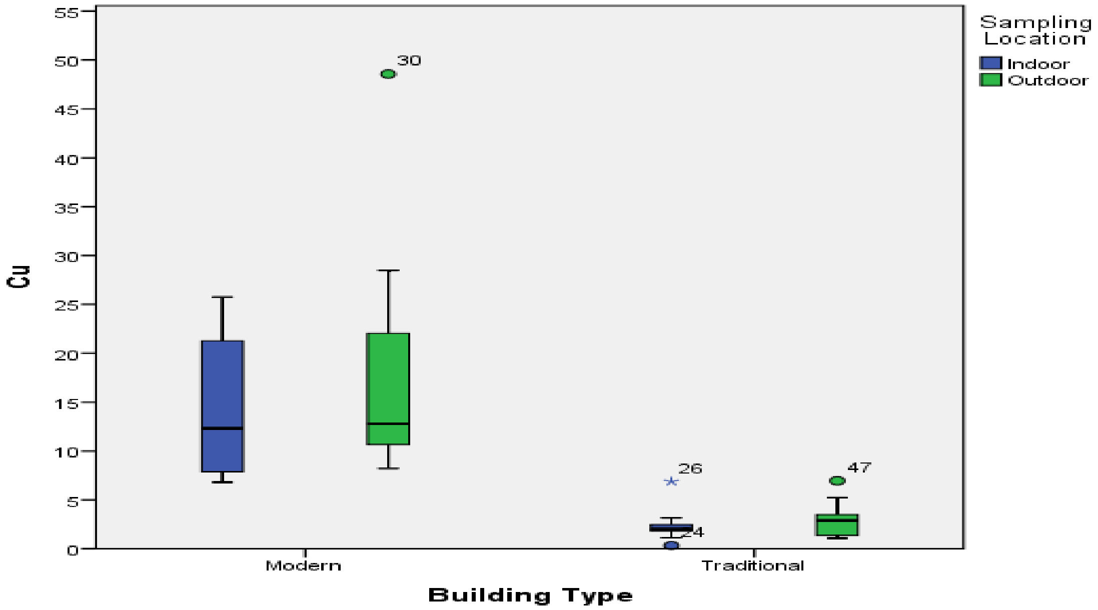
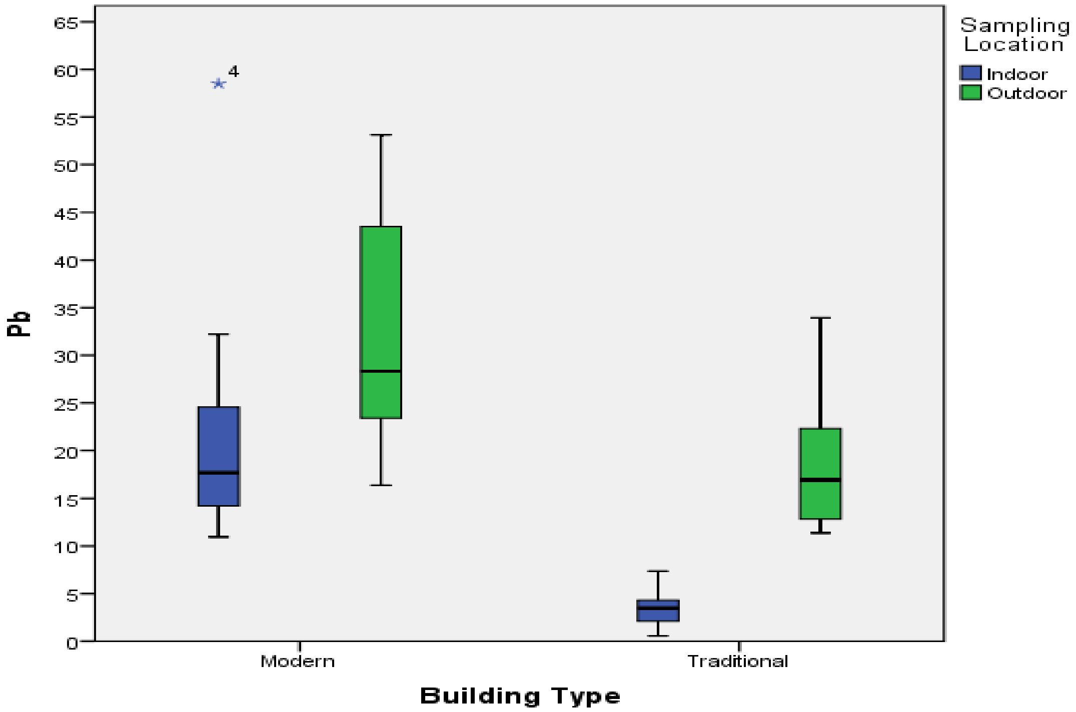
52500
50000
47500
45000
42500
40000
37500
35000
32500
30000
27500
25000
22500
20000
17500
15000
12500
10000
7500
5000
2500
0
2
1
21
15
Modern
Traditional
Building Type
Sampling Location
Indoor
Outdoor



C.4.3 Box plots for metals concentrations in dusts from different Building types




Sampling Location
Indoor
Outdoor
Cu
0
5
10
15
20
25
30
35
40
45
50
55
30
26
24
47
Modern
Traditional
Building Type


Sampling Location
Indoor
Outdoor
Pb
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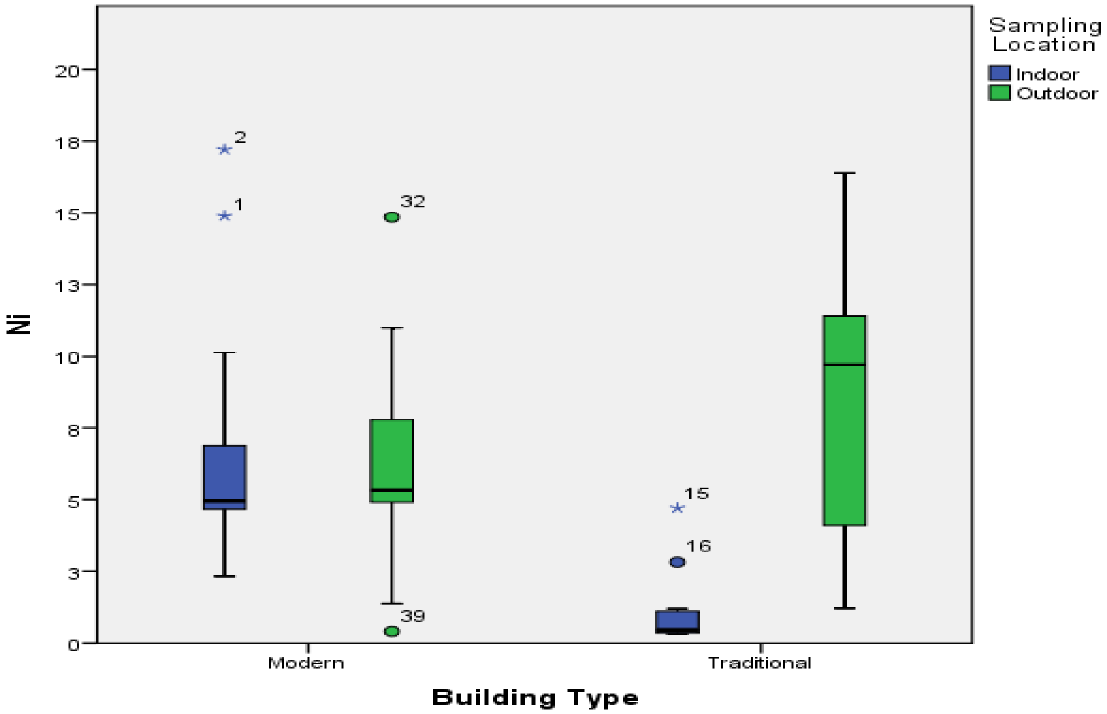
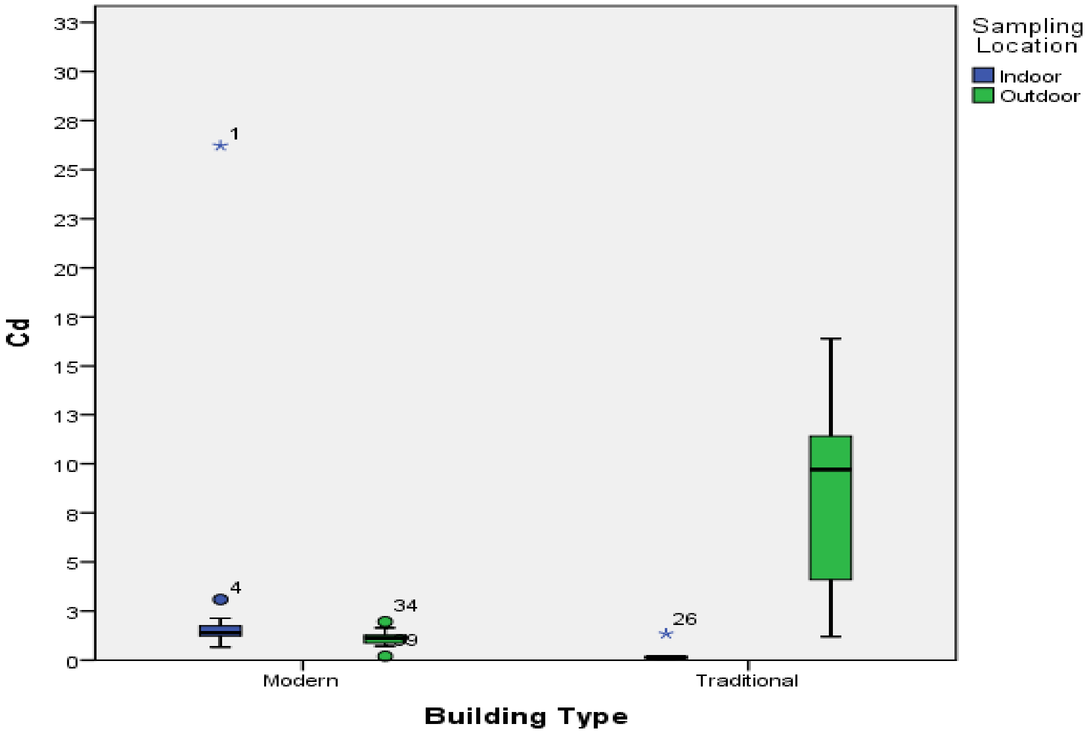
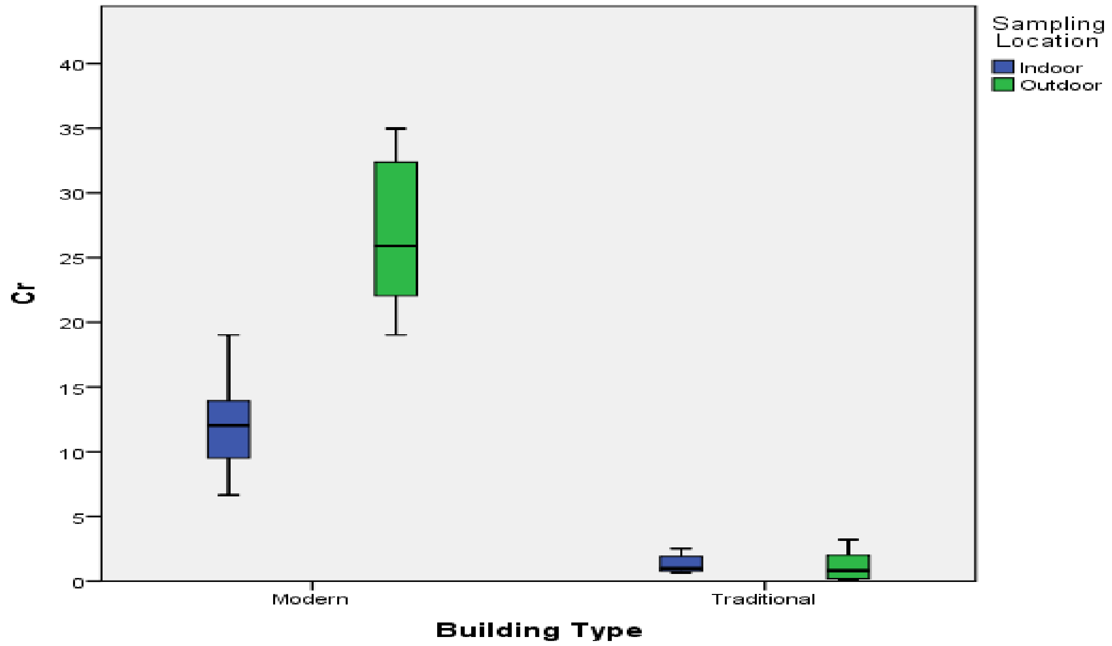
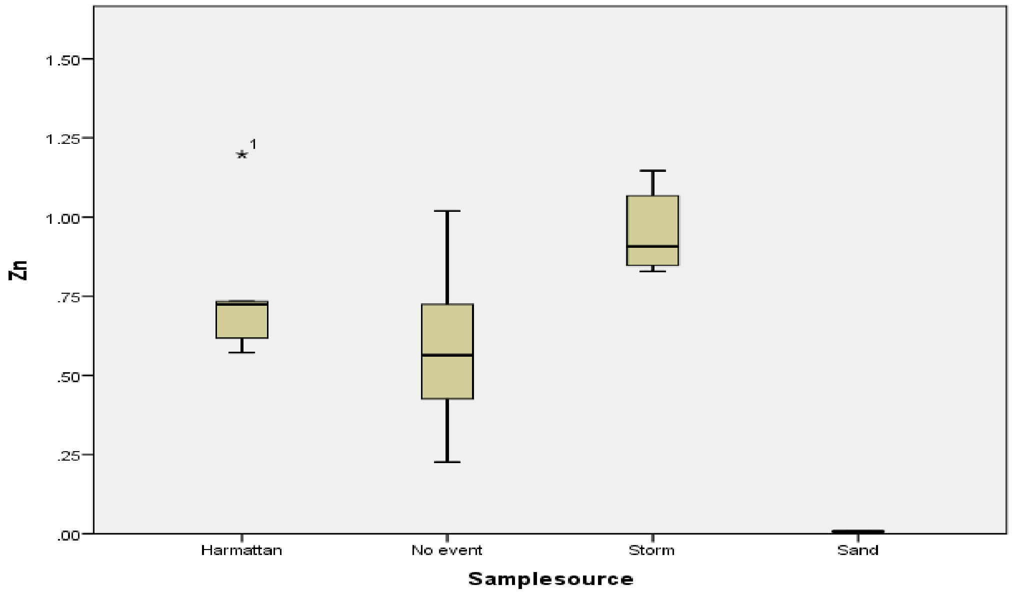
5
10
15
20
25
30
35
40
45
50
55
60
65
4
Modern
Traditional
Building Type

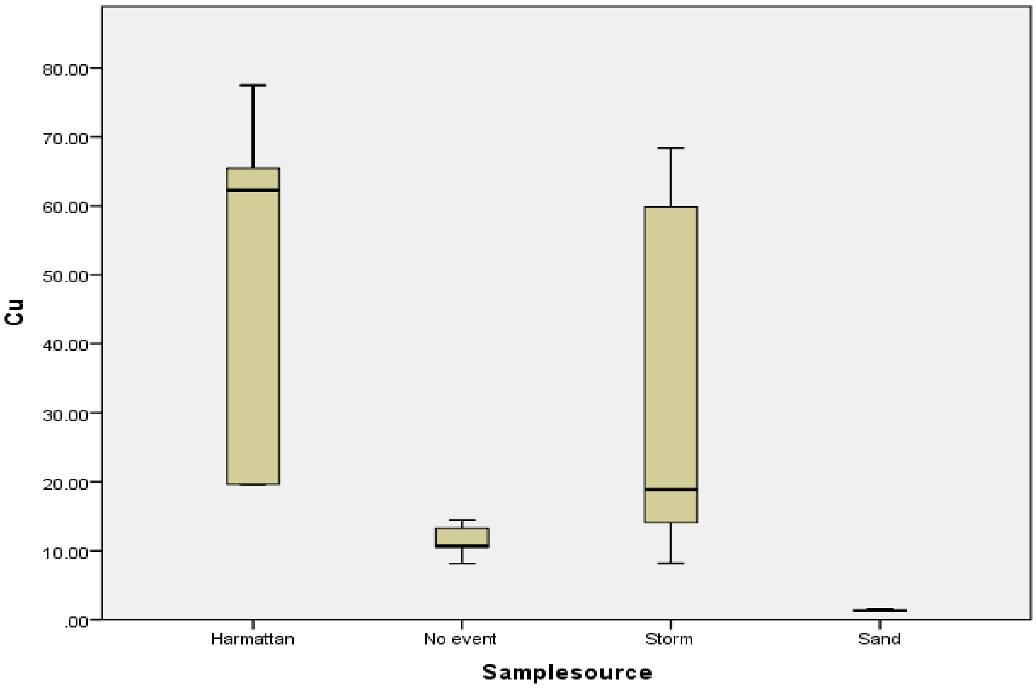

Sampling Location
Indoor
Outdoor
Ni
20
18
15
13
10
8
5
3
0
2
1
32
15
16
39
Modern
Traditional
Building Type

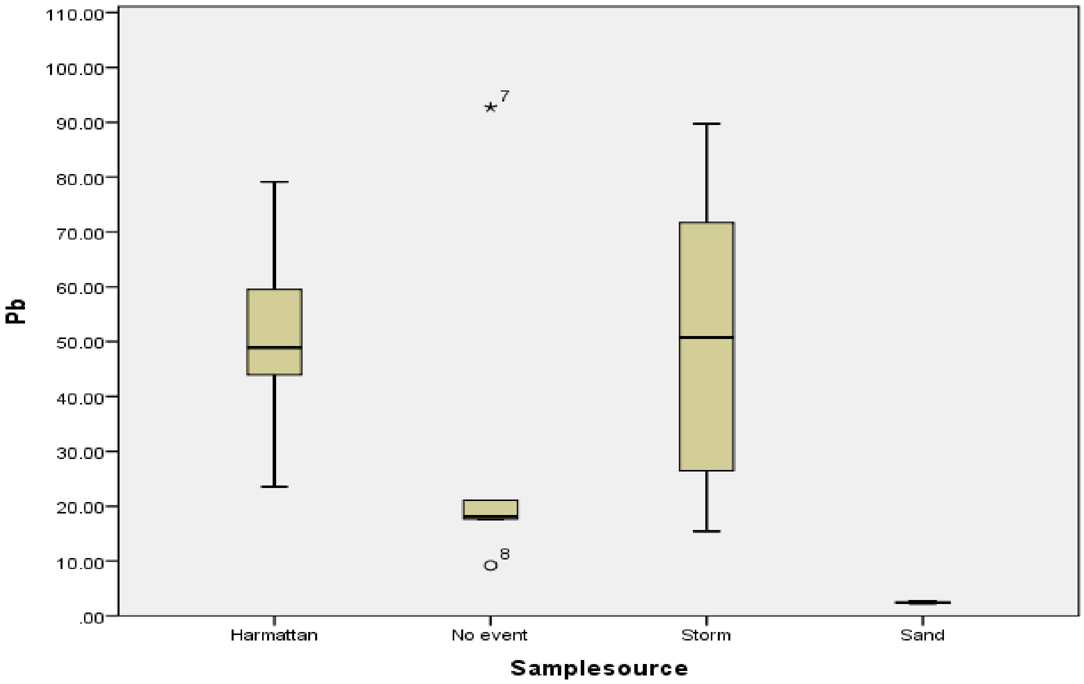

Sampling Location
Indoor
Outdoor
Cd
33
30
28
25
23
20
18
15
13
10
8
5
3
0
1
4
34
9
26
Modern
Traditional
Building Type

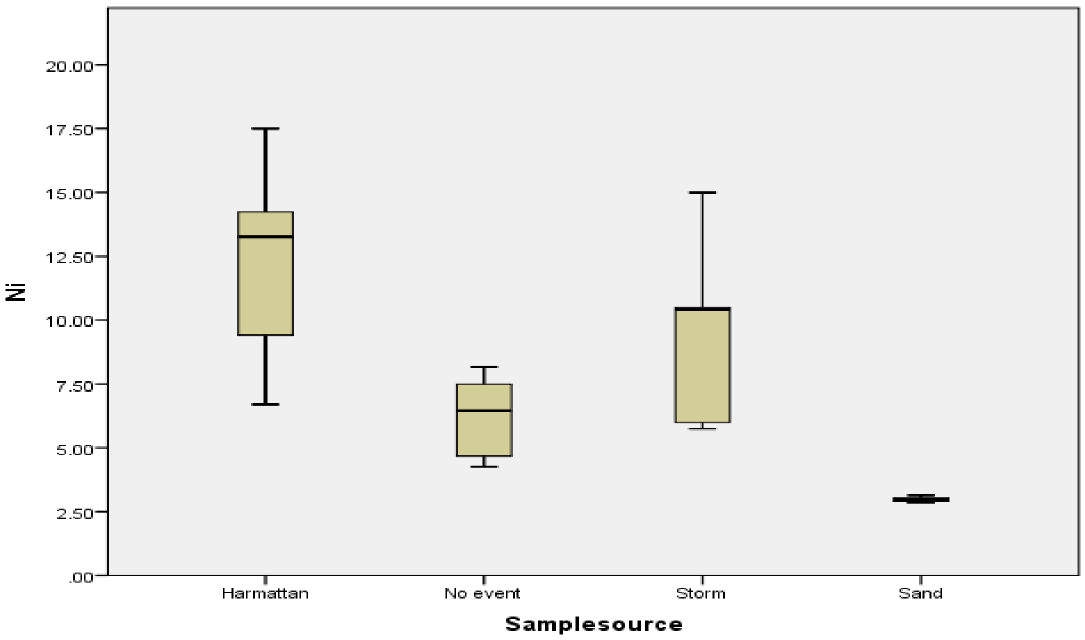


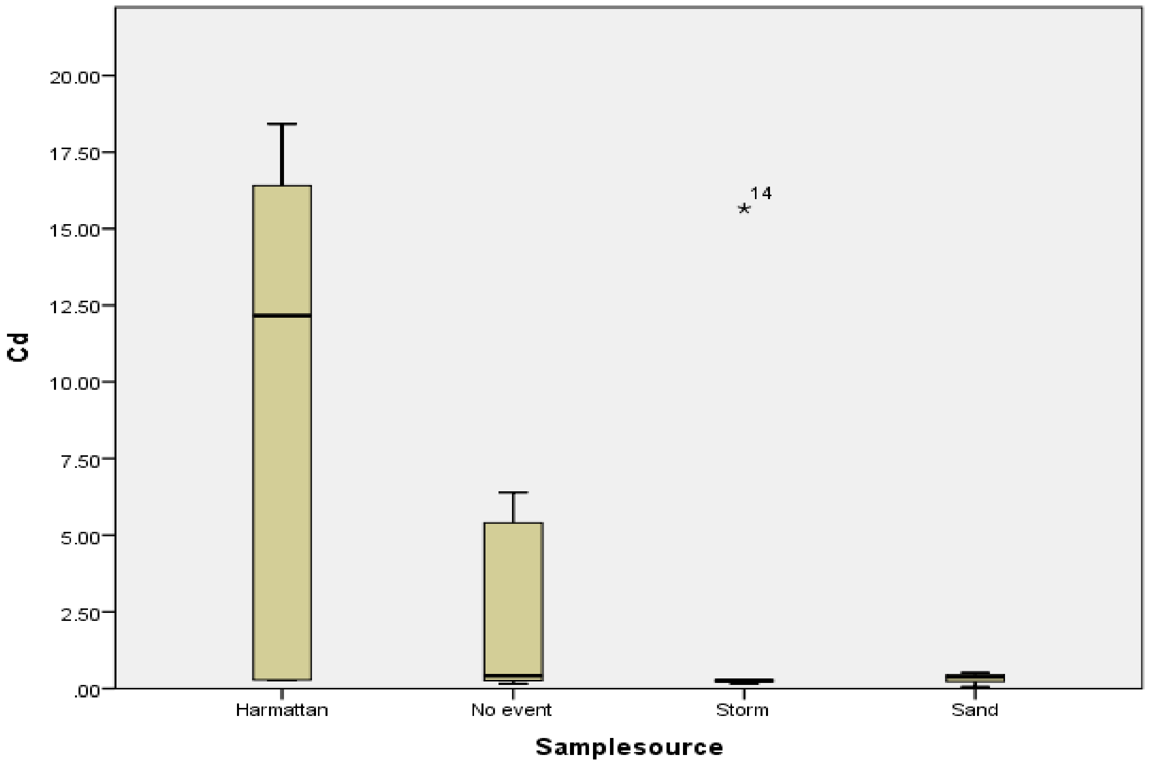
C.4.4 Box plots for metals concentrations in dusts from Different Sources




Cu
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
.00
Harmattan
No event
Storm
Sand
Samplesource


Pb
110.00
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
.00
7
8
Harmattan
No event
Storm
Sand
Samplesource


20.00
17.50
15.00
12.50
10.00
7.50
5.00
2.50
.00
Ni
Harmattan
No event
Storm
Sand
Samplesource


20.00
17.50
15.00
12.50
10.00
7.50
5.00
2.50
.00
Cd
14
Harmattan
No event
Storm
Sand
Samplesource

Appendix D **Publications/Conference papers/Posters**

1) Fatima S. Mohammed and Derrick Crump (2013) *"Characterisation of indoor/outdoor settled dust and air pollutants in Damaturu, Nigeria", International Journal of Engineering and Technology,* vol. Vol. 5, no. No.1. p 104-108.
2) Fatima Sule Mohammed & Derrick Crump *"Harmattan and Dust Storm; Composition, Exposure and Risk to Human Health",* Proceedings of the 2010 Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research, 13–14 April 2010, IEH web report W27, p 79-81, Institute of Environment and Health, Cranfield University, UK.
3) Fatima Sule Mohammed & Derrick Crump *"Sampling and analysis of indoor/outdoor air and settled dust for the determination of pollutants",* Proceedings of the 2011 Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research, 10 & 11 May 2011, IEH web report W28, p 159-162, Institute of Environment and Health, Cranfield University, UK.
4) Fatima Sule Mohammed & Derrick Crump (IEH, Cranfield University) *"Determination of organic chemical pollutants in indoor/outdoor settled dusts during seasonal weather events in Northern Nigeria"* , Proceedings of the 2012 Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research, 3 & 4 May 2012, IEH web report W31, p 69-72, Institute of Environment and Health, Cranfield University, UK.
5) Fatima S. Mohammed and Derrick Crump (IEH, Cranfield Health, Cranfield University. UK) *"Metal concentrations in indoor/outdoor dusts of homes in Damaturu, northern Nigeria".* Proceedings of the 2013 Annual UK Review meeting on outdoor and indoor air pollution research, 23 – 24 April 2013, IEH web report W32, p127-131, Institute of Environment and Health, Cranfield University, UK.