ASSESSMENT OF POLYCHLORINATED DIOXINS/FURANS IN AMBIENT AIR AND SOIL SAMPLES FROM SELECTED INDUSTRIAL SITES USING PALM KERNEL SHELL ACTIVATED CARBON IN A MODIFIED SAMPLE PREPARATION METHOD

by

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LIST OF ABBREVIATION

PHAHs	Polyhalogenated aromatic hydrocarbons
TEQ	Toxicity Equivalence
TEFs	Toxicity Equivalency Factors
USEPA	United State Environmental Protection Agency
PCDDs	Polychlorinated Dibenzo-*p*-dioxins
PCDFs	Polychlorinated Dibenzofurans
PCBs	Polychlorinated Biphenyl
2,3,7,8-TCDD	2,3,7,8 – Tetrachlorodibenzo-*p*-dioxin
1,2,3,7,8-PeCDD	1,2,3,7,8 – Pentachlorodibenzo-*p*-dioxin
1,2,3,7,8 - PeCDD	1,2,3,7,8 – Pentachlorodibenzo-*p*-dioxin
1,2,3,4,7,8 – HxCDD	1,2,3,4,7,8 – Hexachlorodibenzo-*p*-dioxin
1,2,3,6,7,8 – HxCDD	1,2,3,6,7,8 – Hexachlorodibenzo-*p*-dioxin
1,2,3,4,6,7,8 – HpCDD	1,2,3,4,6,7,8 – Heptachlorodibenzo-*p*-dioxin
OCDD	Octachlorodibenzo-p-dioxin
1,2,3,7,8 – PeCDF	1,2,3,7,8 – Pentachlorodibenzofuran
2,3,4,7,8 - PeCDF	2,3,4,7,8 – Pentachlorodibenzofuran
2,3,7,8 - TCDF	2,3,7,8 - Tetrachlorodibenzofuran
1,2,3,6,7,8 – HxCDF	1,2,3,6,7,8 – Hexachlorodibenzofuran
1,2,3,4,7,8 - HxCDF	1,2,3,4,7,8 – Hexachlorodibenzofuran
1,2,3,7,8,9 - HxCDF	1,2,3,7,8,9 - Hexachlorodibenzofuran
2,3,4,6,7,8 – HxCDF	2,3,4,6,7,8 – Hexachlorodibenzofuran
1,2,3,4,7,8,9 – HpCDF	1,2,3,4,7,8,9 – Heptachlorodibenzofuran
1,2,3,4,6,7,8 – HpCDF	1,2,3,4,6,7,8 – Heptachlorodibenzofuran
OCDF	Octachlorodibenzofuran
HRGC – HRMS	High Resolution Gas Chromatography - High Resolution Mass Spectrometry

LIST OF ABBREVIATION (cont.)

PCDEs	Polychlorinated diphenyl ethers
DDE	1,1-Dichloro-2,2-bis(p-chlorophenyl) ethylene

LIST OF UNITS

g	grams
µg	microgram
ng	nanogram
pg	picogram
fg	femtogram
h	hour
L	liter
mL	miliLiter
mg	milligram
%	percentage

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PENILAIAN KANDUNGAN DIOKSIN/FURAN TERPOLIKLORINA DALAM SAMPEL UDARA DAN TANAH DARI KAWASAN PERINDUSTRIAN TERPILIH MENGGUNAKAN KAEDAH PENYEDIAAN SAMPEL YANG DIUBAHSUAI YANG MENGANDUNGI KARBON TERAKTIF DARI TEMPURUNG KELAPA SAWIT

Abstrak

Buat pertama kalinya, satu penilaian paras dioksin/furan dalam udara dan tanah di persekitaran Malaysia telah dilapurkan. Tiga (3) kawasan perindustrian terpilih dan satu (1) kawasan rujukan telah dipilih untuk tujuan ini dan sampel yang diperolehi dianalisa menggunakan kaedah penyediaan (penulenan) sampel yang diubahsuai. Kajian ini melibatkan analisis sebanyak tujuhbelas konjines dioksin/furan yang ujud dalam sampel udara dan tanah. Keputusan kajian mendapati kepekatan tertinggi dioksin/furan dalam udara direkodkan di kawasan Taiping dengan julat 0.056 hingga 0.167 i-TEQ pg/Nm^3. Kepekatan dioksin/furan kedua tertinggi adalah dalam julat 0.080 hingga 0.113 i-TEQ pg/Nm^3 di kawasan Bukit Pelanduk. Seterusnya, di kawasan ketiga iaitu di kawasan Prai, merekodkan kepekatan dioksin/furan terendah iaitu dalam julat 0.029 hingga 0.099 i-TEQ pg/Nm^3. Sementara itu di kawasan rujukan iaitu Taman Negara Kuala Tahan kepekatan dioksin/furan yang dicatatkan adalah dalam julat 0.003 hingga 0.006 i-TEQ pg/Nm^3. Didapati konjines terbanyak dalam sampel di semua lokasi persampelan adalah 2,3,4,7,8 – PeCDF dan 1,2,3,7,8 – PeCDD.

Kajian ini juga membolehkan kadar pelepasan dioksin/furan dari cerobong insinerator diramal menggunakan kepekatan dioksin/furan dalam udara yang diperolehi melalui “data fitting” ke dalam model penyerakan udara Gaussian. Melalui kajian ini juga, semasa berlaku jerebu, ada bukti menunjukkan bahawa terdapat korelasi antara kepekatan bahan pepejal terampai di udara dengan kepekatan dioksin/furan dalam

udara. Selain itu kelajuan dan arah angin utama juga mungkin menyumbang kepada penyebaran dioksin/furan yang dilepaskan daripada insenerator hingga ke jarak yang berbeza-beza.

Sementara itu dalam kajian tanah, kepekatan tertinggi dioksin/furan dalam sampel tanah direkodkan di kawasan Taiping yang berjulat diantara 0.673 hingga 3.655 i-TEQ ng/kg. Kepekatan dioksin/furan kedua tertinggi adalah dalam julat 0.545 hingga 3.253 i-TEQ ng/kg iaitu di kawasan Prai dan kepekatan terendah adalah dalam julat 0.313 hingga 1.462 i-TEQ ng/kg di kawasan Bukit Pelanduk. Di kawasan rujukan iaitu di Taman Negara Kuala Tahan kepekatan dioksin/furan yang dicatatkan adalah dalam julat 0.868 hingga 1.425 i-TEQ ng/kg. Konjines tertinggi yang dicatatkan adalah 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8–PeCDF) bagi PCDF dan octachlorodibenzo-p-dioxin (OCDD) bagi PCDD. Walaubagaimanapun, secara amnya tiada korelasi ditemui antara kepekatan dioksin/furan dalam udara dan dalam tanah di kawasan kajian. Ketiadaan korelasi ini kemungkinan disebabkan aktiviti manusia di kawasan tersebut terutama dalam pembangunan tanah; keadaan ini juga menjelaskan paras dioksin/furan yang tinggi di kawasan Taman Negara Kuala Tahan kemungkinan disebabkan pengumpulan dioksin/furan dalam tanah selama beberapa tahun tanpa gangguan aktiviti manusia.

Kajian ini juga meneroka keberkesanan karbon teraktif yang dijana dari sisa tempurung kelapa sawit sebagai penyerap dan penulen dioksin/furan dalam penyediaan sampel. Sistem penulenan terubahsuai (MCS) yang direka, sebagai kaedah penulenan alternatif kepada sistem PowerPrep^{TM} automatik, didapati lebih menjimatkan kos analisis dioksin/furan terutama kepada sampel alam sekitar (udara dan tanah).

Keputusan analisis menunjukkan peratus purata dapatankembali (recovery) piawai dioksin/furan yang di suntik ke dalam sampel didapati dalam julat 68% hingga 88% untuk tujuh konjines dioksin pada tahap keyakinan 95% (RSD dibawah 20%) sementara bagi sepuluh konjines furan didapati dalam julat 71 hingga 77% pada tahap keyakinan 95% (RSD di bawah 21%).

Adalah dianggarkan kos penggunaan tiga jenis turus penyerap (silica, alumina dan karbon teraktif) dalam sistem penulenan terubahsuai jauh lebih rendah berbanding system PowerPrep^{TM} automatik dengan julat faktor bandingan antara 121 hingga 150 kali. Pengenalan dan penentuan paras dioksin kemudian dilakukan dengan penggunaan Sistem Kromatografi Gas Resolusi Tinggi – Spektrometer Jisim Resolusi Tinggi (HRGC-HRMS).

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ABSTRACT

For the first time an assessment of dioxins/furans in ambient air and soil samples in Malaysian environment is reported. Three (3) industrial sites and one (1) pristine site were selected for this study and samples were analysed using a modified sample preparation method. The analysis involves the quantification of seventeen congeners of dioxins/furans present in the ambient air and soil samples. The highest dioxins/furans concentrations in ambient air were found in Taiping area ranging from 0.056 to 0.167 i-TEQ pg/Nm^3. This was followed by Bukit Pelanduk area with dioxins/furans concentrations ranging from 0.080 I-TEQ to 0.113 i-TEQ pg/Nm^3. The third site, which is in the Prai area recorded the lowest dioxins/furans concentrations, ranging from 0.029 to 0.099 i-TEQ pg/Nm^3, while the pristine site in Kuala Tahan National Park area recorded the dioxins/furans concentration in the range of 0.003 to 0.006 i-TEQ pg/Nm^3. The most abundant congeners in all air samples in these areas were 2,3,4,7,8 – PeCDF and 1,2,3,7,8 – PeCDD.

This study also allows the prediction of dioxins/furans emission rate of different incinerator stacks by data fitting of the observed ambient air dioxins/furans concentration in the Gaussian air dispersion model. Other interesting finding in this study was that during periods of haze, it is evident that there is a correlation between the particulate matter concentrations (indicated by Air Pollution Index) and dioxins/furans concentrations in air. Wind speed and prevailing wind directions were found to

contribute to the distributions of dioxins/furans emitted from incinerators to different distances.

For soil evaluation study, the highest dioxins/furans concentration in soil was found in Taiping area ranging from 0.673 to 3.655 ng/kg. The second highest concentration of dioxins/furans was found in Prai area ranging from 0.545 to 3.253 ng/kg and the lowest concentration ranged from 0.313 to 1.462 ng/kg at Bukit Pelanduk. Background area at Kuala Tahan National Park recorded the dioxins/furans concentration range from 0.868 to 1.425 ng/kg. The most abundant congeners in all soil samples were 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8–PeCDF) and octachlorodibenzo-p-dioxin (OCDD). However, there is generally no correlation observed between the dioxins/furans concentration in air and in soil at all sampling sites. The lack of correlation may be due to the human activities especially in land development in the selected areas; hence, the high levels of dioxins/furans in soil at the Kuala Tahan National Park could be caused by years of accumulation without any effect from human activity.

The study also explored the effectiveness of a laboratory-prepared activated carbon produced from palm kernel shell waste (PKS) and modified cleanup system (MCS) as a cost effective approach for sample cleanup. This simple but effective technology provides an alternative to automated PowerPrep^{TM} System for the analysis of low concentrations of contaminant (traces) especially dioxins/furans from environmental samples (ambient air and soil). Analytical results showed that the mean recovery of spiked standards of dioxin/furan into the environmental samples were in the range of 68% to 88% for the seven dioxin congeners with 95% confidence level (RSD below 20%) and in the range of 71% to 77% for furan congeners with 95% confidence level (RSD below 21%).

It was estimated that the cost of three types of adsorbents (silica, alumina and activated carbon) used in the modified cleanup system were very much lower than the automated PowerPrep^{TM} system by factors ranging between 121 to 150 times. High Resolution Gas Chromatography-High Resolution Mass Spectrometry (HRGC-HRMS) was employed for the identification and quantification of dioxins/furans.

CHAPTER 1

INTRODUCTION

1.1 Introduction

One of the major problems facing the industrialized world today is the contamination of air, surface water, soils, ground water and sediments with hazardous and toxic chemicals. While regulatory measures have been implemented to lessen or eliminate the production and release to the environment of these chemicals, significant environmental contamination has occurred in the past and will probably continue to occur in the future. Among these contaminants, dioxins/furans are well known hazardous and toxic chemicals which have contributed to real environmental problems. In view of this fact, dioxins/furans have received considerable publicity in a majority of industrialized countries with combustion or incineration processes as means of detoxication and destruction of the hazardous contaminants (Bond, 1993, WHO Consultation 1998, Schecter et al., 2006). Furthermore, the perception of the public is that combustion and incineration processes are always associated with the presence of toxicants like dioxins/furans.

Dioxins/furans are a subset of the polyhalogenated aromatic hydrocarbons (PHAHs). These chemicals are stipulated in the Stockholm Convention 2001 as one of the chemical that need special control internationally. They are toxic organic compounds of varying degrees to living organisms including humans. They are present in a variety of environmental media including as low-level contaminants in the food supply. Chemically, there are many PHAH compounds such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polybrominated dibenzo-*p*-dioxins (PBDDs), polybrominated dibenzofurans (PBDFs) and polychlorinated biphenyls (PCBs)(Rappe and Buser, 1989, Abad et al., 1997, McKay, 2002 and Wang et al., 2010). The formation of these compounds depend on the source of the PHAH and the positions of halogen substitution in the molecule. According to Rappe and Buser, (1989) there are 75 different PCDD congeners and 135 different PCDF congeners; of these 210 different congeners, only 17 are of toxicological concern. The most widely studied and most toxic form of PCDD is 2,3,7,8-tetrachloro dibenzo-*p*-dioxin, usually abbreviated as 2,3,7,8-TCDD.

It is worth mentioning that the PHAHs are not intended industrial products as such, but are produced and released or emitted in small amounts during combustion processes including incineration of halogen-containing organic materials and solid wastes. Additionally, the sources of combustion processes that resulted in PCDDs/PCDFs emission are commonly originated from incinerators of municipal solid wastes, clinical wastes disposal and industrial hazardous wastes treatment facilities (Went, 1989, McKay,2002). The PHAHs are also by-product of several chemical manufacturing processes, such as the manufacture of herbicides and the wood pulp and paper bleaching process. However, some dioxin-like chemicals were also synthesized and sold commercially, such as the PCBs. The PCBs in the form of dielectric fluids were used as heat transfer for capacitors and transformers, and other types of PCBs were used as flame retardants and paint addititives (De Vito and Gallo, 2000).

In view of PCDDs/PCDFs toxicity and potential health problems, their emissions to the environment has been curtailed through a provision under the Malaysian legislation known as Environmental Quality Act, 1974. Thus, a new Malaysian environmental legislation for PCDDs/PCDFs formulated under

Environmental Quality Act, 1974 cited as the Environmental Quality (Dioxin and Furan) Regulations 2004 come into operation on 1st May 2004. This regulation is enforced in order to control air emission limit of PCDDs/PCDFs for the incinerators of municipal solid waste, toxic and hazardous wastes, pulp or paper industry sludge and sewage sludge (Appendix A). The permissible concentration limit for air emission of PCDDs/PCDFs originated from incinerators of these wastes categories shall not exceed 0.1 ng/Nm^3 i-TEQ (i-TEQ is abbreviation for International Toxic Equivalent). This regulation specify the air sampling and analytical method for PCDDs/PCDFs parameters to be in accordance with the USEPA Method 8290. The regulation also describes the method of computing air emission limit of PCDDs/PCDFs congeners to be based on Toxicity Equivalency Factors (TEFs). Appendix A also listed the Toxicity Equivalency Factors for PCDDs/PCDFs congeners.

Apart from the sources of PCDDs/PCDFs, their fate and transportation are also of considerable importance. The environmental fate and transport of PCDDs/PCDFs, and their ambient concentrations are dependent on numerous factors including local sources, source emission strengths, and meteorological conditions. The fate and transport of PCDDs/PCDFs enter the food chain via atmospheric deposition. Many airborne sources of PCDDs/PCDFs are contributed by the combustion of wastes and fuels. PCDDs/PCDFs also accumulate in the soil through herbicide/pesticide application and leakage from landfill waste sites (Dwernychuck et al., 2002). These pathways are more important within localized areas with specific problems. Though PCDDs/PCDFs are sparingly soluble in water, aquatic environments have significant amount of PCDDs/PCDFs as a result of their deposition and adsorption to soils and sediments (Dwernychuck et al., 2002).

According to De Vito and Gallo, (2000), PCDDs/PCDFs are chemically and biologically stable as well as relatively lipophilic. For these reasons they bioaccumulate in aquatic organisms. De Vito and Gallo, (2000) reported the pharmacokinetics data on PCDDs/PCDFs which demonstrated that the half-lives of dioxin in humans range from 1 year to more than 20 years depending on their congeners. This aspect is also one of the reasons why PCDDs/PCDFs has received great interests in current research.

At present, it is well-known that, in many countries, emissions from municipal, medical and hazardous waste incinerators can be considered as the major contributor of PCDDs/PCDFs emission into air (Abad et al., 1997a, Basham and Whitwell 1999, Oh et al., 1999, Baker and Hites, 2000, Abad et al., 2000a, Chi et al., 2005, Kim et al., 2008, Aurell and Marklund, 2009, Li et al., 2010, Zhang et al., 2010). However there is lack of information on the PCDDs/PCDFs study done whether in ambient air or in soils even though there were several incinerators of different types in operations for many years at certain places throughout Malaysia. This study is to explore the environmental level of PCDDs/PCDFs especially in ambient air and soils at selected environment in Malaysia. Furthermore the need to survey PCDDs/PCDFs levels in the environment especially in the vicinity of the incinerators has increased with increasing public concern about these compounds due to their persistence and toxicity properties.

In view of analytical aspect, the most fundamental need in PCDDs/PCDFs research is to isolate and purified PCDDs/PCDFs compound from the co-extracted contaminants of samples for the purpose of identification and quantitation of their level in the environment. This isolation and purification processes which are commonly known as sample preparation method is another major concern because their presence in environmental media is usually in traces concentrations and therefore demand complex procedures as well as highly sensitive and reliable instrument for very low detection limit (Rappe and Buser, 1989).

There are several methods of PCDDs/PCDFs analysis (US EPA methods, 1991, 1994, 1997a, 1997b, 1998, 1999 and 2000, German Guidelines VDI 3498, 2002, and Japan International Standards, JIS); however, generally, the analysis has to go through the processes of sampling, extraction, cleanup and finally identification and quantification. These processes are quite complex, costly and time consuming; it has high demands for well trained personnels especially at the extraction and the cleanup stages due to trace presence of the contaminants in matrix. Since it is usually present at low concentration, the standard detection unit used for its measurement is in picogram per cubic meter (pg/m^3).

The extraction process of PCDDs/PCDFs from samples normally involves solvent extraction method such as Soxhlet Extraction method (SE) and Accelerated Solvent Extraction method (ASE); these methods requires the use of solvents such as toluene and acetone. Additionally, the cleanup method involves several adsorption-separation columns such as silica column, alumina column and activated carbon column as well as high volumes of solvents such as hexane, toluene and dichloromethane in order to isolate and purify the PCDDs/PCDFs from co-extracted contaminants present in the samples. This step is necessary before it could be analysed using High Resolution Gas Chromatograph - High Resolution Mass Spectrometer (HRGC-HRMS).

Studies conducted on the analysis of PCDDs/PCDFs especially in enhancing the cleanup process using locally available adsorbent materials such as activated carbon adsorbent is still lacking. Investigation on the performance of palm kernel shell activated carbon as the adsorbent in the cleanup process of PCDDs/PCDFs analysis is novel and yet to be carried out in Malaysia. Although from the engineering and cost standpoints, the automated cleanup process is convenient, the cost of adsorbents used in this automated process particularly activated carbon is quite expensive and its procurement problematic, especially for developing countries. In order to reduce the cleanup cost, an alternative adsorbent material which is effective but cheaper in cost compared to the disposable adsorbents that are manufactured for the automated process, would be of great benefit to the PCDDs/PCDFs analysis. Due to the extensive palm oil industry in Malaysia (Basiron and Weng, 2004), palm kernel shell wastes are found in abundance and may therefore proved to be advantages as an alternative material for activated carbon in this analysis.

The study also involves some modification on the length of adsorbent columns by replacing the commercially adsorbent columns with the laboratory-prepared adsorbent columns. From the analyst standpoint, modifications of the adsorbents column may benefit the analyst by reducing the cost of cleanup process. The modification also involves the fabrication of the cleanup tool to incorporate the modified adsorbent columns prepared. Hence, the purpose of this research was also to evaluate the suitability of a prepared palm kernel shell (PKS) activated carbon as an alternative to activated carbon used in automatic cleanup techniques, particularly for the isolation and purification of PCDDs/PCDFs from other contaminants during sample extraction. For this reason, the process of PCDDs/PCDFs purification practices in developing countries can be economically minimized by the use of this modified cleanup system which intergrates the palm kernel shell activated carbon in the adsorbent columns and more over, the column length can be adjusted.

1.2 Statement of the Problem

At present, important data pertaining to the distribution and dispersion of PCDDs/PCDFs congeners in air and soil within the vicinity of industrial, hazardous and clinical wastes treatment facilities in this country is still lacking due to limited research. Similarly, the major aspect on the emission of PCDDs/PCDFs from different types of incinerators that may contribute to elevated PCDDs/PCDFs concentrations in air and soil as well as source is still puzzling. No doubt, such data are important for decision making process on pollution control and management especially in setting up industrial incinerators and developing national policies and regulations regarding PCDDs/PCDFs acceptable levels. However, due to the lengthy and costly process of the extraction and cleanup of the PCDDs/PCDFs samples, development of such policies and regulations have to be dependent on secondary data or literatures from temperate countries. Consequently, the development of policies and regulations pertaining to PCDDs/PCDFs control will suffer from a number of difficulties due to lack of defensible, definitive and confirmatory data.

In the early years, researchers were largely unsuccessful in determining the levels of PCDDs/PCDFs in the environment, mainly because of the lack of appropriate methods. Currently, with the development of analytical methods and equipments, trace levels PCDDs/PCDFs, with detection limits down to picogram per kilogram (ppt) of the contaminants could be reported (Rappe and Buser, 1989). Presently, PCDDs/PCDFs cleanup could easily be conducted by using the automated PowerPrep™ System manufactured by Fluid Management System Inc. This system is comprised of integrated cleanup multicolumns of silica, alumina and activated carbon, as well as pumps and computerised system that could purify PCDDs/PCDFs extract in a single cleanup unit.

The purified PCDDs/PCDFs extract could subsequently be analysed for the presence of various congeners by using HRGC-HRMS system. However, the cleanup columns used are quite costly (US Dollar 57 per sample treatment) and required the use of large volume of solvents (a total of 834 mL per sample) comprising of hexane, toluene and dichloromethane (PowerPrep™ Operation Manual). These factors significantly influence the cost of operating the system and subsequently affect the overall frequency of PCDDs/PCDFs sampling analysis especially by industries and hazardous waste facilities to comply with the increasingly stringent regulation on PCDDs/PCDFs emission monitoring from industrial incinerators.

The majority of studies on cleanup methods used adsorbent materials such as silica, alumina and activated carbon for low concentration contaminants analysis such as PCDDs/PCDFs. Activated carbon used are normally produced from plant materials such as wood, nut shells, fruit stones, almond shell, pistachio shell, walnut shell, etc (Hayashi et al., 2002, Aygun et al., 2003, Stavropoulus and Zabaniotou, 2005). However, indigenous materials from tropical countries such as palm kernel shells have not been exploited as a value-add adsorbent material particularly for PCDDs/PCDFs analysis. In addition information in the literature on the use of this indigenous materials particularly in Malaysia is still scarce. Most literature discuss the use of palm kernel shell activated carbon in the areas of wastewater treatment and air pollution control (Hussein et al., 1996, Guo and Lua, 2001, 2002a, 2002b, Che Ibrahim, 2006).

It is worth mentioning that the air samples matrix collected for PCDDs/PCDFs analysis do not significantly interfere with the other contaminants as compared to soil samples. It is observed that the adsorbent columns such as silica, alumina and carbon columns used for the cleanup process for air and soil samples are of equal length. Normally, for samples with less interference from other contaminants, it is sufficient to use a shorter column for the cleanup in order to minimise cost and wastage of absorbents and solvents used. This study explores an alternative solution to minimise the cost and wastage through the use of local materials. Another factor that significantly contributed to the problem of the cleanup method is the complexity involving high maintenance of the instrument and solvent flow setup of the automated PowerPrep™ System.

1.3 Significance of the Study

This study contributes to the assessment of the real time PCDDs/PCDFs level in ambient air and soil particularly near the industrial, clinical and the hazardous waste disposal facilities. Research has found that the significant level of PCDDs/PCDFs that could be easily detected are within the vicinity of the incinerators (Ohsaki et al., 1995, Sandalls, 1998, De Vito and Gallo, 2000,McKay, 2002, Uegaki and Otani, 2006, Li et al., 2008, Colombo et al., 2009, Caneghem et al., 2010). The data obtained will provide firm basis for justifying an appropriate emission control limit for dioxins and their congeners in air and soil generated from the industrial areas as well as hazardous and clinical wastes disposal facilities. This study also demonstrates the applicability of the generated dioxins emission rate for quantifying the distribution and dispersion of the congeners by data fitting into an established atmospheric dispersion model.

Another contribution of this study is in the applicability of the new Malaysian regulation with respect to ambient air and soil sampling and analytical method for PCDDs/PCDFs. This study is timely because of the new regulation that focuses more on sampling and analytical method employed for PCDDs/PCDFs levels emitted from incinerator stacks only. More importantly, this study also explores an alternative sampling strategy or model that is useful for the sampling of PCDDs/PCDFs in environmental samples (ambient air and soils) without immediately embarking into stack emission sampling strategy commonly practiced by the enforcement agencies and industries. This study will assess the applicability as preliminary predictors for overall screening prior to direct investigation on multiple sources of PCDDs/PCDFs contaminants from stack emission. The feasibility of the outcome of this study may assist in minimizing environmental management bureaucracy and enforcement complexity and resources.

As mentioned earlier, the current cleanup method in PCDDs/PCDFs analysis is based on a fully automated system with integrated multicolumn (silica, alumina and activated carbon columns) cleanup and computerised control pump. State-of-the-art automated PowerPrep™ System is very costly in terms of consumables usage as well as maintenance of the instruments. The modified cleanup system as reported in this study will achieve optimal results for purified PCDDs/PCDFs with reasonable savings on cost of solvent and multicolumn used without affecting the analysis time of each sample, i.e. within 2-3 hours. Thus, the significant contribution of this study is to provide an alternative reliable technique on the performance of the cleanup system for PCDDs/PCDFs samples at a reasonable cost and efficiency comparable to the automated cleanup method and also as a model for future practice.

Another significant contribution of this study is that it has explored the potential use of activated carbon prepared from palm kernel shell wastes as a component in the modified cleanup system for determining the trace level of PCDDs/PCDFs. The automated cleanup system uses the ready-made multicolumn including activated carbon column, which costs very much higher than the columns prepared in this study (refer to Table 4.20). The automated PowerPrep™ System uses PX21 activated carbon which is generated from mixture of petroleum coke, coconut shell char and other raw materials (Fluid Management System Inc). Thus, the viability of activated carbon from palm kernel shell wastes as the adsorbent will also contribute significantly to the literatures on trace analysis of organic chemicals especially PCDDs/PCDFs analysis.

1.4 Hypothesis

The major objective of the study was to evaluate the level of PCDDs/PCDFs in air and soil in selected industrial area in Malaysia. It is predicted that the level of PCDDs/PCDFs in soils samples in the selected areas are higher than the levels in air due to the continuous deposition of the pollutant. It is hypothesized that the level of PCDDs/PCDFs in the Malaysia environment is comparable to the levels obtained from the rest of the world.

The next main objective of this study was to investigate the feasibility of using the custom-made palm kernel shell (PKS) activated carbon column by integrating it with the silica and alumina columns to purify PCDDs/PCDFs extract using a laboratory fabricated modified cleanup system (MCS). The MCS is a new idea of exploiting the adsorptive capacity of palm kernel shell activated carbon in the purification process. It is hypothesized that MCS can be a viable and effective technology and provide an alternative to automated commercial cleanup technology for PCDDs/PCDFs analysis from environmental samples (air and soil). Recovery performance testing on the MCS was conducted with PCDDs/PCDFs standards solutions to study the purification capacity of the system. Subsequently, the MCS performance studies were conducted to investigate the PCDDs/PCDFs level in air and soil resulting from industrial incinerator stacks emission within the vicinity of industrial and unpolluted sites. The specific objective of this study to test the above hypothesis are enumerated below.

1.5 Objectives of the Study

The specific objectives are:

(a) To assess the level of PCDDs/PCDFs in ambient air and soil collected from the vicinity of three selected industrial sites (Prai, Taiping and Bukit Pelanduk) and a selected pristine area (Kuala Tahan National Park) in Malaysia.

(b) To evaluate the possible distribution of PCDDs/PCDFs dispersed from the selected industrial sites specifically from stacks emission of industrial, clinical and hazardous wastes treatment facilities; the data will be fitted into Gaussian air dispersion model to calculate the PCDDs/PCDFs emission rate in order to demonstrate its applicability to predict the ambient concentration of PCDDs/PCDFs from the incinerators stack at a certain distance.

(c) To characterize the adsorptive capacity of laboratory prepared activated carbon from candidate palm kernel shell (PKS) wastes, and conducting preliminary studies to evaluate performance characteristics of modified cleanup columns comprising the PKS activated carbon and activated chromatography grade of silica and alumina adsorbents, integrated with the MCS.

(d) To compare the effectiveness of the MCS with those of commercial automatic cleanup system (PowerPrep^{TM} System) in cleanup process for PCDDs/PCDFs extract from spiked and real samples.

1.6 Limitations of the Study

Ideally, in the ambient air PCDDs/PCDFs sampling, the site chosen should be based on the wind direction. Theoretically, the concentrations of PCDDs/PCDFs in air are higher in the areas located in downwind direction and low in the other opposing sites. However, the sampling points have to be selected according to accessibility and availability of power supply even though they are not in the downwind direction.

Preferably, the best practice of PCDDs/PCDFs study is to compare PCDDs/PCDFs levels emitted from incinerators stack with the levels in ambient air and soil within the vicinity of the incinerators study areas. However, due to some tight security procedures within the restricted area of these incinerators, the study areas are limited to these sampling processes. Moreover, owing to geographical distances, variation in climate condition, time, number of air sampler units and resource constraints adds further to the limitation of PCDDs/PCDFs sampling processes.

A study on PKS activated carbon characteristics can be very broad and cover various aspects (Slejko 1985, Smith, 1992 and Jumasiaha et al., 2005). However, the emphasis of this research was based on the adsorption isotherms data determined by Micromeritics ASAP 2000 for the purpose of PCDDs/PCDFs cleanup process. The candidate samples of PKS wastes converted into laboratory prepared activated carbon were obtained from an existing palm oil mill at Kuala Gula, Taiping District, Perak.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this study, several different scientific literature topics of interrelated subjects were reviewed. Although the major topics are on the PCDDs/PCDFs level assessment and cleanup method, other important topics include basic information of PCDDs/PCDFs, behaviour and modelling studies on PCDDs/PCDFs in environment, cost analysis and legislation pertaining to PCDDs/PCDFs control. The amount of published literatures for PCDDs/PCDFs cleanup analysis is vast. But most of the earlier works tend to be the predecessors of the most recent literature of the subject. These temporal progresses help in understanding the advancement of the knowledge for both chemistry of PCDDs/PCDFs and PCDDs/PCDFs analysis methods. Various topics will be covered in this chapter.

2.2 Basic Information of PCDDs/PCDFs

2.2.1 Structures of PCDDs/PCDFs

PCDDs/PCDFs are two series of almost planar tricyclic aromatic compounds with very similar chemical properties and can be represented by general formulas as in Fig 2.1. Chlorine atoms can be attached to 8 different carbon atoms on the molecule, numbered from 1 to 9. These compounds differ from one another primarily by the location and number of chlorine atoms on the molecule, and their degree of toxicity varies greatly. The higher the number of chlorine atoms that are on the molecule, the lower the toxicity (Rappe and Buser, 1989).

In chemical notation, the site number of the chlorine atom refers to these congeners. For instance, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, (commonly abbreviated as 2,3,7,8-TCDD, or just TCDD), is a PCDD congener with chlorine atoms located at the 2,3,7 and 8 positions. The term "dioxin" is also sometimes used to refer specifically to 2,3,7,8-tetrachlorodibenzo-p-dioxin, the most toxic and thoroughly researched and widely publicized form of dioxins and furans. It is one of 22 possible isomers of tetrachlorodibenzo-*p*-dioxin.

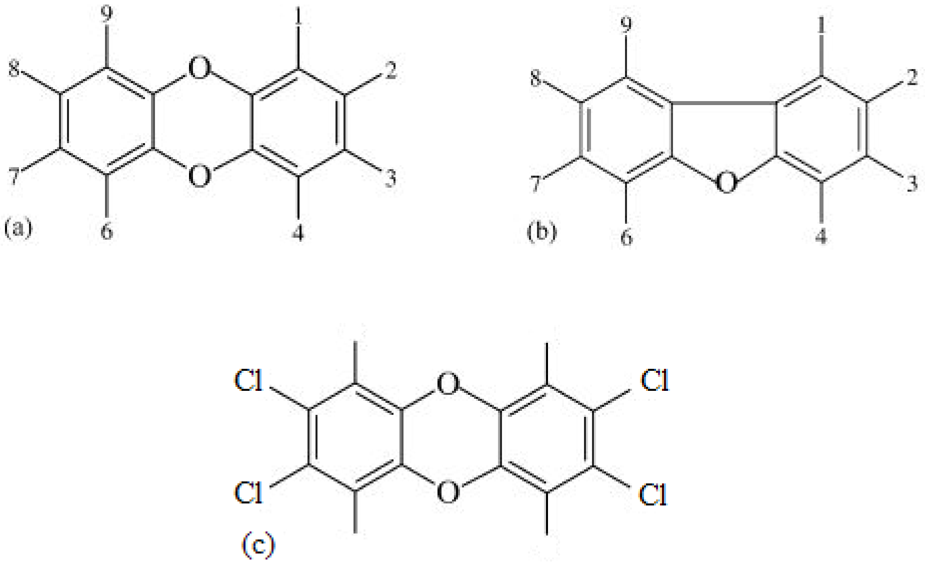

Figure 2.1: Molecular Structure of (a) PCDDs, (b) PCDFs and (c) 2,3,7,8 – TCDD

The term isomer refers to comparisons between compounds with the same empirical formula, in all there are 75 dioxins and 135 furans (Rappe and Buser, 1989, McKay, 2002). Table 2.1 shows the number of PCDDs/PCDFs isomers with the seventeen 2,3,7,8 – substituted isomers in toxic tetra-,penta-, and hexachloro groups.

Table 2.1 Summary of PCDDs/PCDFs Isomer

Compounds	**Number of PCDDs/PCDFs isomer**	
	Total	**2,3,7,8- type***
MonoCDDs	2	-
DiCDDs	10	-
TriCDDs	14	-
TetraCDDs	22	1
PentaCDDs	14	1
HexaCDDs	10	3
HeptaCDDs	2	(1)
OctaCDDs	1	(1)
Total	*75*	*7*
MonoCDFs	4	-
DiCDFs	16	-
TriCDFs	28	-
TetraCDFs	28	1
PentaCDFs	38	2
HexaCDFs	16	4
HeptaCDFs	4	(1)
OctaCDFs	1	(1)
Total	*135*	*10*

* Number of 2,3,7,8-substituted isomers; number in parentheses are not in the toxic tetra-,penta-, and hexachloro group.
(Source: Rappe and Buser, 1989)

2.2.2 Physical and Chemical Properties of PCDDs/PCDFs

The properties of PCDDs/PCDFs influence their availability, toxicity, fate and the analysis of the compounds. The knowledge of their properties is crucial to the understanding as well as modelling of the environmental transport and transformation of the compounds. Among the most important properties of these compounds are solubility, vapour pressure and photolysis. Rappe and Buser, (1989) reported that PCDDs/PCDFs are almost insoluble in water. However, PCDDs/PCDFs are slightly soluble in most organic solvents. Table 2.2 shows the solubility of 2,3,7,8 – TCDD in some common organic solvents and water.

Table 2.2 Solubility of 2,3,7,8 – TCDD in various solvents

Solvent	**Solubility at 25°C g/L**
O-Dichlorobenzene	1.8
Chlorobenzene	0.8
Perchloroethylene	0.68
Chloroform	0.55
Benzene	0.47
Acetone	0.09
Dimethylsulfoxide	< 0.1
Methanol	0.01
Water	2×10^{-7}

(Source: Rappe and Buser, 1989)

Another important property of PCDDs/PCDFs as stated by Ryan et al., 2005 and Mader and Pankow, (2003) is vapour pressures which play an important parameter for modelling of the environmental fate and incinerator behaviour of PCDDs/PCDFs. Vapour pressure can be used to assess the distributions of a chemical among air, air particles, water, soil and plants. Wu, et al., (2005) stated that PCDDs/PCDFs in the environment could be transformed by photo degradation. Photolysis half-life ($t_{1/2}$) is an important parameter in characterizing photochemical reactions of PCDDs/PCDFs (Kim and O'Keefe, 2000).

Geyer et al., (2002) claimed that the half-lives ($t_{1/2}$) of PCDDs/PCDFs in organisms including humans is an important criterion in hazard assessment. This value provides a convenient measure for the persistence of PCDDs/PCDFs in living aquatic and terrestrial organisms. The average half-life of TCDD in adult humans is approximately 2840 days, while in Sprague-Dawley rats is 19 days, which is about 150 times that in humans. This factor was frequently quoted in the half-life calculation of other PCDDs in humans.

2.2.3 Toxicity

Although PCDDs/PCDFs have been found in the environment in low concentration, their toxic property is a major concern because it is extremely toxic to human. PCDDs/PCDFs are side product contaminants in the production of 2,4,5 – Trichlorophenoxyacetic acid, which has led to restrictions in its use (Sawyer et al, 1994). The toxicity of the 210 individual chlorinated PCDDs/PCDFs congener varies widely. Seventeen of these congeners have chlorine atoms in all of the 2, 3, 7 and 8 positions, and are considered to be the most toxic (Hay, 1982, Rappe and Buser, 1989, McKay, 2002). As quoted earlier, the congener with the greatest toxic potency, and for which the greatest amount of toxicological information is available, is 2,3,7,8-TCDD.

Since 2,3,7,8-TCDD is the most toxic, and by convention is assigned a toxicity rating of 1.0 (called a toxic equivalent factor or TEF). The remaining 2,3,7,8-positional congeners are then assigned lower TEFs comparable to their toxicity, relative to that of 2,3,7,8-TCDD. The toxicity of any mixture of PCDDs/PCDFs, relative to 2,3,7,8-TCDD, can then be expressed by multiplying the concentrations of the 2,3,7,8-positional congeners present in the mixture by their respective TEF. The resulting products for each congener are called toxic equivalents (TEQ), with units identical to that in which the concentrations of the individual congeners are expressed (McKay, 2002).

Indeed, currently, most international standards of PCDDs/PCDFs measurement were based on TEQ (Dyke and Stradford, 2002, Quaβ et al.,2004, Wittsiepe et al., 2005, Murphy and Morrison, 2006 and 2007, Hong et al., 2009, Gao et al., 2009, Li et al., 2010). There are two schemes of reporting the toxicity of PCDDs/PCDFs i.e., i-TEQ which is the older International Toxic Equivalent (i-TEQ) scheme by the North Atlantic Treaty Organisation (NATO) initially set up in 1989 and later extended and updated and WHO-TEQ which is more recently, the World Health Organization (WHO) suggested modified Toxic Equivalency Factor (TEF) in 1998 than re-evaluated in 2005 (Wittsiepe and Wilhelm, 2007). On average, the result of TEQ-calculations is about 10% higher when i-TEFs are used compared to when WHO-TEFs are used. All quantitative results reported in this thesis are in international-TEQ (i-TEQ). The i-TEQ of the mixture is obtained by summing the individual i-TEQ. The i-TEF and WHO-TEF for the seventeen 2,3,7,8-positional congeners of PCDD/PCDF are presented in Table 2.3; all other congeners that may be present in a sample are assigned a TEF value of 0.0. The summation of individual TEQ for a mixture of PCDDs/PCDFs is termed the international toxic equivalent or i-TEQ of the mixture. (McKay, 2002, Dyke and Stratford, 2002 and Wittsiepe and Wilhelm, 2007).

Table 2.3: Toxicity Equivalency Factors (i-TEF) For Determining of The Toxicity Equivalence (TEQ) of PCDDs/PCDFs

Congener	**i-TEF**	**WHO-TEF**
PCDDs		
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.001	0.0003
PCDFs		
2,3,7,8-TCDF	0.1	0.1
2,3,4,7,8-PeCDF	0.5	0.3
1,2,3,7,8-PeCDF	0.05	0.03
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.001	0.0003

Source: Wittsiepe and Wilhelm, 2007

2.2.4 Origin of PCDDs/PCDFs

PCDDs/PCDFs were detected for the first time in emissions of municipal solid waste incinerators in 1977 (Abad et al., 1997a). Then Dyke et al., (1997) reported that PCDDs/PCDFs were mostly found in the stack gas emission of solid waste incinerators. They are persistent and bio-accumulative chemicals. They have never been commercially manufactured but are unintentional by-products of incineration and chemical processes that involve chlorinated substances. These PCDDs/PCDFs are widespread contaminants in the environment. They have been found virtually in almost all areas of the globe including marine and fresh water ecosystems, urban and rural settings and remote areas such as the polar region.

Many surveys dealing with sources of PCDDs/PCDFs have been published within the last years. Huang and Beukens, (1995) studied the PCDDs/PCDFs from municipal solid waste incinerator (MSWI), concluded that very high PCDDs/PCDFs formation in municipal solid waste incinerator was due to highly sooting flame, highly metal content and unsteady state combustion in the incinerator compared to other sources. Fiedler, (1996) found that sintering plant for recycling materials and sintering plant for iron-ore were among the major sources of the PCDDs/PCDFs emissions into the environment instead of incinerators. Coutinho et al., (1998) found that hospital produced higher PCDDs/PCDFs emission level compared to MSWI, traffic, and landfill gas in Lisbon and Porto regions. Buekens et al, (2000) compared the PCDDs/PCDFs level from iron and steel manufacturing plants, copper smelters and aluminium plants with MSWI and found that the PCDDs/PCDFs congener produced were comparable.

This similarity in congeners was also found in coal combustion studied by Gullett and Wikstrom, (2000). Several studies in Taiwan and Japan also resulted that MSWI was the major source of PCDDs/PCDFs emission to the environment (Chang and Lin, 2001, Cheng et al., 2003, Chang et al., 2003, 2004). As reported by Assuncao et al., (2005), PCDDs/PCDFs were also found in the site where there is influence of industrial activities and heavy vehicular traffic fuelled by gasohol, diesel, and ethanol when studied the PCDDs/PCDFs sources in the Sao Paulo city in Brazil. Gao et al., (2009) also concluded that the stack gas emission from hospital waste incinerator in China was also a major source of PCDDs/PCDFs even though the emission level meets the China emission standard (0.5 ng i-TEQ/Nm^3. A recent study by Mai et al., (2007) in Southern Vietnam revealed that soils in the areas were highly contaminated with PCDDs/PCDFs (47 – 437 i-TEQ ng/kg) compared to other studied areas. It was concluded by Mai et al., (2007) that the contamination was took place since the Vietnam War 30 years ago.

From the information available three main categories of PCDDs/PCDFs sources can be identified: chemical-industrial sources, thermal or combustion sources, and reservoir. The industrial sources include manufacture of chlorinated chemicals, pulp and paper industry, steel industry, dry cleaning distillation residues, and others. Incinerators for municipal solid waste, clinical waste and hazardous waste, sewage sludge, sintering plant and various types of recycling plants as well as diffuse sources such as automobile exhaust, home heating and combustion of landfill gas were among the thermal or combustion sources. Reservoirs include sewage sludge, compost, and contaminated soils. Under certain environmental conditions, such as composting, micro-organisms can produce PCDDs/PCDFs from chlorinated phenolic compounds (De Vito and Gallo, 2000, Gao et al., 2009).

Several natural processes can result in the production of PCDDs/PCDFs. Hepta- and Octa- chlorodibenzo-p-dioxin are the predominant congeners produced in forest fires. However current estimates of all emissions sources suggest that forest fires are a minor source compared to anthropogenic sources (Kim et al., 2003, 2005 and Shih et al., 2008). Table 2.4 shows PCDDs/PCDFs emission from various sources.

Table 2.4 : PCDDs/PCDFs emission from various combustion sources

Combustion sources	**PCDDs/PCDFs in flue gas (i-TEQ ng/Nm^3)**	**PCDDs/PCDFs in fly ash (i-TEQ ng/Nm^3)**
Municipal waste incineration	0.2 – 63	1 – 28
Hazardous waste incineration	0.1 – 0.5	NA
Wood combustion:		
- Natural wood	0.02 – 1.8	NA
- Waste wood	2.7 – 14	0.08 – 8
Coal combustion	ND	ND – 10
Plastics pyrolysis	Detected	Detected
Oil combustion:		
- Oil furnace	0.03 – 0.3	NA
- Leaded gasoline in vehicle	0.01 – 0.06 (ng/L)	NA
- Lead-free gasoline in vehicle	0.035 (ng/L)	NA
Gas combustion	0.07 – 100	NA

NA = not available, ND = not detected
(Source: Huang and Buekens, 1995)

2.2.5 PCDDs/PCDFs Formation from Waste Incineration

Combustion systems are a primary source for the production of PCDDs/PCDFs. Included in this category are waste incinerator, such as municipal solid waste, medical waste, sewage sludge, and hazardous waste incinerators. At present, it is well-known that, in many countries, emissions from municipal, medical and hazardous waste incinerators can be considered as the major contributor of PCDDs/PCDFs emission into air. Abad et al., (1997a), reported that the ambient air PCDDs/PCDFs determinations in Northern Spain studied areas were in the range of 0.05-0.55 pg I-TEQ/Nm^3. Oh et al., (1999) found that PCDDs/PCDFs emission of municipal solid waste incinerators (MSWI) exhibited a large variation (0.07~36.5 ng I-TEQ/Nm^3) and the emission of industrial waste incinerators (IWI) was the least of all incinerators following a study in Korea.

However, a study by Abad et al., (2000a) indicated that stack gas levels constitute a minor contribution to the total dioxin emitted by the MWI which complies with the limit of 0.1 ng i-TEQ/Nm3, but the highest concentration of PCDD/PCDF was found in fly ash. Caserini et al., (2004) reported that PCDDs/PCDFs level in proximity to MSWI plants in Italy were found to be in a range of 0.022 – 0.125 pg i-TEQ/Nm^3 in the air samples and 0.7 – 1.5 ng i-TEQ/kg in the soil samples. Chi et al., (2005) reported that the average PCDDs/PCDFs concentrations from stack gases of two studied MSWI in Taiwan were 0.17 and 0.043 i-TEQ ng/Nm^3 respectively. Coutinho et al., (2007) found that the presence of a seasonal pattern is very clear in the data obtained in Porto and Lisbon. The mean value (0.067 ng i-TEQ/Nm^3) and the concentration range (0.010 – 0.171 ng i-TEQ/Nm^3) measured in Porto during summer are significantly lower than during winter (mean: 0.224 ng i-TEQ/Nm^3, range: 0.069 – 0.817 ng i-TEQ/Nm^3). Note that the ratio of summer to winter values is approximately 1:3 for the mean but it reaches a ratio of about 1:6 at the extreme values.

In national monitoring of PCDDs/PCDFs in environmental media around incinerators in Korea, Kim et al., (2008) reported the PCDD/DFs concentrations in the flue gas samples ranged from 0.02 to 16.41 ng i-TEQ/Nm^3, in the air samples ranged from 0.032 to 0.965 pg i-TEQ/Nm^3 and in the soil samples between N.D. and 153 ng i-TEQ/kg-dry. The average PCDD/PCDFs levels in the soil samples decreased with increasing distance from the incinerator. Air monitoring of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (PCBs) was carried out in June 2008 and January 2009 by Li et al., (2010) to investigate the concentrations, profiles and estimated the potential inhalation risks to the local residents around a steel plant area in northeast China. The WHO-TEQs of PCDDs/PCDFs obtained was in the range of 0.003 – 0.247 i- TEQ pg/Nm^3.

2.2.5.1 Medical Waste Incineration (MWI)

Incineration has been the most widely used treatment technology for the disposal of medical wastes. The major advantages are a significant reduction in the volume of material, and destruction of pathogens and hazardous organics. The main disadvantage is that incineration may emit trace amounts of unwanted pollutants such as PCDDs/ PCDFs, usually in cities due to the typical location of hospitals. Typically, medical waste is incinerated locally at the hospital or any other medical facility in small furnaces in a batch-type mode (United Nation Environment Programme, 2001).

Medical waste is considered to be all type of wastes generated due to medical activities regardless if these activities take place in a hospital or are performed by a medical doctor, dentist or any other physician. The waste generated contains in many cases infectious materials, secretes, blood, pharmaceuticals and packaging materials and/or tools used during or for the medical treatment of people or animals. Further, due