Monitoring of Polychlorinated Dibenzo (p) Dioxins and Furans in Cement Kiln Emission Using Different Kinds of Fuel

S. El-Kabbanya, H. Khairallah, A. El-Marsafey and S. El-Safty
1Department of Pesticide, Faculty of Agriculture, Cairo University, Egypt
2Central Laboratory of Residue Analysis of Pesticides and Heavy Metal in Food, Agriculture Research Center, Cairo, Egypt

Corresponding Author: S. El-Kabbanya, Department of Pesticide, Faculty of Agriculture, Cairo University, Egypt

ABSTRACT

Monitoring of polychlorinated dibenzo (p) dioxins and furans (PCDD/Fs) in cement kiln emission were conducted using different kinds of fuel at different location in Egypt. A total of 97 samples provided data on PCDD/F congener concentrations during which the kilns combusted a varied mix of fuels, including coke, mazout and natural gas. The use of coke to fuel the kilns was found to generate significantly different emission-profiles relative to the use of mazout rather than natural gas, the total PCDD/Fs WHO-TEQ levels in coke, mazout and natural gas were determined by High Resolution Gas Chromatography-High Resolution Mass Spectrometer (HRGC-HRMS) ranged from 0.282-0.001 (ng WHO-TEQ Nm$^{-3}$) in mazout, natural gas ranged from 0.774-0.001 (ng WHO-TEQ Nm$^{-3}$) and coke ranged from 0.026-0.001 (ng WHO-TEQ Nm$^{-3}$). A total of 9 samples provided data on PCDD/Fs congener concentrations from ambient air in 4 different Egyptian governorates. Results obtained confirm the presence of PCDD/F in Natural gas followed by Mazout followed by coke 30% with mazout 70%, this means that the different operating conditions must be controlled. All of the kiln emission profiles were found to be same markedly from profiles in ambient air. However, the small absolute dioxin emission rates from the kilns suggested that kiln impacts would be detectable via ambient air monitoring.

Key words: Monitoring, PCDD/Fs, cement, Egypt

INTRODUCTION

Egypt is an Afro-Asiatic country spanning the northeast corner of Africa and southwest corner of Asia. Egypt is the largest country in North Africa and the Arab World, the third-largest in Africa and the fifteenth-most populous in the world. The cement industry is today distributed throughout the world and in 2003 produced approximately, 1940 million t of cement (Cembureau, 2009). The cement industry consumes billions of tons of raw materials and more than 300 million t of coal and is believed to contribute to about 5% of the global anthropogenic CO$_2$ emissions (Oss and Padovani, 2003). Approximately, 60% of the CO$_2$ originates in calcination of limestone; the remaining 40% is due to combustion of fossil fuel. Depending on how the raw material is handled before being fed to the kiln, basically four different types of rotary kiln processes can be distinguished: The dry, semi-dry, semi wet and wet processes. Egypt is one of the greatest cement producers all over the world with 13 companies and the leading country in the Middle East, Africa and the Arabian Region with a total production capacity of 50 million t of cement. Vertical shaft kilns is still the dominating production technology in China accounting for 60% of the Chinese production
(approximately, 4000 vertical shaft kilns existed in 2005), which was 1065 billion t in 2005 and accounting for approximately, 50% of the world production (Karstensen, 2006b). Major sources of dioxins (PCDDs and PCDFs) in the environment are combustion of waste materials and many other high-temperature processes commonly used in industrial settings (Lustenhouwer et al., 1980). The chemical reactions involved in dioxin formation are extremely complex and heterogeneous (Huang and Buekens, 1996). Dioxins are generated in two places in an incinerator, a combustion chamber and a cham ber for exhaust gas treatment, such as an electric precipitator. In particular, it is quite difficult to know precisely, what the formation mechanisms of dioxins in a combustion chamber are because their formation varies over different combustion conditions. Combustion of organic material generates, among other things, myriad Products of Incomplete Combustion (PICs). Since, the late 1970s, combustion chemists and others have studied the many interacting factors that appear to govern the extent and pattern of PCDD/F emissions from combustion sources and industrial processes. The relative amounts of various PCDD/F congeners emitted from a given source (the source’s congener profile or congener “fingerprint”) are of interest for two primary reasons. First, the pattern of congeners emitted from a source might provide insight into the processes that lead to PCDD/F formation. Second, the fingerprints generated from various sources or source types, when compared with the profiles found in air or other environmental media might allow identification and apportionment of the sources affecting specific locations. The PCDD/F emission data have been published for a number of cement manufacturing facilities (Zemba et al., 2011) but few studies have focused on PCDD/F congener profiles. Abad et al. (2004) found no marked differences in PCDD/F emissions or congener profiles in a facility using tires and meat meal as alternative fuels. However, the problems with hazardous chemicals and wastes remain unsolved in many countries. These problems are represented by accumulation of Organo Chlorine Pesticide (OCP) residues in different environmental samples and hosting of at least 50,000 t of obsolete pesticides, as well as tens of thousands of tons of contaminated soil. Within the framework of the Africa Stockpiles Program (ASP), at regional level (i.e., African Countries), a strategic plan for monitoring and getting rid of POPs in the continent should be set up and implemented through coordination between all governments. In Egypt, for example a large amount of hazardous wastes are also produced for solid hazardous chemicals produced in the country is 12017 t annually and amount of liquid hazardous chemicals produced in the country is 4269306 m$^3$ annually, where amount of obsolete chemicals hazardous in Egypt is about 277.58 t. Most of these chemicals are used in industry, agriculture and for public health control. In particular, in the year of 2009 the amount of stockpiled Obsolete Pesticides (OPs) was estimated to constitute up to 263,500 t (metric ton or tone) in the European Union (EU), the European Neighborhood Policy (ENP), the Russian Federation and Central Asia, while for Africa was at least 50,000 t also indicated that stock piled OPs amounted to 30,000 t in Central and South America in 2010 and the amount in the Southeast Asia (SEA) was estimated at 6500 t. Similarly, a large amount of hazardous chemicals is found in other SEA countries. Several SEA countries have also conducted destruction of stock piled. The POPs in Thailand, the “National Implementation Plan of Basel Convention and the Stockholm Convention on POP’s aims to destroy all stockpiled POPs before 2025. Several treatment technologies for hazardous wastes are available in the country. Around 20% of the hazardous wastes are burnt in cement kilns, 0.02% is burnt in High Temperature Incinerator (HTI) and 79% of hazardous wastes were disposed of in secured landfills. Thermal treatment in dedicated incinerators is a proven destruction method for hazardous wastes, including hazardous chemicals and the use of treatment in cement kilns or HTI is recommended by the Basel Convention.
However, there is a risk of releasing unintentional POPs (U-POPs) and other toxic substances from the combustion into the environment. The goal of this study was to determine the dioxin emissions levels in Egyptian air with different operating conditions of the fuels and compare it with the European levels and it is availability to use alternative fuel. In this paper, we present a study of PCDD/F congener profiles in the exhaust-stack emissions from 5 different cement companies factories with more than 18 chimney around Egypt using the stack sampler (Apex Instrument 5000) tested under normal operating conditions and using a variety of fuels. A total of 9 samples provided data on PCDD/Fs congener concentrations from ambient air in five different Egyptian governorates Alex, Helwan, Cairo, Giza and beni sweaf to determine the dioxin emissions levels in Egyptian air and compare it with the European levels and it is availability to use alternative fuel.

MATERIALS AND METHODS

Chemicals and reagents: N-hexane, dichloromethane, cyclo-hexane, methanol and toluene were from Merck, HPLC grade purity not less than 99%, Silica gel and basic Alumina were purchased from Aldrich (Brockmann I, Standard grade, Milwaukee, USA). Calibration standard solutions, $^{13}$C labeled standard and $^{13}$C injection solutions as specify in EPA Method 1613B and obtained from Cambridge Isotopes Laboratories (Andover, USA).

Sampling and sample processing: The procedures of sampling method were following the Environmental Protection Agency (U.S. EPA 23) were evaluates around 97 dioxin/furan stack emission measurements collected samples during 2008-2014 were represented from 5 Egyptian cement factories with more than 18 chimney around Egypt using the stack sampler (Apex Instrument 5000). Sampling and analytical determination of PCDD/F levels in the kilns exhaust gases were performed in accordance with EPA 23. Flue gas (including dust) was extracted isokinetically from the exhaust stack via a titanium enclosed water-cooled glass probe, which rapidly cooled the sample before it entered the collection system. This collection system consisted of a condensate flask in an ice bath (receiving condensate and a part of the dust) and two collection cartridges. The first cartridge contained a flat filter and the second one a resin sorbent with proven efficiency for the separation of organic substances. The filters were followed by a gas drying tower, gas pump, gas volume meter, temperature and pressure meters. Quantification was carried out using internal/external standard mixtures. Quantitative determinations of PCDD/Fs were made using the isotope dilution method with $2, 3, 7, 8$-substituted $^{13}$C-IL internal standards and by whether supplemental hazardous fuels were used in conjunction with the use of coke.

The data represents emission levels from large capacity processing technologies, including wet and dry process cement kilns, performed under normal and worst case operating conditions with and without the utilization of a wide range of waste-derived alternative fuel. A passive air sampler comprising a Polyurethane Foam (PUF) disk impregnated with XAD-4 powder has been used. This Sorbent-Impregnated PUF (SIP) disk builds on previous work using PUF disk passive air samplers that have been effective in spatial air mapping studies of nonpolar hydrophobic chemicals without the need of electricity or expensive air sampling equipment, it is used for 28 days for sampling. Samples were taken from 5 governorates Alex, Helwan, Cairo, Giza and beni-Sweaf.

Extraction: Toulene were used for extraction for at least 18-24 h, a resin (XAD) and PUF were spiked with known amounts of mixture of $^{13}$C labeled PCDD/Fs, are extracted using Soxhlet after
mixing the Resin or PUF sample with anhydrous sodium sulfate, the extract solvent was evaporated using a rotary evaporator to concentrate the aliquot.

**Clean-up:** Clean up steps were conducted according to EPA Method (U.S.A Environmental Protection Agency, 1994), using Anthropogenic, Multilayer silica gel, Alumina and active Carbon column.

**HRGC/HRMS instrument:** Analyses were conducted using HP 6890 plus gas chromatograph coupled with Micromass/Autospec Ultima mass spectrometer operating in EI+ mode at 35 eV and with a resolution of 10,000 (5% valley). Sample injections were performed in the splitless mode on DB5 MS column (60 m, 0.25 mm id, 0.1 µm film thickness). The oven program was started from 90°C then takes 15 min, to reach 220°C then held for 15 min, then from 220-290 in 8 min then held for 17 min. Helium (Ultra high purity) at a flow rate 0.8 mL min⁻¹ was used as a carrier gas. Injector temperature was 225 C, 1 µL of the sample was injected using splitless mode.

**Quantitative determination:** PCDD/Fs were performed by an isotope dilution method using relative response factors previously obtained from five standard solutions. The TEQ concentrations were calculated guided to World health Organization-toxic equivalent factor (WHO-TEFs) in 1998 (Van den Berg *et al.*, 1998) the result values are presented in (ng WHO-TEQ Nm⁻³) for resin Multiplied by the associated WHO-TEF. It was assumed that non-detected isomer concentrations were equal to the limits of determination. As recommended by the European Regulation (EU Directive 2000/76/EU), Detection and quantification limits, as well as recoveries, for all PCDD/Fs congeners were in good agreement with requirements laying down the sampling methods and the methods of the analysis for the official control of PCDD/Fs. For each run the samples were prepared including a method blank and quality control samples are performed. All steps of Analysis were conducted according to (U.S.A Environmental Protection Agency, 1994).

**RESULTS AND DISCUSSION**

**PCDD/Fs (ng WHO-TEQ Nm⁻³) levels in different operating conditions of the fuels:** Cement kilns are known to emit (PCDD/Fs) but estimates of the amounts and patterns of these emissions vary widely. These variations may stem from a combination of factors, including the design and operating conditions of the kiln and the fuels and raw materials fed into the kiln. The mean levels measured by HRGC/MS Multiply by Toxic Equivalent Factor (TEF) (Van den Berg *et al.*, 1998) in mazout were 0.06, natural gas were 0.086, Coke were 0.008 (ng WHO-TEQ Nm⁻³) as described in Table 1 and ambient air were 0.062 (ng WHO-TEQ Nm⁻³).

**PCDD/Fs (ng WHO-TEQ Nm⁻³) levels with mazout fuel:** The mean levels measured by HRGC/MS Multiply by Toxic Equivalent Factor (TEF) in Mazout were 0.06 (ng WHO-TEQ Nm⁻³) as shown in Table 1. The range of the highest and lowest levels in all samples, No. of samples violated, Maximum levels and Sum of dioxins (ng WHO-TEQ Nm⁻³) according to Environment regulation limits in European Union (2000/76/EC).

Seventeen 2, 3, 7, 8-substituted congeners of PCDD/Fs Profile in the 26 mazout samples have been collected samples during 2008-2014 were represented from 5 Egyptian cement factories with more than 18 chimney around Egypt. The mean levels of PCDD/Fs are shown in Table 1, the profile of the PCDD/Fs in mazout samples have been shown in Fig. 1. This study shows that the ΣPCDFs
Fig. 1: PCDD/Fs (% in WHO-TEQ Nm$^{-3}$) in mazout, natural gas, coke and ambient air.

Table 1: Monitoring data of dioxin in cement samples with different fuel.

| Fuel type | No. of samples | Mean | Range | No. of samples violated | Violation (%) |
|-----------|----------------|------|-------|-------------------------|---------------|
| Mazout    | 26             | 0.06 | 0.28-0.00 | 4                       | 15            |
| Natural gas | 61             | 0.11 | 1.13-0.00 | 13                      | 21            |
| Coke      | 10             | 0.01 | 0.05-0.00 | 0                       | 0             |

Maximum levels sum of dioxins (ng WHO-TEQ Nm$^{-3}$) was 0.1.

Table 2: Mean concentration (ng WHO-TEQ Nm$^{-3}$) of dioxin congeners.

| Dioxin congeners | Mazout (%) | Natural gas (%) | Coke (%) | Ambient air (%) |
|------------------|------------|-----------------|----------|-----------------|
| 2, 3, 7, 8-TCDD  | 0.003      | 0.018           | 0.005    | 0.001           |
| 1, 2, 3, 7, 8-PeCDD | 0.009      | 0.038           | 0.016    | 0.011           |
| 1, 2, 3, 4, 7, 8-HxCDD | 0.001      | 0.006           | 0.001    | 0.008           |
| 1, 2, 3, 6, 7, 8-HxCDD | 0.001      | 0.009           | 0.001    | 0.013           |
| 1, 2, 3, 7, 8, 9-HxCDD | 0.001      | 0.007           | 0.001    | 0.010           |
| 1, 2, 3, 4, 6, 7, 8-HxCDD | 0.001      | 0.046           | 0.001    | 0.096           |
| 1, 2, 3, 4, 6, 7, 8-OCDD | 0.000      | 0.301           | 0.000    | 0.205           |
| 2, 3, 7, 8-TCDF  | 0.004      | 0.070           | 0.005    | 0.041           |
| 1, 2, 3, 7, 8-PCDF | 0.002      | 0.111           | 0.003    | 0.059           |
| 2, 3, 4, 7, 8-PeCDF | 0.017      | 0.045           | 0.032    | 0.035           |
| 1, 2, 3, 4, 7, 8-HxCDF | 0.004      | 0.092           | 0.007    | 0.065           |
| 1, 2, 3, 6, 7, 8-HxCDF | 0.003      | 0.074           | 0.005    | 0.049           |
| 2, 3, 4, 6, 7, 8-HxCDF | 0.004      | 0.040           | 0.005    | 0.032           |
| 1, 2, 3, 7, 8, 9-HxCDF | 0.001      | 0.018           | 0.001    | 0.014           |
| 1, 2, 3, 4, 6, 7, 8-HpCDF | 0.001      | 0.185           | 0.002    | 0.153           |
| 1, 2, 3, 4, 7, 8, 9-HpCDF | 0.000      | 0.011           | 0.000    | 0.024           |
| 1, 2, 3, 4, 5, 6, 7, 8-OCDF | 0.000      | 0.019           | 0.000    | 0.141           |

Sum of PCDDs 0.015 0.425 0.26 0.347 0.002 0.030 0.018 0.074
Sum of PCDFs 0.036 0.666 0.061 0.612 0.006 0.049 0.044 0.354
Sum of PCDF/PCDs 0.051 1.091 0.086 0.966 0.008 0.079 0.062 0.430

was higher than ΣPCDDs where contribute 70 and 30%, respectively from ΣPCDD/Fs. 2, 3, 4, 7, 8-PeCDF is 0.017 (ng WHO-TEQ Nm$^{-3}$), where the most abundant congener contribution was remarkable with 34% followed by 1, 2, 3, 7, 8-PeCDD is 0.009 (ng WHO-TEQ Nm$^{-3}$), which contributes about 17% and 2, 3, 4, 6, 7, 8-HxCDF is 0.004 (ng WHO-TEQ Nm$^{-3}$), which contributes about 9% from ΣPCDD/Fs as presented in Table 2.

Heidelberg cement (Haegermann, 2004a) made a comparison between kilns using a high substitution rate of alternative fuels and kilns using fossil fuel only. Nine plants with a substitution
rate of minimum 40% showed an average value of 0.007 ng TEQ m$^{-3}$ (minimum 0.001 ng TEQ m$^{-3}$, maximum 0.016 ng TEQ m$^{-3}$), while the average of eight kilns using fossil fuel only was 0.016 ng TEQ m$^{-3}$ (minimum 0.002 ng TEQ m$^{-3}$, maximum 0.031 ng TEQ m$^{-3}$). (Haegermann, 2004b). The European Cement Association reported 230 PCDD/PCDF measurements from 110 cement kilns and 11 countries in 2003 (Van Loo, 2004). The countries covered by the survey were Belgium, Czech Republic, Denmark, France, Germany, Hungary, Italy, Norway, Spain, Netherlands and United Kingdom; most countries practice co-processing of wastes. The measurements showed that the average concentration was 0.017 ng ITEQ m$^{-3}$ for all measurements. The lowest and highest concentrations measured were <0.001 and 0.163 ng I-TEQ m$^{-3}$, respectively. Overall, 98% of the 230 kilns had emission concentrations below 0.1 ng TEQ m$^{-3}$ and the majority of the kilns emitted concentrations lower than 0.01 ng TEQ m$^{-3}$. Other examples can be found from Italy (Caserini and Monguzzi, 2002), Russia (Kucherenko et al., 2001a, b) and Taiwan (Chen, 2004). These emissions factors lead to cement industry contribution estimates ranging from 5% and up to a worst case scenario estimate of 59% of total emissions by Brzuzy and Hites (1996).

**PCDD/Fs (ng WHO-TEQ Nm$^{-3}$) levels with natural gas:** The mean levels measured by HRGC/MS Multiply by Toxic Equivalent Factor (TEF) (in natural gas were 0.086 (ng WHO-TEQ Nm$^{-3}$) as shown in Table 1. The range of the highest and lowest levels in all samples, No. of samples violated, maximum levels and sum of dioxins (ng WHO-TEQ Nm$^{-3}$) for environment.

Seventeen 2, 3, 7, 8-substituted congeners of PCDD/Fs Profile in the 61 natural gas samples have been collected samples during 2008-2014 were represented from 5 Egyptian cement factories with more than 18 chimney around Egypt. The mean levels of PCDD/Fs are shown in Table 2, the profile of the PCDD/Fs in natural gas samples have been shown in Fig. 1, this study shows that the $\Sigma$PCDFs was higher than $\Sigma$PCDDs where contribute 70 and 30%, respectively from $\Sigma$PCDD/Fs. 2, 3, 4, 7, 8-PeCDF is 0.032 (ng WHO-TEQ Nm$^{-3}$), where the most abundant congener contribution was remarkable with 37% followed by 1, 2, 3, 7, 8-PeCDD is 0.016 (ng WHO-TEQ Nm$^{-3}$) which contributes about 19% and 1, 2, 3, 4, 7, 8-HxCDF is 0.007 (ng WHO-TEQ Nm$^{-3}$) which contributes about 8% from $\Sigma$PCDD/Fs as presented in Table 2.

Environment Australia (2002) has measured a range of Australian cement plants representing different operating and process conditions, different fuel sources and different raw materials, as plants using gas and coal as primary fuels sources as well as plants using waste-derived fuels. No significant difference in PCDD/PCDF emissions due to use of waste-derived fuels have been observed within plants. Results of repeated measurements over a decade showed that levels of PCDD/PCDF emissions from Australian cement manufacturing have consistently been below 0.1 ng I-TEQ m$^{-3}$. Fifty-five measurements showed the range 0.001-0.07 ng I-TEQ m$^{-3}$ with subsequent emissions factors covering the range 0.0032-0.216 lg I-TEQ t$^{-1}$ cement. The Japanese cement industry utilizes a broad range of Alternative Fuels and Raw (AFR) materials in their cement production and approximately 78 million t of clinker was produced in 62 dry suspension preheater kilns in Japan in 2003. Fifty four measurements performed in 2000 showed that all kilns were below 0.0941 ng TEQ m$^{-3}$, Fifty three measurements performed in 2001 showed that all kilns were below 0.126 ng TEQ m$^{-3}$ and Fifty seven measurements performed in 2002 showed that all kilns were below 0.096 ng I-TEQ m$^{-3}$; all measurements corrected to 10% O$_2$ (MOE., 2004). In the first phase of the Spanish PCDD/PCDF inventory, 20 cement kilns (18 dry and 2 wet processes) were measured for PCDD/PCDF emissions under baseline operating conditions (Fabrellas et al.,
2002). The mean emission value was 0.00695 ng I-TEQ m⁻³ and the mean emission factor 0.014464 lg I-TEQ t⁻¹ cement. In the period 2000-2003 samples from 41 kilns were collected, representing 69.5% of the industry and 40.2 million t cement. Fifty eight samples were taken when using conventional fuels and 31 when alternative fuels were used. No evidence of higher PCDD/PCDF emissions when using alternative fuels could be found (Fabrellas et al., 2004).

**PCDD/Fs (ng WHO-TEQ Nm⁻³) levels with coke:** The mean levels measured by HRGC/MS multiply by Toxic Equivalent Factor (TEF) in coke were 0.008 (ng WHO-TEQ Nm⁻³) as shown in Table 1 the range of the highest and lowest levels in all samples. No. of samples violated, Maximum levels and Sum of dioxins (ng WHO-TEQ Nm⁻³) according to (2000/76/EC) for Environment. It is mixed with mazout with 70% Mazout and 30% Coke.

Seventeen 2, 3, 7, 8-substituted congeners of PCDD/Fs Profile in the 10 coke samples have been collected samples during 2008-2014. The mean levels of PCDD/Fs are shown in Table 2, the profile of the PCDD/Fs in Coke samples have been shown in Fig. 1. This study shows that the ΣPCDFs was higher than ΣPCDDs where contribute 70 and 30%, respectively from ΣPCDD/Fs. 2, 3, 4, 7, 8-PeCDF is 0.031 (ng WHO-TEQ Nm⁻³) where the most abundant congener contribution was remarkable with 31% followed by 2, 3, 7, 8-TCDF is 0.002 (ng WHO-TEQ Nm⁻³) which contributes about 24% and 2, 3, 7, 8-TCDD is 0.001 (ng WHO-TEQ Nm⁻³) which contributes about 15% from ΣPCDD/Fs as presented in Table 2.

Five measurements from two German preheater kilns feeding a mix of coal and plastics to the main burner and tyres to the kiln inlet showed concentrations from <0.0021 ng TEQ m⁻³ up to 0.0057 ng TEQ m⁻³ (Haegermann, 2004a). Among the kiln, fuel-to-fuel comparisons, the use of coke as a fuel produced significantly different profiles, when others used was used, elevated emissions were found to be associated with de novo PCDD/F formation in particulate control systems (electrostatic precipitators and bag houses) operating at temperatures above 450 K, irrespective of hazardous waste utilization. Recent investigations indicate that PCDD/F formation-rates typically depend not on the fuel but instead on the trace organic chemical content of the raw materials (limestone, sand, shale, clay and iron ore) and the temperature of flue gases as they pass through air pollution control devices (Karstensen, 2008).

**PCDD/Fs (ng WHO-TEQ Nm⁻³) levels with ambient air:** Sampling and analytical determination of PCDD/F levels in the ambient air were performed by using a passive air sampler comprising a Polyurethane Foam (PUF) without the need of electricity or expensive air sampling equipment, it is duration for 28 days around Egypt. The mean levels measured by HRGC/MS multiply by Toxic Equivalent Factor (TEF) in ambient air were 0.062 (ng WHO-TEQ Nm⁻³) as shown in Table 1.

Seventeen 2, 3, 7, 8-substituted congeners of PCDD/Fs Profile in the 9 ambient air samples have been collected samples during 2008-2014. The mean levels of PCDD/Fs are shown in Table 2, the profile of the PCDD/Fs in ambient air samples have been shown in Fig. 1, this study shows that the ΣPCDFs was higher than ΣPCDDs, where contribute 71 and 29%, respectively from ΣPCDD/Fs. The 2, 3, 4, 7, 8-PeCDF is 0.022 (ng WHO-TEQ Nm⁻³) where the most abundant congener contribution was remarkable with 35% followed by 1, 2, 3, 7, 8-PeCDD is 0.012 (ng WHO-TEQ Nm⁻³) which contributes about 20% and 2, 3, 7, 8-TCDF is 0.007 (ng WHO-TEQ Nm⁻³) which contributes about 11% from ΣPCDD/Fs as presented in Table 2.

PCDD/F congener profiles are of interest in part because, if robust and unique profiles can be established for specific types of PCDD/F sources, it might be possible to identify and apportion...
source contributions to ambient total PCDD/F concentrations or TEQ levels (Rivera-Austrui et al., 2011). Lanier et al. (1996) demonstrated that PCDD/PCDF emissions from cement kilns increase exponentially with increases in inlet temperatures to the air pollution control device Air Pollution Control Device (APCD), within the PCDD/PCDF formation window (250-450°C). The very low emissions of PCDD/PCDFs from cement kilns, regardless of the type of fuel used can generally be attributed to the high temperatures and long residence times within the kiln (Karstensen et al., 2006).

The height of the bars indicates the fraction of each congener's concentration relative to the total concentration of all seventeen listed congeners. As shown, there is substantial congeners' level variability within different kind of fuel. Visually, the profiles for the three different kind of fuel having a more pronounced enrichment in 2, 3, 4, 7, 8-PeCDF, examination of the kiln-specific data analyzed by Cleverly et al. (1997) indicates that PCDD/F in cement kiln burning hazardous wastes and 2, 3, 7, 8-TCDF in cement kilns not burning hazardous waste. Assuming a global cement production of approximately 2 billion t and using the highest emission factor of the Tool kit as the worst case scenario, 5 Lg TEQ t⁻¹, would imply a contribution from the cement industry of 10 kg year⁻¹. A best scenario estimate would be to use the lowest emission factor of the Tool kit, 0.05 Lg TEQ t⁻¹, making the contribution from the cement industry to be 100 g year⁻¹. A more reasonable contribution estimate would be to assume that the eight international cement companies, representing approximately 20% of the total clinker production, is currently representative of the global industry. More than 500 recent measurements from around the world, representing all technologies and local raw material conditions as well as feeding AFR, show an average flue gas concentration of 0.021 ng I-TEQ m⁻³. Assuming a global cement production of 2 billion t year⁻¹, or 1.6 billion t year⁻¹ of clinker and an exhaust-gas volume of 2300 Nm³ t⁻¹ clinker, the contribution from the cement industry would constitute 77 g year⁻¹. When compared with the 1420 kg estimated by Brzuzy and Hites (1996) in their worst case scenario, it becomes evident how unreliable early emission factors are.

Clinker is hard spheres which are difficult to crush and contamination during sample preparation in the laboratory is not unlikely. Comparing the concentration levels of solid materials used in cement production with other known materials may provide a perspective (Santillo et al., 2001). The International POPs Elimination Network claim that the PCDD/PCDF emissions in 2004 from a long dry kiln in the UK reached 136 ng TEQ m⁻³ and averaged more 50 ng TEQ m⁻³ over the year with total emissions of more than 40 g TEQ. The kiln, now closed, was operating with relatively high temperatures in the electrostatic precipitator and used raw material with high organic content together with waste pulverized fuel ashes. This information cannot be confirmed in scientific literature but is referred in UNEP (2007). The contribution estimate made by (Brzuzy and Hites, 1996) showed that the cement industry were supposed to contribute with 1420 kg PCDD/PCDF year⁻¹, or 59% of estimated total global emissions as a worst case scenario. This calculation can be redone by using recent data, for example from the UNEP Toolkit (UNEP, 2005). We know that PCDD/PCDFs can result from a combination of formation mechanisms, depending on kiln and process configuration, process and combustion conditions, feed characteristics and type and operation of the air pollution control devices APCD (Everaert and Baeyens, 2002). In another study, 106 PCDD/PCDF measurements of 37 kilns showed that all values were below 0.065 ng I-TEQ m⁻³ (10% O₂) and in seven cases no PCDD/PCDF was detected. More recent inventories are usually based on real measurements, resulting in significantly lower emission factors and a release contribution estimates, constituting from about 0.5% or less of total emissions. Fabrellas et al. (2004) used 0.0144 gL-TEQ t⁻¹ cement in the Spanish inventory; 0.2 Lg TEQ t⁻¹ were used for the Newly Independent States and the Baltic
countries (Kakareka and Kukharchyk, 2002); 0.025-1.2 Lg I-TEQ t$^{-1}$ cement was used in the UK, covering also wet kilns burning a mix of fossil and waste-derived fuel (Alcock et al., 1999). In the absence of real measurements, the (EPDKH, 2000) assumed an exit gas concentration of 0.1 ng I-TEQ m$^{-3}$, a flow rate of 7000 m$^{3}$ min$^{-1}$ and an operation of 7680 h of per year for their cement plant, leading to a contribution estimate of 0.96-1.39% of total emissions. The worldwide measurements performed by Holcim showed an average emission factor of 0.104 Lg TEQ, 0.073 Lg TEQ and 0.058 Lg TEQ t$^{-1}$ clinker, representing a clinker production of 35.1, 46.7 and 57.6 million t, respectively (Lang, 2004). The availability of chlorine does not seem to be a limiting factor, i.e., there will be enough chlorine in the raw materials or in the fossil fuels (Bragg et al., 1991) to form PCDD/PCDFs under unfavourable conditions. It has been believed that the highly alkaline environment in cement kilns scavenges available chlorine, making it unavailable for chlorination of organic material (Eduljee, 1998). One positive correlation identified both in US and German studies (Kuhlmann et al., 1996) was that between PCDD/PCDF concentration and ESP/stack temperature, at high temperatures. This was confirmed by Schreiber (1993) which tested a cement kiln with the ESP temperature between 255 and 400°C, the PCDD/PCDF emissions were highest at 400°C and decreased 50-fold at 255°C. We have seen evidence, especially from data of newer origin that fuels and wastes fed through the burners are properly destroyed, also hazardous wastes (Stobiecki et al., 2003). Evidence from the US has shown that naturally occurring PCDD/PCDFs in the raw materials can be emitted from the system, probably through volatilization. This study have identified and quantified two sources of input materials containing PCDD/PCDFs; raw material kiln feed and fuel (Karstensen, 2006a).

PCDD/Fs (ng Nm$^{-3}$) levels in different operating conditions of the fuels

PCDD/Fs (ng Nm$^{-3}$) levels with Mazout fuel: The mean levels is measured by HRGC/MS in Mazout were 1.091 (ng Nm$^{-3}$) as shown in Table 2. The mean levels of Seventeen 2,3,7,8-substituted congeners of PCDD/Fs Profile in the 26 Mazout samples have been analyzed this study shows that the $\Sigma$PCDDs was higher than $\Sigma$PCDFs where contribute 61 and 39%, respectively from $\Sigma$PCDD/Fs as shown in Fig. 2. The 1, 2, 3, 4, 6, 7, 8, 9-OCDD is 0.30 (ng Nm$^{-3}$), where the most abundant congener contribution was remarkable with 28% followed by 1, 2, 3, 4, 6, 7, 8-HpCDF is 0.185 (ng Nm$^{-3}$), which contributes about 17% from $\Sigma$PCDD/Fs and 1, 2, 3, 7, 8-PeCDF is 0.111 (ng Nm$^{-3}$) which contributes about 10% from $\Sigma$PCDD/Fs as presented in Table 2.

PCDD/Fs (ng Nm$^{-3}$) levels with natural gas: The levels is measured by HRGC/MS in natural gas were 0.966 (ng Nm$^{-3}$) as shown in Table 2. The mean levels of Seventeen 2, 3, 7, 8-substituted congeners of PCDD/Fs Profile in the 61 natural gas samples shows that the $\Sigma$PCDFs was higher than $\Sigma$PCDDs, where contribute 63 and 37%, respectively from $\Sigma$PCDD/Fs as shown in Fig. 2. The 1, 2, 3, 4, 6, 7, 8, 9-OCDD is 0.205 (ng Nm$^{-3}$) where the most abundant congener contribution was remarkable with 21% followed by 1, 2, 3, 4, 6, 7, 8-HpCDF is 0.153 (ng Nm$^{-3}$) which contributes about 16% and 1, 2, 3, 4, 6, 7, 8, 9-OCDF is 0.141 (ng Nm$^{-3}$) which contributes about 15% from $\Sigma$PCDD/Fs as presented in Table 2.

PCDD/Fs (ng Nm$^{-3}$) levels with coke: The levels measured by HRGC/MS in samples using Coke fuel were 0.079 (ng Nm$^{-3}$). The mean levels of Seventeen 2, 3, 7,8-substituted congeners of PCDD/Fs profile in the 10 coke shows that the $\Sigma$PCDFs was higher than $\Sigma$PCDDs, where contribute 62 and 38%, respectively from $\Sigma$PCDD/Fs as shown in Fig. 2. The 1, 2, 3, 4, 6, 7, 8, 9-OCDD is 0.022 (ng Nm$^{-3}$), where the most abundant congener contribution was remarkable with
28% followed by 2, 3, 7, 8-TCDF is 0.019 (ng m\(^{-3}\)), which contributes about 24% and 1, 2, 3, 7, 8-PeCDF is 0.011 (ng Nm\(^{-3}\)) which contributes about 13% from \(\Sigma\)PCDD/Fs as presented in Table 2.

**PCDD/Fs (ng Nm\(^{-3}\)) levels with ambient air:** Sampling and analytical determination of PCDD/F levels in the ambient air were performed by using a passive air sampler comprising a Polyurethane Foam (PUF) without the need of electricity or expensive air sampling equipment, it is duration for 28 days around Egypt.

The levels measured by HRGC/MS in ambient air were 0.43 (ng Nm\(^{-3}\)). The mean levels of Seventeen 2, 3, 7, 8-substituted congeners of PCDD/Fs Profile in the 9 ambient air samples have been analyzed shows that the \(\Sigma\)PCDFs was higher than \(\Sigma\)PCDDs, where contribute 83 and 17%, respectively from \(\Sigma\)PCDD/Fs as shown in Fig. 2. The 2, 3, 7, 8-TCDF is 0.069 (ng Nm\(^{-3}\)), where the most abundant congener contribution was remarkable with 16% followed by 1, 2, 3, 4, 7, 8-HxCDF is 0.051 (ng Nm\(^{-3}\)), which contributes about 12% and 1, 2, 3, 7, 8-PeCDF is 0.051 (ng Nm\(^{-3}\)), which contributes about 12% from \(\Sigma\)PCDD/Fs as presented in Table 2.

The profiles for the three different kind of fuel having a more pronounced enrichment in 2, 3, 4, 7, 8-PeCDF, examination of the kiln-specific data analyzed by Cleverly et al. (1997) indicates that PCDD/F in cement kiln burning hazardous wastes and 2, 3, 7, 8-TCDF in cement kilns not burning hazardous waste. Overall, the profiles for the fuels are similar with PCDDs and PCDFs congeners. Visually, the profiles for the fuels appear same emissions having a more pronounced enrichment in OCDD and 1, 2, 3, 4, 6, 7, 8-HpCDF, while ambient air emissions have a different congeners than the emission from the cement. Also, it is interesting that some of the fuel-specific patterns in the profiles (notably the levels for 2, 3, 7, 8-TCDF) appear similar for the kind of fuel. The OCDD and 2, 3, 7, 8-TCDF are most frequently the peak congeners for facilities that both use and do not use hazardous waste. The long history of pulp/paper bleaching along the Swedish coast has been a major source of 2, 3, 7-TCDD, 1, 2, 3, 7, 8-PeCDD and 2, 3, 7, 8-TCDF (Rappe, 1994; Sundqvist et al., 2009; Tanabe et al., 2004). Another source of the PCDD/Fs in the Swedish environment has been the manufacturing of iron and steel (Rappe, 1994). More PCDFs than PCDDs have been released from these industrial processes. The chlor-alkali industry has been another source particularly, when graphite electrodes were used this produced a higher proportion of
PCDFs than PCDDs, with a dominance of the 2, 3, 7, 8-substituted congeners including penta-, hexa-, hepta- and octa PCDF (Rappe et al., 1991). Chlorophenol products have been used for wood and preservation for a long time in Sweden and were prohibited at the end of the 1970s. The main congeners in the Pentachlorophenol Products (PCP) were HpCDD and OCDD. More broadly, destruction of fuel-contaminants in cement kilns depends on several factors, including high production temperatures, long residence times, surplus oxygen during and after combustion and inherent dry scrubbing by the alkaline nature of limestone (Karstensen, 2008). Tests performed two decades ago on various cement kilns in the U.S. had indicated relatively high emission rates of PCDD/Fs, including facilities combusting hazardous waste but, as noted above, these earlier tests had been intentionally conducted under sub-optimal combustion conditions (Cleverly et al., 1997; Brzuzy and Hites, 1996). Because the gas and raw materials in the cement manufacturing process flow in opposite directions, there is significant potential for semi-volatile components to build up in a recycle loop in the back end of the process. It is likely that the more chemically stable PCDDs exit the process without being altered from how they were formed, or they are present in the raw materials, in which the fully chlorinated OCDD dominates. With regard to the PCDFs, in contrast, the higher molecular weight congeners likely condense onto particulates and recycle back through the process, where these less thermodynamically stable compounds are converted to more volatile, lesser chlorinated congeners. These are then emitted without the opportunity for condensation and recycling back through the process. Brzuzy and Hites (1996) estimated the total global annual emission of PCDD/Fs to air to be 3000±600 kg. The cement industry burning and not burning hazardous waste was assigned an emission factor of up to 4160 Lg t$^{-1}$ cement and 320 Lg t$^{-1}$ cement, respectively.

CONCLUSION

More than 106 PCDD/Fs samples measurements have been evaluated in this study, representing most all kind of fuel used in production technologies exhibited fluctuation, so, the lowest (0.01 ng WHO-TEQ Nm$^{-3}$) level were in the mixture of coke 30% and mazout 70%, while 0.11 (ng WHO-TEQ Nm$^{-3}$) level were the highest in natural gas fuel. It was found that mostly all cement kilns can meet an emission level of 0.1 ng WHO-TEQ Nm$^{-3}$ and that proper and responsible operation and maintenance condition are important factor influencing the formation of PCDD/PCDFs and prevent any use of organic hazardous and other wastes to replace parts of the fossil fuel is an important factor until a good control operation and modern technologies are used to prevent the formation of PCDD/Fs. This may explain that the main influencing parameter stimulating formation of PCDD/Fs seems to be the availability of organics/precursors in the raw material and the temperature of the air pollution control device. Feeding of materials containing elevated concentrations of organics as part of raw-material-mix should therefore be avoided and the exhaust gases should be cooled quickly in wet and long dry cement kilns. The detailed understanding how PCDD/Fs are formed in cement production is not yet complete but it seems that a combination of heterogeneous surface-catalyzed reactions and de novo synthesis in the preheater and the post-preheater zones are the most important. The PCDD/Fs could be identified and quantified in all raw materials, products and residues used and produced in the industry but the concentrations were generally low, in the same magnitude as normal earth crust materials, soil and sediments. Finally, it may also concluded that monitoring of emissions from cement factories need restricted operating conditions and periodically maintenance to prevent any emissions that can be detected.
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