

Influence of alternative fuels on the formation of dioxins in a cement production plant

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Abstract

Cement kilns can emit polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), but estimates of the amounts and pattern of PCDD/Fs emissions vary widely. These variations may stem from a combination of factors including operating conditions of the kiln, temperature of air pollution control devices (APCD), the fuel used to heat the cement kiln and raw meal fed to the kiln. The goal of this study was to examine the dioxin emission at one of the Cements cement production plant in southeast of Sweden, that used a variety of alternative fuels. These alternative fuels comprising of RDF, SPA and KEO that were combusted with a varied mixes. This study was divided into two parts; in the first part, an evaluation of PCDD/Fs emission data from the time period 2009 to 2012 were performed to elucidate whether the emissions could be attributed to the fuel parameters or process parameters and possibly gives an indication where in the plant, the elevated PCDD/Fs concentrations occur. In the first part, one of the production lines was found at more risk due to the toxic concentration (TEQ value) exceeded the toxic level set by the world health organization (WHO) 0.1 ng/m³ for stack emissions. In the second part, samples were taken at different sampling points in the production line that was found at more risk (before ESP, after ESP and chimney) to clarify where in the production line, the increased concentrations of PCDD/Fs occur. In addition to that, samples of the ESP ash, coal and raw meal were also analyzed. The toxic concentration (TEQ value) in the flue gas samples were higher than the limit set by the authorities. The toxic concentration increased between the sampling points after the ESP and the chimney. Moreover, the dioxin emission profile changed on changing the fuel mixes in the Cements cement production facility.

Some important abbreviations and definitions:

APCD	Air pollution control devices
Dg	Dry gas
RDF	Refused derived fuel
KEO	“Konverted Eldnings Olja” means used oil
PUFP	Polyurethane foam plug
EPA	Environmental protection agency
GC-HRMS	Gas chromatography with high-resolution mass spectrometer
PAH	Polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
PCBz	polychlorinated benzenes
PCDDs	polychlorinated dibenzo- <i>p</i> -dioxins
PCDFs	polychlorinated dibenzofurans
PCDTs	polychlorinated dibenzothiophenes
PCPhs	polychlorinated phenols
POPs	persistent organic pollutants
TeCDD	Tetra chlorinated dibenzo- <i>p</i> - dioxins
TEF	Toxic equivalent factor
TEQ	Toxic equivalent

Congeners:	A general term used to describe the individual species of a class of compound.
Isomer	Species having the same molecular formula but different structural formula.
Homologue	A group of species (isomers) with the same number of chlorine atoms but substituted on different positions.
Pattern	The relative abundance of the individual isomers in a group of homologues.

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1. Introduction

Cement manufacturing is energy intensive processes because of rotary kilns operate at high temperature, i.e. about 1450°C. Generally, conventional fuels (coal, petroleum coke and natural gas) are used to heat up the kilns. Due to increasing conventional fuel prices, limited natural resources for conventional fuels and environmental concerns, alternative fuels are becoming more popular in cement industries (1). Alternative fuels comprising all non-conventional fuels, such as waste oils, plastics, waste tires, biomass and sewage sludge (1) (2) (3). Nowadays, cement manufacturers are using blends of alternative fuels with conventional fuels for sustainable development.

The replacing ratio of conventional fuels with alternative fuels differs from country to country and some European countries are leading ahead and they are pursuing to increase the proportion of alternative fuels even more until 2020 (4). Cement kilns have also been used for burn and destruct hazardous wastes, with even the more complex chlorinated hydrocarbons such as dioxins, being destroyed at normal burning conditions (5). However, the amount of dioxins seems to increase when alternative fuels are used in the cement kilns (6). The term dioxin includes polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs). These compounds are unintentional by products of combustion process and show adverse effects on human health (7).

The Stockholm Convention on persistent organic pollutants (POPs) to prevent and reduce unintentionally emission of (PCDD/Fs) identified the cement kilns as an increasingly important source of pollutants. Cement kilns firing hazardous waste are mentioned precisely in the Convention, Annex C part II, as “industrial source having the potential for relatively high formation and release of PCDD/Fs to the environment” (8). Co-combustion of waste material in cement industries thus seem to increase the emission of PCDD/Fs (9).

Many researchers have investigated the formation, emission and distribution of dioxins in the environment (10), but the formation pathways are still not fully understood. However, they are supposed to form in the lower temperature region (250-400°C) of the post combustion zone in combustion plants.

2. Aim of the project

The main objective of this work is to elucidate the influence of alternative fuels on the formation of dioxins in the Cementa cement production facility at Degerhamn southeast of Sweden.

3. Background

3.1 Cement manufacturing

There are different types of cement and the most common type is Portland cement, which is being used worldwide. It is a hydraulic binder, which forms the paste upon addition of water due to hydration reaction (11). Over the last few decades, the incremental production in cement worldwide reveals its importance. Cement is a binder used in the manufacturing of concrete, mortars and to binding of other materials. Concrete and mortars are used for the construction of buildings, roads, dams and bridges to maintain life cycle. Mortar is a mixture of cement, water and sand (used between bricks or stone to bind individual masonry units to each other). On the other hand, when stone or gravel added to the mortar, the resulting product is called concrete. The world production of concrete per annum is about 12 billion tons and it consumes 1.6 billion tons of Portland cement (12). According to European cement association (CEMBUREAU), in 2012 the total world production of cement was 3.6 billion tons (13). Cement and concrete are of fundamental importance for a modern society. Cement plants form a network throughout Europe providing not only essential construction products but also an important waste treatment capacity without the need for separate waste treatment technology. Co-processing of waste in the cement industry provides an effective local waste management solution and energy recovery from the waste (14). The unique benefits of co-processing recognized in a revised EU waste treatment hierarchy to ensure that the selection of this waste treatment option prioritized and encouraged. The essential benefit of co-processing materials in the cement industry is that both the energy content and the material content of the waste materials are used for producing the intermediate product clinker (13). Clinker is the

intermediate product produced in the rotary kiln, which is ground and mixed with gypsum to form the cement (15). Manufacturing of cement consists of drilling and blasting of rocks containing limestone along with oxides of calcium, silicone, aluminum, and iron. This raw material is crushed and milled into homogenized form and then blended and heated in a preheating section of cyclone preheater to convert calcium carbonate into calcium oxide and carbon dioxide. The conversion process of calcium carbonate into calcium oxide and carbon dioxide is called calcination. The calcined material is then fed to the rotary kiln and heated up to 1450°C. In the rotary kilns, the formation of silicates of calcium and aluminum takes place by the reaction of calcium oxide and other elements. After the kiln, the product obtained is called clinker. The clinker is mixed with gypsum and ground to a fine powder to form the cement (16)- (17). The schematic diagram (in Figure 1) shows the manufacturing of cement from raw material to final product.

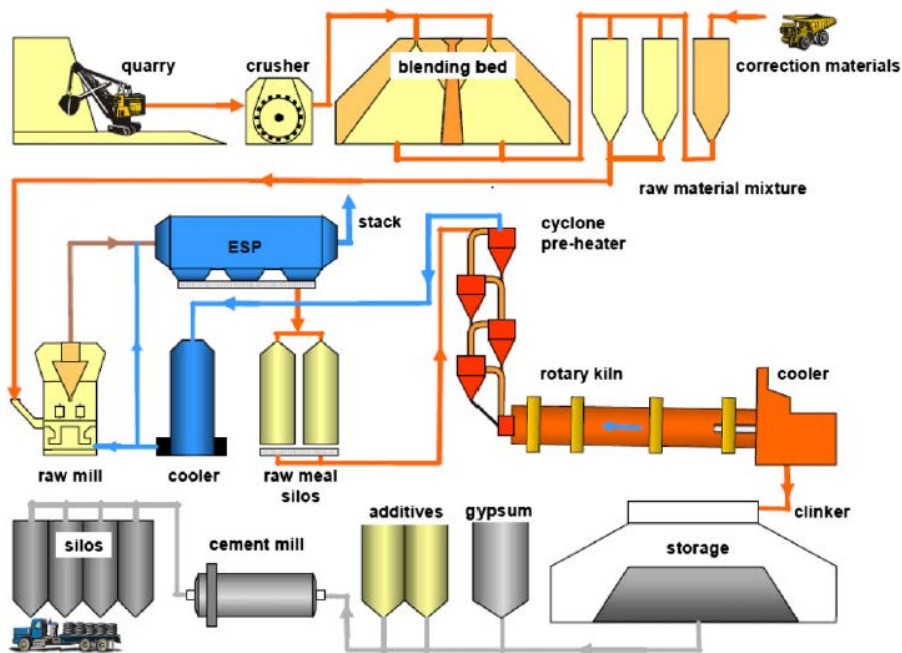


Figure 1 Schematic description of cement production from raw material to final product (18)

3.2 Rotary kiln process

Rotary kilns are inclined cylinders lined with heat resistant bricks. Heating, calcining and blending of raw materials are the general steps for the manufacturing of cement. It is necessary to maintain the temperature 1450°C for clinker production. The chemistry involved in the cement manufacturing starts with the decomposition of calcium carbonate at 900°C into calcium oxide and carbon dioxide called calcination. After calcination, clinkering process starts in which the calcium oxide reacts with the other chemical species preset in the rotary kiln such as silica, alumina and ferrous oxide at high temperature, i.e. 1400-1500°C to produce silicates, aluminates and ferrites to produce the clinker.

In the rotary kiln, the raw material is fed at the cold or upper end of the kiln and fuel used for heating on other end of the kiln to achieve the high temperature. The rotation of the kiln moves raw material towards the hotter end. The raw material and kiln hot gases produced from combustion of kiln fuels move in opposite direction to create favorable conditions for thorough mixing and efficiently heat transfer between gases and raw materials. The hot gas also known as flue gas contains various pollutants, such as dioxins, when it is discharged from the rotary kiln (6).

Generally, conventional fuels are used to heat up the kilns but due to increasing conventional fuels prices, limited natural resources for conventional fuels and environmental concerns, alternative fuels are being introduced in the cement industries for sustainable development (2). No doubt replacing conventional fuels with alternative fuels decreases the cost of production but they are polluting the environment by releasing harmful pollutants. Burning of hazardous waste in cement kilns as alternative fuels identified the increase in PCDD/Fs level in stack emissions compared to cement kilns that used conventional fuels (19). Many researchers worldwide proposed the possible remediation technologies for dioxins in the flue gas with different techniques (20).

In modern rotary kilns, the facility for high temperature, long residence time, excess of oxygen for complete combustion, thorough mixing, counter current flow of raw material and gases, scrubbers to scrub the gases and removal of heavy metals maintained. These features make rotary kilns more attractive in terms of energy recovery from the waste and destruction of waste in a safe way (14).

Modern rotary kilns are however equipped with pollutant cleaning system such as air pollution control devices (APCD) used for removal of acid gases, heavy metals and PCDD/Fs along with additional advantages of heat recovery system. For example, ammonia used as cleaning agent for removal of NO_x from the flue gases, acid gases removed with the help of lime or caustic soda, and PCDD/Fs adsorb on the surface of activated carbon. The gases coming from rotary kilns are of high temperature and used to heat the raw materials prior to stack. In this way, heat is used for heating the process; it may also be used for electricity production. In some cement kilns, APCD are used to screen the pollutants and recycled back in the raw material again or dumped into the landfills (21).

The Cementa plant in Degerhamn is the market leader in Sweden in producing ready mixed concrete, prefabricated concrete and aggregates. Ready mixed concrete is the mixture of cement, water, sand and gravel manufactured at the facility and transported to the construction sites directly in cement trucks. Pre-fabricated concrete products produced by casting the concrete into specific shapes according to the requirement and cured in a controlled environment. These products transported to the construction sites and fit there as such. Aggregates are the coarse particulate materials used in the construction including sand, gravel, asphalt, crushed stone slag etc. High temperature and long residence time in cement kilns create favorable conditions for combustion of waste, but under some legislation that there must be no increase in the emission levels of air pollutants such as dioxins, acid gases and heavy metals (22).

3.3 Alternative fuels

Cement industries are facing high pressure from the environmental protection agencies to reduce their emission levels of pollutants. Replacing conventional fuels with alternative fuels conserve not only non-renewable conventional fuel resources; it also has significant advantages of reducing the price and reduction in CO₂ emission level arising from burning of conventional fuels (23) (24). Alternative fuels consist of different types of fuels such as used tires, biomass residues, sewage sludge, different commercial wastes, solvents, waste oils, plastics and all kinds of slaughterhouse waste (3). Refuse derived fuel (RDF) is an alternative fuel derived from municipal or industrial waste consisting of combustible portion such as plastics and biodegradable material. It is produced by separating the non-combustible materials like glass, grit and ferrous materials from the municipal solid waste by shredding and dehydration through waste converter technology (25). RDF produced according to European standard method called as solid recovered fuel (SRF) (26).

KEO is also another alternative fuel used in Cementa plant. KEO is derived from Swedish word "Konverterad Eldnings Olja" (KEO) waste oil from households, shops, municipalities and other industries. The waste oil is treated at a small number of processing Plants; where water and slurry are separated and the oil is quality assured. The treated waste oil is also called Recovered Fuel Oil (RFO) that is particularly suitable for the cement industry. Cementa has special permission for the use of RFO as fuel. Copper slag is a material consisting of granulated slag obtained from metal smelting industries. It is available in the form of granulated slag of copper and used for cleaning of metal surfaces. Cementa had added this to increase the sulphur contents in the clinker, but they have stopped using it since it increased the PCDD/Fs concentrations too much.

Alox is a waste solvent used as lubricating material in the industries, also rust protection. Cementa also using this material as an alternative fuel. The proportion of alternative fuels in relation to conventional fuels differs from country to country and in this cases some European countries are far ahead and are trying to increase this proportion even more until 2020 (4). According to WBCSD (27), CO₂ the major greenhouse gas released from cement industries contributes 5% to the total anthropogenic emission of CO₂ to the environment. During cement manufacturing, 60% CO₂ released from calcination and 40% from combustion of fossil fuels. One possible way of sustainable development for cement industries is to replace fossil fuels with alternative fuels.

In Heidelberg cement group usage of alternative fuels contributes to the protection of natural resources, provides a suitable solution to the waste management and sustainable development of the cement production. Heidelberg group has released their sustainability report on September 16, 2013 for the year 2011/2012 (28) describing in Europe at five of their cement production plants, the proportion of alternative fuels was almost 70% and alternative fuels utilization in entire group was 21.7% with 21% net reduction of CO₂ as compared with 1990. The usage of alternative fuels increases as compared with 2011 that was 14.6%.

In cement industries, waste not used as such especially in European countries where well-developed techniques for sorting the waste into RDF has installed. Because of using waste, they can affect the quality of the product and emit some pollutants into the environment. In some European countries mechanical biological treatment (MBT) technique used for conversion of waste into RDF (29). MBT technique is a type of waste processing facility, which combines the sorting and shredding with biological treatment such as composting or anaerobic digestion. In this technique mixed household waste, industrial waste as well as commercial waste are treated to transform them into alternative fuels.

4. Chemical structures and properties of dioxins

The term dioxins is often used for both polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs). These compound groups are suspected to be the underlying cause for many environmental and human health problems (30). PCDDs are consisting of two benzene rings interlinked through oxygen atoms in a bridge form as shown in figure 2. While PCDFs consist of two benzene rings fused together through one oxygen atom and one carbon-carbon single bond. These main structures are then substituted with chlorine atoms ranging from one to eight chlorine atoms on different positions as designated position 1-4 and 6-9 in figure 2.

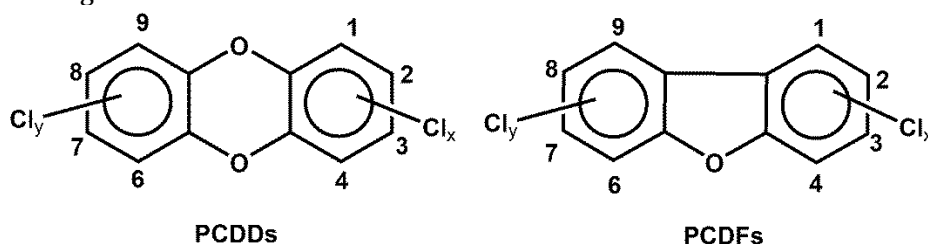


Figure 2 Chemical structure of PCDDs and PCDFs

There are 75 possible congeners of PCDDs with different number of chlorine atoms on different positions and 135 congeners of PCDFs, which together sum up to 210 possible PCDD/Fs congeners in total. Amongst these 210 compounds, 17 congeners have chlorine atoms on the 2,3,7,8 positions of the molecule. These seventeen 2,3,7,8 substituted congeners have shown particular toxicity towards many laboratory animals and also caused other adverse health effects such as teratogenicity, liver damage, carcinogenic and decrease in reproduction (7). These compounds come into the environment through both natural and anthropogenic sources. Dioxins were identified in historical times when there was no large-scale manufacturing of industrial products and no use of chlorinated compounds showing the natural release of dioxins (31).

However, numerous studies show that most of the environmental release of dioxins are due to anthropogenic sources including combustion processes (cement kilns, wood burning, and coal-fired utilities), industrial processes (paper and pulp industry) and chemical processes (20).

A general term used to describe the individual members of the dioxin group is called as congener. A group of congeners with the same number of chlorine atoms constitutes a homologue. The distribution of congeners within each homologue group is referred to as a congener distribution pattern. The possible number of different congeners for each PCDD and PCDF homologue group is shown in table 1.

Table 1 Possible number of congeners within each homologue group

Homologue	Number of congeners for PCDD	Abbreviation	Number of congeners for PCDF	Abbreviation
Monochloro	2	MoCDD	4	MoCDF
Dichloro	10	DiCDD	16	DiCDF
Trichloro	14	TriCDD	28	TriCDF
Tetrachloro	22	TeCDD	38	TeCDF
Pentachloro	14	PeCDD	28	PeCDF
Hexachloro	10	HexCDD	16	HexCDF
Heptachloro	2	HepCDD	4	HepCDF
Octachloro	1	OCDD	1	OCDF
Total	75		135	

The distribution of dioxins in the environment depends on the physical and chemical properties of the compounds and properties of the environment. Dioxins are found in air, sediments and biota (32). Dioxins are non-polar in nature, which means that they are hydrophobic and lipophilic compounds. Due to this, they accumulate in biota including food, dairy products, meat and fish through which humans may be exposed (33). As the number of chlorine increases, their water solubility and reactivity tend to decrease and solubility in organic solvents and fatty tissues increases. Dioxins attached with particulate matter seem to be resistant to degradation (34).

4.1 Formation of dioxins

There are two main types of mechanisms of formation of dioxins in combustion systems, Homogeneous formation (gas phase) and heterogeneous (gas phase-solid surface interaction) formation. These mechanisms take place at different temperature profiles, with homogeneous formation taking place at high temperature between 500-800°C and heterogeneous formation taking place at comparatively lower temperature profile between 200-400°C (35). The concentration of PCDDs and PCDFs in the flue gases are the net result of formation and degradation reactions (Figure 3). The formation and degradation reactions compete at higher temperature whereas at lower temperature formation reaction is favored (36). This usually results in increasing concentration of dioxins at lowering temperatures.

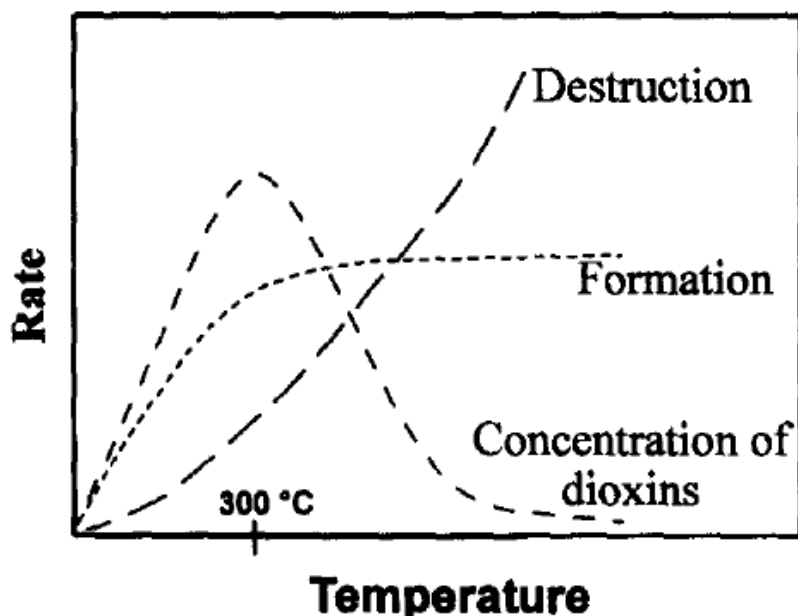


Figure 3 The formation and degradation of dioxins with temperature.

Adapted from Wehrmeier *et al.* (36)

It has been shown that formation of PCDD/Fs via the homogeneous pathways is very low (37). According to Vogg and Stieglitz, the concentrations of PCDD/Fs in flue gases are very low at temperature 600°C as compared with temperature 300°C suggesting that the main formation occurs at a relatively low temperature, which makes the heterogeneous pathways more important (38). Heterogeneous formation proceeds through surface catalyzed reaction and may be divided into two sub-pathways, De novo formation and formation from precursors.

4.1.1 De novo synthesis

Formation of dioxins from carbon residues present in the fly ash matrix and deposited on surfaces of the post combustion zone. De novo synthesis involves the chlorination and oxidation of carbon structures leading to new formation of dioxins (39). Weber *et al.* (40) described the formation of PCDDs and PCDFs through de novo synthesis from PAH but with very low concentrations suggesting there might be an additional mechanism for the formation of these compounds. It means that not only de novo mechanism contributes to the formation of dioxins there are some other routes for the formation of dioxins.

4.1.2 Formation from precursors

Dioxins form through smaller organic molecules present in the flue gas that can act as precursors. There are large varieties of precursor molecules present in the combustion system, which form during combustion or produced in the post combustion zone. For example, polychlorinated benzene (PCBz), polychlorinated phenols (PCPh) and various other chlorinated hydrocarbons that can act as precursors and react with each other to form PCDD/Fs through condensation or radical reaction mechanism (41). These type of precursors present as a gaseous phase or deposited on the surface of the fly ash particles. One of the strongest precursor molecule for the formation of PCDD/Fs is PCPh. PCPh, which often are found together with the PCDD/Fs and may be used as an indicator for the presence of PCDD/Fs (42). Formations of PCDDs have been proposed to occur mainly via condensation reaction involving precursors, and PCDFs through de novo synthesis (43). The PCDD/Fs ratio may be used to check whether de novo or precursor mechanism is dominant. If the PCDD/Fs ratio is less than 1, it means de novo synthesis dominant and if the PCDD/Fs ratio is greater than 1 then precursor formation is dominant (44).

4.2 Dioxin formation in cement kilns

The long residence time and high temperature in the cement kiln as compared with municipal waste incinerators lead to very low amount of PCDD/Fs. In fact, PCDD/Fs and other components of hazardous waste may actually be destroyed properly in cement kilns if added directly to the burner (45). Majority of the research done on formation of dioxins in cement kilns suggest that these compounds mainly are formed at the cooler parts of the processes, including the preheater region (red color zone) and post preheater region (blue color zone), see figure 3. In this figure, there are three regions highlighted with different colors: yellow color represents the rotary kiln (the high temperature region), red color represents cyclone preheater region and blue color represents the post preheater region in figure 3 (9).

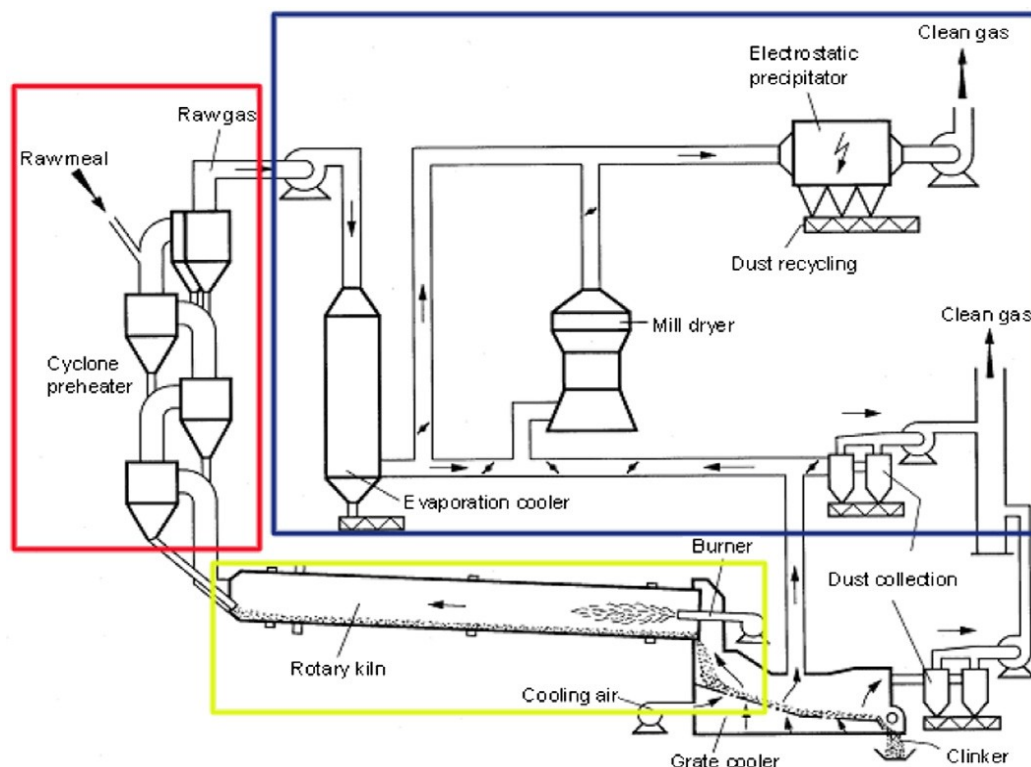


Figure 3 Rotary kiln with dust collector and cyclone preheater, yellow color represents the rotary kiln, the high temperature zone, red color cyclone preheater and blue color dust collector the lower temperature zone. Adapted from Karstensen K.H 2008 (9)

The destruction of hazardous waste in cement kilns, including chlorinated hydrocarbons have been analyzed by many researchers and found more than 99.99% destruction efficiency (46) (47). Due to high temperature in cement kilns, all the organics are destroyed, therefore formation of dioxins in cement kilns may be attributed to the preheater zone and post preheater zone. In the preheater region (red), raw meal is added, heated with the hot gas coming from rotary kiln and calcination occurs in this region. The temperature in this region varies from approximately 250-850°C with lower part of pre heater zone at higher temperature and upper part at lower temperature. The raw meal may constitute many particle surfaces, which may facilitate the surface catalyzed formation of PCDD/Fs (35). At the same time, the lower part of preheater zone may facilitate the homogeneous gas phase formation and upper part may participate in heterogeneous formation of dioxins. The organic material present in the raw meal, volatilize in the preheater zone and become available in the gas stream. Usually there is enough chlorine present in the raw meal to maintain the formation reactions of the chlorinated organic compounds (chlorophenols, chlorobenzene etc.) needed for PCDD/Fs formations (48). The raw gas (kiln gas), may contain carbon residues and deposited on surfaces of the walls of air pollution control devices (APCD) blue color region. The temperature and oxygen concentration may also be responsible for the formation of dioxins in APCD. APCD such as

electrostatic precipitator (ESP) is used in cement industries to remove the particulate matter from the flue gas. This particulate matter may adsorb some dioxins on their surfaces.

In modern preheater kilns, the emission is lower because of lower temperature of APCD. The raw gases from the rotary kilns go through the preheater then through raw mill dryer to heat the raw meal, enter into APCD and then stack gas. This operational mode decreases the hot gas temperature and increase the possibility for adsorption of PCDD/Fs in APCD. Due to lower temperature and adsorption of PCDD/Fs, low level of dioxins detected in stack gas.

On the other hand, some studies show that there are more chances for the formation of dioxins in APCD, due to adsorption of carbon structures and temperature profile almost 250-350°C (39).

Karstensen *et al.*, 2006 (49) identified the following main sources for the dioxins emissions in cement kilns:

(i) Raw meal, containing naturally occurring PCDD/Fs

(ii) PCDD/Fs formed in the preheater zone

(iii) PCDD/Fs associated with cement kiln dust (CKD), originating from the ESP. CKD, containing adsorbed dioxins collected and reintroduced into the process along with raw meal. Karstensen *et al.*, 2006 (50) proposed that there is region between ESP and preheater region where PCDD/Fs produced and are present in gaseous as well as adsorbed form. Once dioxins are produced, they will circulate between gaseous and particle adsorbed form.

Hence, in cement industry dioxins formation could be attributed to the already dioxins present in the raw meal and the combination of homogeneous and heterogeneous mechanism in the preheater and post combustion zone for the formation of PCDD/Fs are significant (36).

Homologue profile or congener pattern of dioxins within each homologue group may be used to identify the major sources and formation pathways, responsible to the dioxins formation in a specific case. Homologue profile provides the information about the relative proportions of mono to Oct- chlorinated compounds and simply described as a single number indicating the average degree of chlorination. The degree of chlorination varies between 1 and 8, where 8 indicates the PCDD or PCDF as OCDD or OCDF. Some studies show that homologue profile differs if there are changes in fuel composition and combustion conditions (51)- (50).

5. Factors affecting the Dioxin formations

5.1 Chlorine

The chlorine contents in the fuel has significant effects on the formation of dioxins, i.e. if it is organic or inorganic (51). The most common source of chlorine in flue gas is hydrogen chloride (HCl) produced e.g., when waste containing plastic and inorganic chloride are used as fuel (52). Molecular chlorine (Cl₂), the more reactive form in the formation of dioxins is produced from HCl through Deacon Process in which HCl is converted to Cl₂ in a reaction catalyzed by copper chloride (53). Wikström *et al.*, 1996 (51) investigated the formation of dioxins by varying level of chlorine in the fuels and found the increased level of dioxins, when chlorine level exceeded 1% and no correlation was found below 1%. Eduljee, 1998 (48) proposed that high alkaline conditions in the cement kilns scavenges available chlorine, creating unfavorable conditions for chlorination of organic compounds. However, on the other side, Dellinger *et al.*, 1993 (54) found that at temperature above 200°C, the scavenging of chlorine is no more effective even in more alkaline medium such as calcium hydroxide. This influences the conversion of HCl into Cl₂ through Deacon Process. High temperature and less oxygen in the preheater zone favors the conversion of HCl into Cl₂ through Deacon Process. Organic chlorine as Cl₂ in the preheater zone (55) participates in chlorination of hydrocarbons through alkali metal oxides and hydroxides present in the feed materials (48). So different kinds of precursors are formed in the preheater zone, which are needed for the formation of dioxins.

5.2 Effect of temperature

The temperature and residence times both are important for the formation of dioxins in the post combustion zone. In a previous study conducted (56) on cement kiln burning hazardous waste, PCDD/Fs emissions were measured in ESP at two different process temperatures, i.e. 255°C and 400°C. Overall, they found higher emissions of PCDD/Fs at higher temperature. In another study it was observed that the maximum concentration of PCDDs were at 300°C-400°C, while the PCDFs peaked at 400°C-500°C, supporting the theory of different formation mechanism for these two compound groups (57). This effect could be explained by the fact that at higher temperature, the concentrations of chlorophenols are low, which are the most important precursors for the formation of PCDDs. This would lead to a disadvantage for the PCDDs formation and thereby favor the relative proportion of PCDFs at higher temperature (43).

5.3 Water

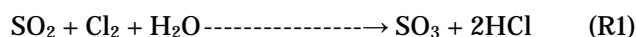
Many researchers have reported the potential effect of water for the formation of dioxin. Sakurai *et al.* (58), Ross *et al.* (59) Investigated this effect and showed that the water content increased the dioxins formation. On the other hand, Jay and Stieglitz (60) showed the reverse effect of water. It has also been shown that water may influence the emission of hydrogen chloride, which is the major form of chlorine in combustion system (61). Moisture contents along with sulfur reduce the Cl₂ production and ultimately reduction in PCDD/Fs formation (62).

5.4 Catalyst

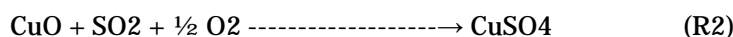
Copper is believed to have a strong catalytic effect on Deacon Process (54). Some other metals such as iron and aluminum have also showed to have catalytic effects on the formation of chlorinated hydrocarbons. Nevertheless, copper is the most effective and has about 25 times stronger catalytic power than iron (63). Even copper contents as low as 0.006 and 0.007% in the fuel have shown the effect on formation of PCDD/Fs (64). Copper naturally present in the raw meal and fuel participates in the catalytic reaction.

5.5 Sulfur

In cement production, sulfur may be present in raw meal, fuel and coal. It has shown an inhibitory effect on the formation of PCDD/Fs in combustion process (65). In a previous study conducted during co-combustion of refused derived fuel (RDF) with coal containing high contents of sulfur, they found a large reduction in PCDD/Fs (66). This effect may be due to the fact that, SO₂ produced in the process, suppresses the precursors, which are needed for the formation of dioxins. According to Griffin (62) SO₂ added in the process, can react with Cl₂ in the presence of water and transform Cl₂ it to less reactive HCl and SO₃ (R1).



HCl is not a strong chlorinating agent, so sulfur was found to inhibit the formation of PCDD/Fs by converting molecular chlorine to HCl. In another study (67), SO₂ showed to interfere with Deacon Process by reacting with CuO, the most reactive catalyst in the Deacon Process and transform into less reactive CuSO₄ (R2).



In conclusion, reduction in dioxin formation is expected in the presence of sulfur. However, according to Chang *et al.* 2006 (68) excessive addition of sulfur contents in the fuel composition can result in a lower effect.

6. Toxicity associated with dioxins

Dioxins are present in air, water, soil and food (69) as mixtures containing varying levels of the different congeners. The congener's toxicological effect depends on their affinity to the aryl hydrocarbon receptor (AhR) (70). The AhR receptor is a ligand activated transcription factor responsible for the regulatory biological responses to planar dioxins molecules. Dioxins penetrate fatty tissues and accumulate in food chains, ultimately ending up in human beings. These compounds are known as highly toxic to humans and animals including dermal toxicity,

reproductive and developmental toxicity, immunotoxicity, hepatotoxicity, carcinogenicity, teratogenicity, neurobehavioral, Endocrine and metabolic alterations (71) (72). The toxic equivalency factor (TEF) concept was developed to facilitate the comparisons of the congener's relative toxicities. The standardized TEF was developed the first time in 1998, and then reevaluated in 2005 (73). In the TEF scale, the toxicity of each congener is related to the toxicity of the most toxic congener 2,3,7,8-TCDD, which is assigned TEF value 1, giving all other congeners TEF values between 0 and 1 shown in table 2. Compounds having values close to 1 are more toxic. The toxicity of a single PCDD/F in a sample is described by its toxic equivalent (TEQ), which is the product of the concentration in the sample and its TEF value. The TEF values for all 2,3,7,8 substituted PCDD/Fs re-evaluated in 2005 by world health organization and shown in table 3 (73). According to European Union directives (EU Directive 2000/76/EC) with the aim to prevent or limit as far as practicable negative effects on the environment particularly in emission of dioxins to air and the resulting risks to human health from the incineration and co-incineration of waste in cement kilns. Half hour average values shall be needed to measure the daily average values for dioxin emission from cement industries. The measured results for dioxins in the exhaust gas should be compliance with the emission limit 0.1 ng/m³ at temperature 273 K, pressure 101.3 KPa, 10% oxygen and dry gas.

Table 2 Toxic equivalent factors (TEFs) for different congeners of dioxins according to WHO 2005 (73).

Specific isomer	Homologue name	TEF values
2,3,7,8-TCDD	Tetrachlorodibenzo- <i>p</i> -dioxins	1
1,2,3,7,8-PeCDD	Pentachlorodibenzo- <i>p</i> -dioxins	1
1,2,3,4,7,8-HxCDD	Hexachlorodibenzo- <i>p</i> -dioxins	0.1
1,2,3,6,7,8-HxCDD	Hexachlorodibenzo- <i>p</i> -dioxins	0.1
1,2,3,7,8,9-HxCDD	Hexachlorodibenzo- <i>p</i> -dioxins	0.1
1,2,3,4,6,7,8-HpCDD	Heptachlorodibenzo- <i>p</i> -dioxins	0.01
OCDD	Octachlorodibenzo- <i>p</i> -dioxins	0.0003
2,3,7,8-TCDF	Tetrachlorodibenzo furans	0.1
1,2,3,7,8-PeCDF	Pentachlorodibenzo furans	0.03
2,3,4,7,8-PeCDF	Pentachlorodibenzo furans	0.3
1,2,3,4,7,8-HxCDF	Hexachlorodibenzo furans	0.1
1,2,3,6,7,8-HxCDF	Hexachlorodibenzo furans	0.1
1,2,3,7,8,9-HxCDF	Hexachlorodibenzo furans	0.1
2,3,4,6,7,8-HxCDF	Hexachlorodibenzo furans	0.1
1234678-HpCDF	Heptachlorodibenzo furans	0.1
1234789-HpCDF	Heptachlorodibenzo furans	0.01
OCDF	Octachlorodibenzofurans	0.0003

7. Material and method

The evaluation of dioxin formation during cement production in Cementa Plant in Degerhamn was divided into two parts. In the first part, we had dioxin analysis data between 2009 and 2012 from two different production lines named as oven 3 and oven 4 and the second part was based on the results from part 1.

In part 1, samples in oven 3 had been taken only from the stack gas, while in oven 4 the samples had been taken from chimney as stack gas and flue gases from raw mill and coal mill. Apparently, from the part 1 results, we observed oven 4 was at more risk due to increased concentrations of dioxins in oven 4. However, the sampling sites in part 1 were not enough to draw a clear picture where dioxin formation actually occurs. Therefore, we decided to collect more samples from different points during the cement production process in oven 4, which are discussed in part 2.

The selection of sampling points in part 2 was based on the different conditions on all the sampling points, and on a hypothesis that dioxin could form on these points. We had two types of samples in part 2, one was flue gas sample and other was solid sample during September 2013 shown in figure 4. In figure 4, at points A and B in ESP and raw material were solid samples and other sampling points were flue gas samples. The extraction and cleaning up of both types of samples in part II done according to the method described elsewhere by Liljelind *et al.* 2003 (74). The dioxin analysis consists of three steps extraction, cleaning and analysis.

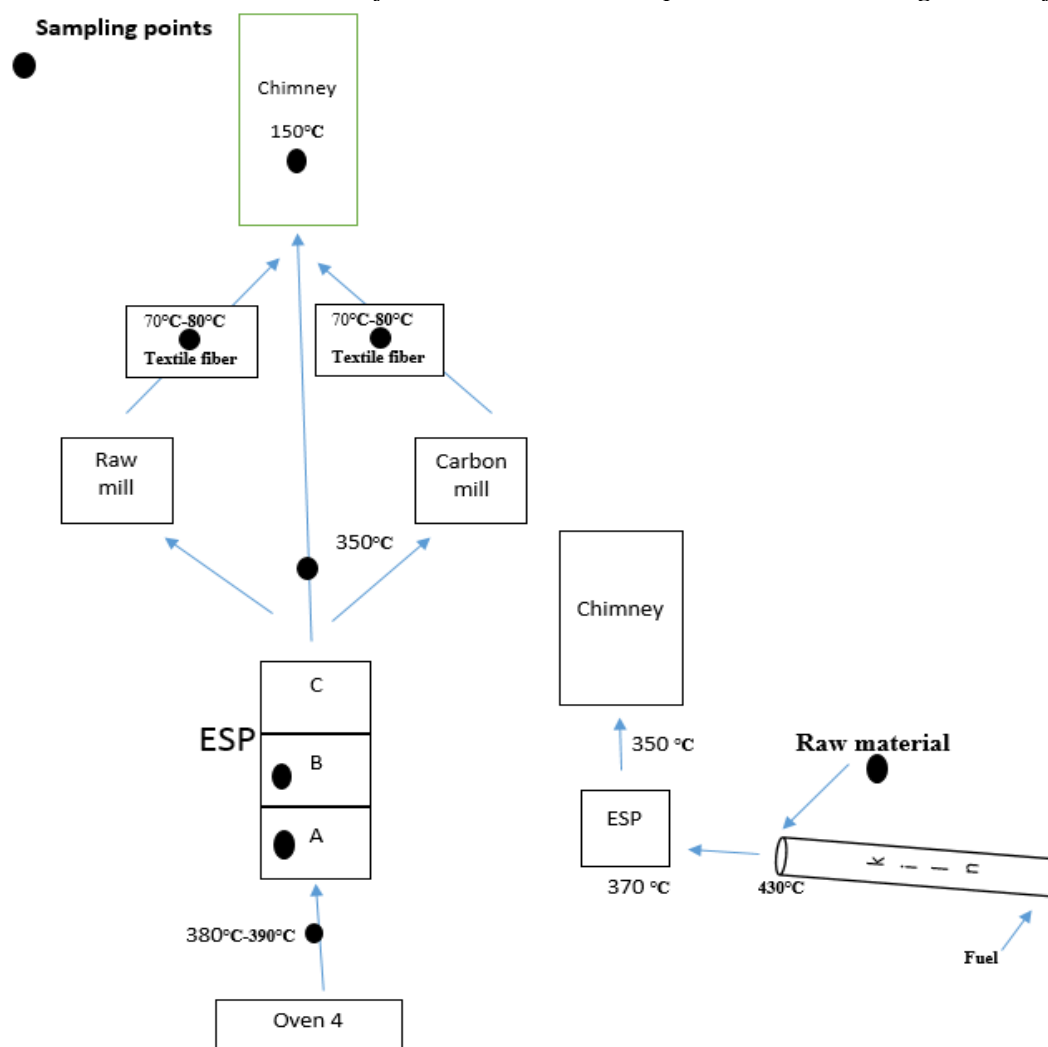


Figure 4 sampling point at the Cementa cement production facility in part 2

7.1 Extraction of gaseous samples

In the very first step of extraction, we took out the filters and XAD adsorbent from the sampling device and put into the Soxhlet Dean Stark apparatus. The glassware was rinsed with toluene into Soxhlet apparatus. 40 micro liter of ¹³C labeled internal standards of mono to octa-chlorinated dioxins and 40 micro liters of ¹²C labeled quantification standards were also added to the Soxhlet apparatus along with 40 micro liters of PCBs standards. The samples were extracted with 400 ml of toluene overnight. The extracts were evaporated into a few milliliters by vacuum evaporation. The sample flasks were rinsed with a few milliliters of cyclopentane. The extracts were divided into two halves, one-half for dioxin analysis and one-half for storage and back up.

7.2 Extraction of solid samples

We took 10 g of toluene washed sand in a glass extraction thimble. 3 g of ash sample added into the same thimble and 10 g of toluene washed sand added again and mixed thoroughly. 40 micro liters of internal standards for PCBs and mono-octa chlorinated dioxins were added. 10 ml of acetic acid was added to increase the extraction efficiency of PCDDs and PCDFs and allowed to react for one hour. 200 ml toluene and 15 ml deionized water were added to the round bottom flasks and the samples were then extracted for 48 hours in a Soxhlet apparatus. The extracted samples were evaporated into a few milliliters by vacuum evaporation. The flasks were rinsed with a few milliliters of cyclo-pentane. The extracts were divided and treated as the extracts of the gas samples.

7.3 Clean-up of the samples

The clean-up of the extracts were done by a four step procedure based on several open chromatographic columns, i.e. multilayered silica column, a super Alox column, an AX21-carbon/ Celite column and finally another miniaturized multi layered silica column. First of all the extracts were cleaned up with multilayered silica column consisting of glass wool, 1.5 ml basic silica, 1.0 ml neutral silica, 2 ml 40% H₂SO₄ impregnated silica and anhydrous sodium sulfate from bottom to top. The column was rinsed with 2-column height of n-hexane. In the second step, the Super-Alox column consisting of glass wool, 10 ml Alumina super-B I and 3 g sodium sulfate from bottom to top was prepared and rinsed with 30 ml of n-hexane.

The extracted samples applied on multilayered silica column with 3*1 ml of n-hexane, eluted with 30 ml n-hexane into the super Alox column. This eluate was discarded and after that, 100 ml dichloromethane/cyclohexane (1:1) was added to the Alox column to elute the PCDD/Fs into separate flasks. 40 microliter of tetradecane was added to the eluate and concentrated to a few milliliters, using a vacuum evaporator.

In the third step, a carbon column was prepared using glass wool, 0.5 g AX21-carbon/celite and then glass wool. The carbon should be approximately in the middle of the column. The column was rinsed with 10 ml toluene, 10 ml dichloromethane/ methanol/ toluene (15:4:1), 2 ml dichloromethane/n-hexane (1:1) and finally with 5 ml n-hexane. The concentrated sample from the super-Alox column was applied on this column with 3*1 ml n-hexane, eluted with 40ml dichloromethane/n-hexane (1:1), to collect the PCBs and then back flushed with 40 ml toluene to collect dioxins in the separate flasks. 40 micro liters of tetradecane was added to each sample, which then were concentrated to 40 micro liters using vacuum evaporation.

Finally, the multilayered silica columns were prepared with the same proportions as the first one, but miniaturized in Pasteur pipette this time. The column was rinsed with n-hexane equal to two column heights, after which the samples were applied and the dioxins were eluted with 8 ml of n-hexane. 40 microliters of recovery standards for dioxins were added to each flask. The samples were concentrated using vacuum evaporation without adding tetradecane because it is already present in the samples from previous step, left the samples for overnight and next day the samples transferred into GC vials for GC-MS analysis.

To be sure, about the reliability of the laboratory procedures, a blank was processed in the same way as the samples. The levels in the blank were in most cases well below 10% of what was detected in the samples and those that were higher has been omitted from the results as presented in the appendix. The recoveries were between 30% and 130%, which were within the limits for the EN 1948 standard. The analytical procedures for PCDD/Fs analysis performed in

accordance with the European Standard Method for PCDD/F analysis (EN: 1948 standard) by HRGC/HRMS using a Waters auto spec ULTIMA NT DB-5 mass spectrometer.

The degree of chlorination was calculated by using the equation R3.

$$\text{Degree of chlorination} = (\sum_{i=1}^8 niCDD/F*i) / (\sum_{i=1}^8 iCDD/F) \quad \text{R3}$$

Where i is the number of chlorines substituted on carbon backbone and n is the amount of the homologue group in moles.

8. Results and discussion

We have two data sets one based on previous samples collected between 2009 and 2012 at Cementa's cement production plant and a second based on new samples at the same plant in September 2013. The collection of the latter samples were based on the results from previous samples. The information about the raw meal and amount of different kinds of fuels used on different occasions in both studies for oven 3 and oven 4 are presented in table 3. The information about the fuels used during November 2011 in oven 4 was not available due to some technical reasons.

Table 3 Amount of raw meal and different kinds of fuels used on different occasions in Oven 3 and Oven 4

Oven 3	Raw meal (ton/h)	Coal (ton/h)	KEO (ton/h)	EO1 (ton/h)	RDF (ton/h)	SPA (ton/h)
June 2009	30.7	2.3	0.3	0	0	0
June 2010	28.3	2.26	0	0	0	0
October 2010	28.7	1.94	0.33	0	0	0
June 2011	29.4	2.4	0.17	0.34	0	0
November 2011	28.7	2.17	0.3	0.2	0	0
may 2012	30.6	2.24	0.72	0.12	0.32	0
sep-12	30.6	2.24	0.13	0	0.47	0
September 2013	25.2	1.69	0	0	0	0
Oven 4						
June 2009	32	2.7	0	0	0	1
October 2010	30.7	2.92	0	0	0	0.69
November 2010	29.9	2.8	0	0	0	0.66
Jun-2011	30.75	2.99	0.33	0	0.6	0
Jan-2012	29.94	3.27	0.5	0	0	0
May-2012	31.7	2.49	0	0	0.2	0.01
Sept-2012	30.3	2.6	0	0	0.5	0.78
September 2013	25.3	1.88	0	0	0.6	0.41

8.1 Part 1 dioxin data about the previous study

In this part, we received the dioxin data analyzed by the industry and the results in relation to the fuel and combustion conditions. The concentration of the dioxins expressed in pmol/m³ for gaseous samples and normalized to 1 atm, 0°C, dry gas and 11% O₂. For these data, no information was available about mono to tri-chlorinated dioxins; only tetra-octa chlorinated dioxins had been analyzed. Moreover, for oven 3 the homologue profile was available during June 2011, November 2011, May 2012 and September 2012. Similarly, the homologue profile for oven 4 was available during June 2011, January 2012, May 2012 and September 2012.

Generally, the concentrations of PCDFs were 2-15 times greater than the PCDDs as shown in table 4. The concentrations of dioxins in exhaust gases from raw mill and carbon mill in oven 4 were very low and had TEQ value below 0.1 ng/m³ that is why these are not included in the table 4 but presented in appendix.

Table 4 Amount of total PCDDs and PCDFs measured in pmol/m³ along with TEQ value measured in ng/m³ for both oven 3 and oven 4 on different sampling occasion.

Oven 3	Total PCDDs (pmol/m³)	Total PCDFs (pmol/m³)	I-TEQ (ng/m³)
June 2009	0.18	1.18	0.04
June 2010	0.02	0.19	0.01
October 2010	0.11	0.29	0.01
June 2011	0.13	1.17	0.05
November 2011	0.16	1.01	0.05
May 2012	0.47	2.77	0.11
September 2012	0.51	1.17	0.05
Oven 4			
June 2009	0.01	0.11	0.00
October 2010	0.07	0.43	0.02
November 2010	0.06	0.72	0.03
June 2011	0.18	2.80	0.13
November 2011	0.48	5.22	0.28
January 2012	0.31	1.36	0.08
May 2012 chimney	0.72	4.24	0.14
May 2012 chimney	0.21	2.41	0.11
September 2012 chimney	0.22	1.29	0.06
September 2012 before filter	0.56	2.50	0.11
September 2012 after filter	1.84	6.47	0.29

The homologue profile for PCDDs and PCDFs in oven 3 are shown in figure 5-6. The homologues of PCDFs show the similar pattern with TeCDF, the highest concentration, while PCDDs show different pattern during May 2012 and September 2012. This difference may be due to the different formation mechanism of these two compound groups. During May 2012 and September 2012, Cementa introduced RDF as an alternative fuel along with other alternative fuels (table 3). RDF consists of combustible portion of waste including plastic and biodegradable materials, which upon combustion may produce different kinds of precursors than other fuels. Precursors may be present in the fuel, formed during combustion or formed in the post combustion zone (36) which are responsible for the formation of dioxins. We can see in table 3, during June 2011, November 2011, May 2012 and September 2012 different alternative fuel mixes were used, due that reason we got different pattern of the dioxins during

these measurements as shown in figure 5-6. In a previous study, it has been shown that, homologue profile changes on changes in fuel composition (51)- (50). The homologue profile for PCDFs also changes, but they are produced in higher concentrations than PCDDs, therefore they are not account much as shown in figure 6 but can be seen in the appendix.

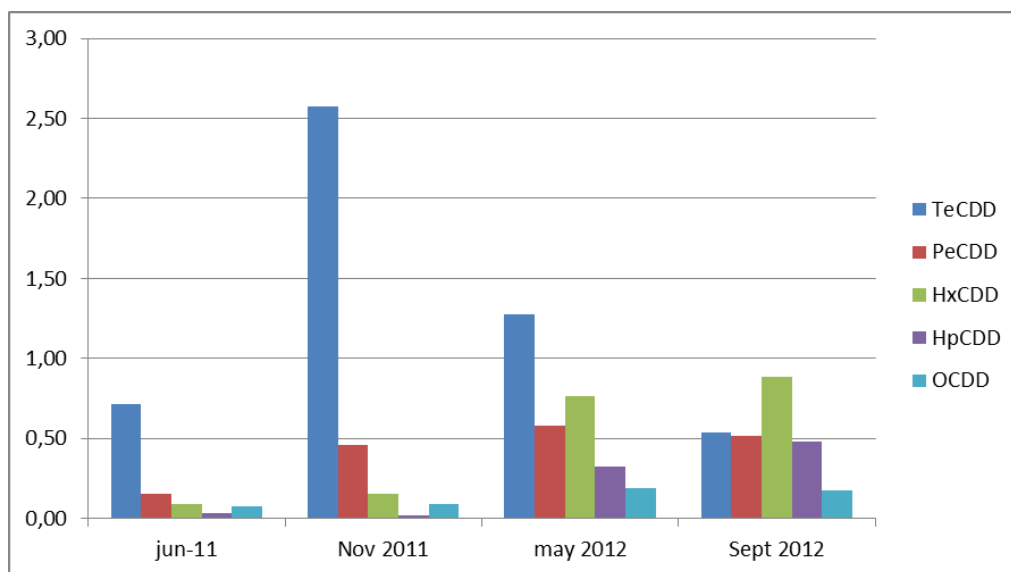


Figure 5 Homologue profile for tetra to octa chlorinated dibenzo-*p*-dioxins on different sampling occasions measured in pmol/m³ in oven 3

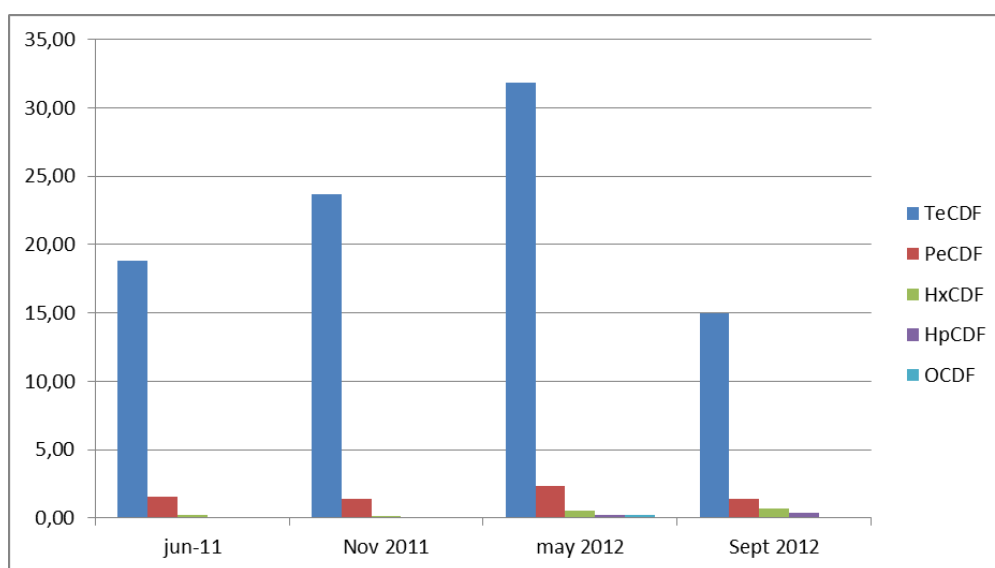


Figure 6 Homologue profile for tetra to octa chlorinated dibenzofurans on different sampling occasions measured in pmol/m³ in oven 3

The distribution of congener pattern for both PCDDs and PCDFs in oven 3 at different occasions are shown in figure 7-8. Hepta and octa-chlorinated congeners were dominant in case of PCDD with higher concentrations during May and September 2012, while in case of PCDF, tetra chlorinated congener was dominant with the highest concentration during May 2012.

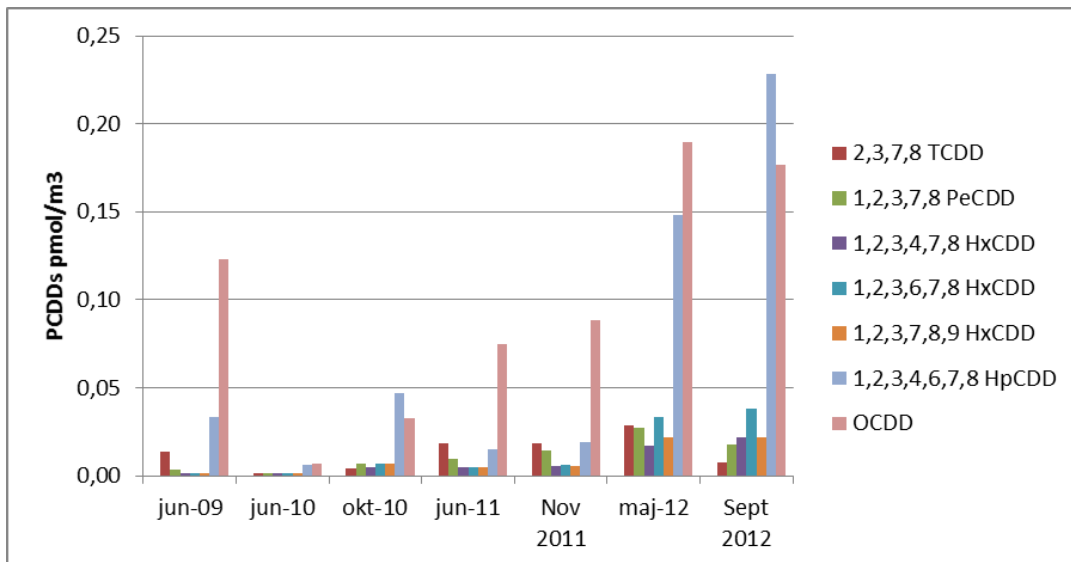


Figure 7 Congener distribution of PCDD at different sampling occasions in oven 3

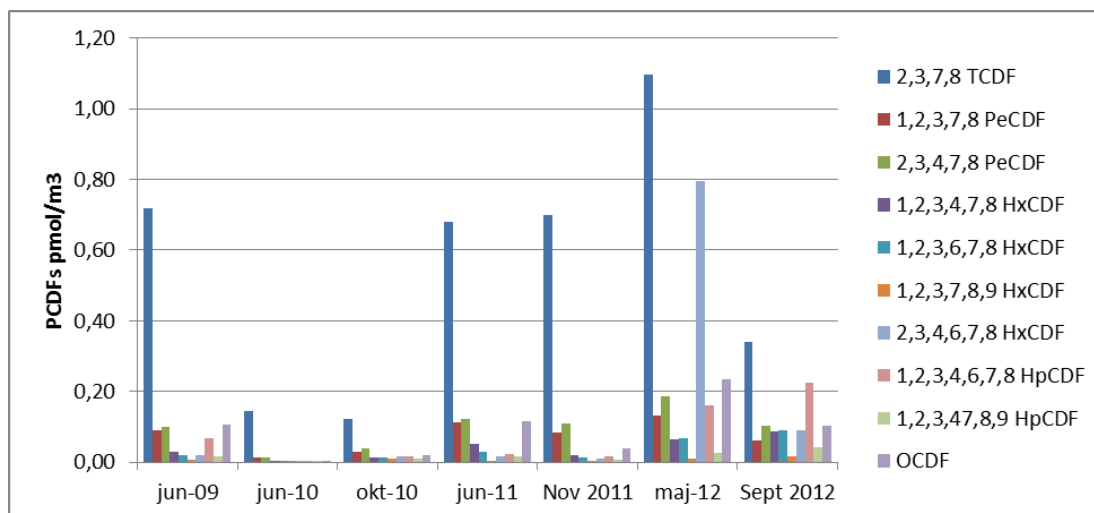


Figure 8 Congener distribution of PCDF at different sampling occasions in oven 3

The congener pattern for PCDDs show a dominating formation of higher chlorinated congeners during all the occasions. This type of behavior may be due to increased level of chlorine in the flue gas, which previously has been shown to increase both the PCDD/Fs and the degree of chlorination (57) (75). During May and September 2012, the congener profile for PCDDs show that there is more chlorine present during these occasions as compared with other occasions. This may be due to the introduction of RDF during these measurements in the Cementa plant because RDF is proposed as the main source of chlorine in the solid waste incineration process (76). Similarly, in case of PCDF (figure 8), the congener pattern during May and September 2012 was different from the other sampling occasions. However, here only the concentration of highly chlorinated congeners increased. This also supports the availability of chlorine during these occasions and as a result, less chlorinated congeners undergo chlorination and converted to highly chlorinated congeners.

The homologue profile for PCDDs and PCDFs in oven 4 are shown in figure 9 and 10, with clear dominance of tetra-chlorinated homologue in both cases.

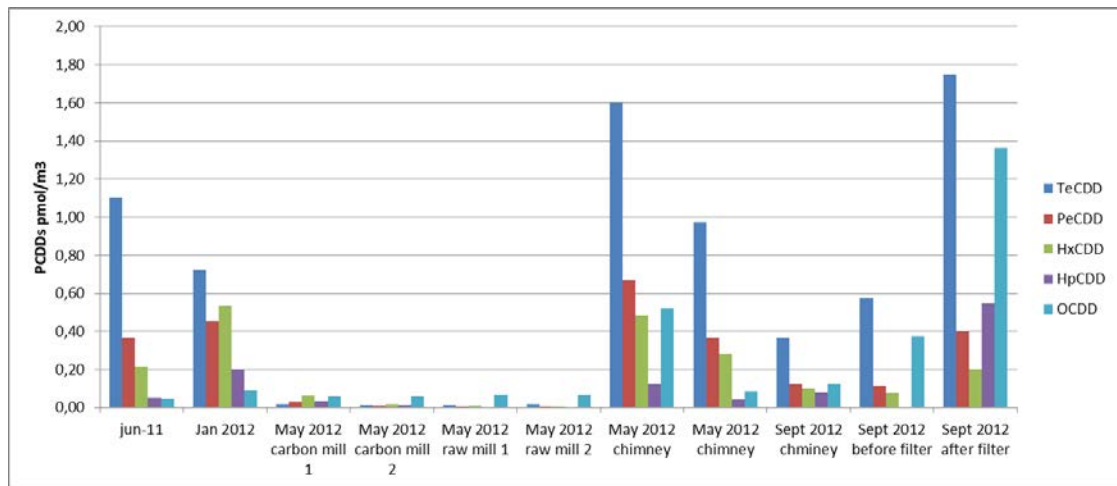


Figure 9 Homologue profile from tetra to octa chlorinated dibenzo-*p*-dioxins in oven 4 on different sampling occasions.

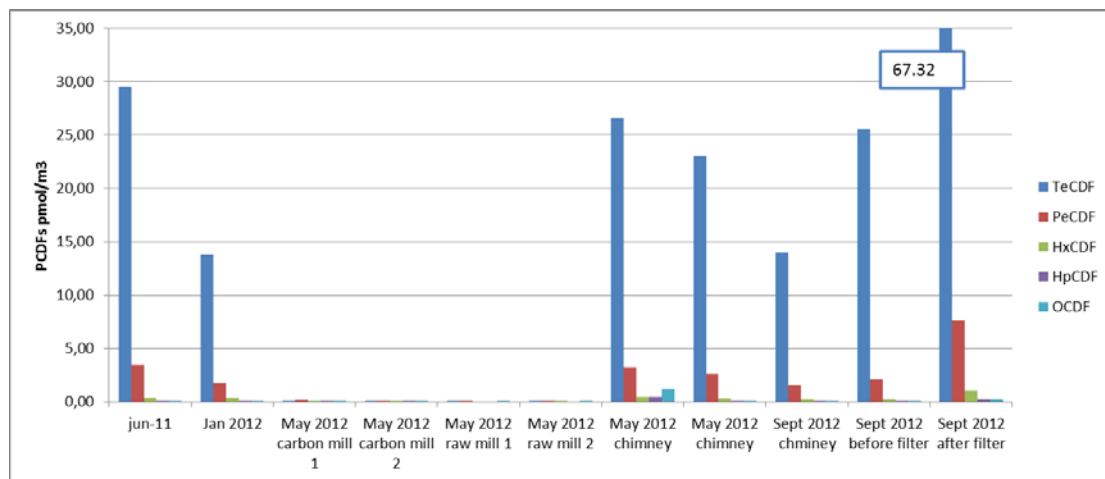


Figure 10 Homologue profile from tetra to octa-chlorinated dibenzo furans in oven 4 on different sampling occasions

The homologue profile for PCDDs (figure 9) shows different pattern on different sampling occasions. This difference may be attributed to the different fuel mixes were used on different occasions (table 3). Because of different fuels mixes, different precursors formed during combustion. The concentrations of dioxins were very low in flue gas samples taken at raw mill and carbon mill. During September 2012, we had two samples one before ESP (before filter) and other after ESP (after filter). For PCDDs, the levels of individual species of homologue in after filter were higher than before filter. The increase of dioxin levels in ESP could be attributed to availability of chlorine, carbon structure, oxygen, temperature and residence time. Since temperature and residence time are both important for the formation of dioxins in the post combustion zone. The temperature of ESP is normally set at 250-400°C. This temperature window facilitates the heterogeneous formation of dioxins in ESP and as a result, higher levels of dioxins detected after filter as compared with before filter. These results are consistent with the findings: catalytic potential of fly ash for the formation of dioxins have been proposed by Shaub and wing (37). The homologue profile for PCDFs, presented in figure 10, was similar at all sampling occasions but varying individual species with a clear dominance of tetra CDF. PCDFs after filter were higher than before filter in September 2012 due to the same reason explained above.

The congener profile for PCDDs in figure 11 shows that highly chlorinated congeners are formed more than less chlorinated. The increased proportions of higher chlorinated dioxins after filter

in September 2012 as compared with before filter may be attributed to the chlorination of lower chlorinated dioxins or dioxin formation in the ESP explained as above (37). Similarly, the congener pattern for PCDFs are different for different occasions explaining the different fuel mixes used and with increased concentrations of all the congeners after filter in figure 12.

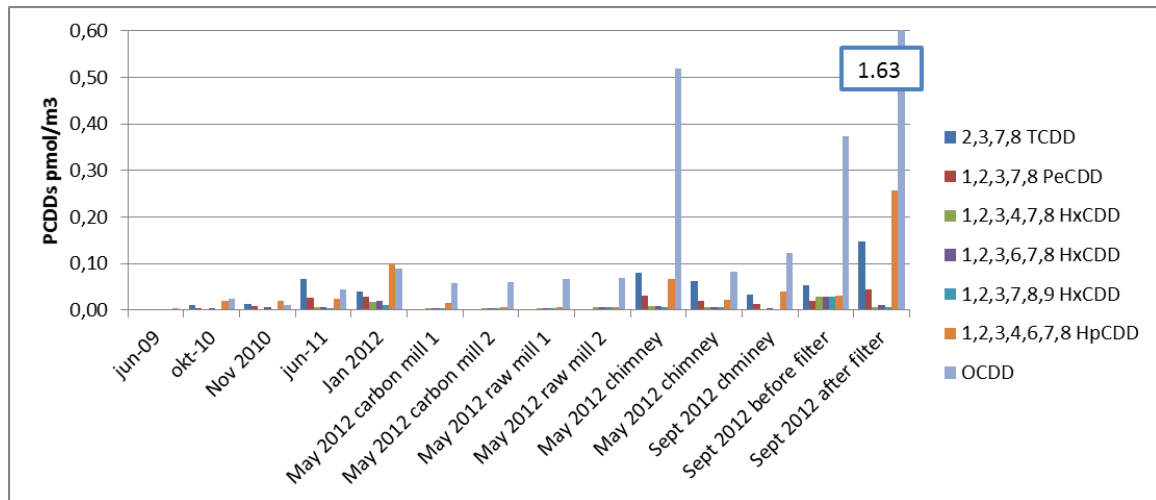


Figure 11 Congener distribution of PCDD at different sampling times

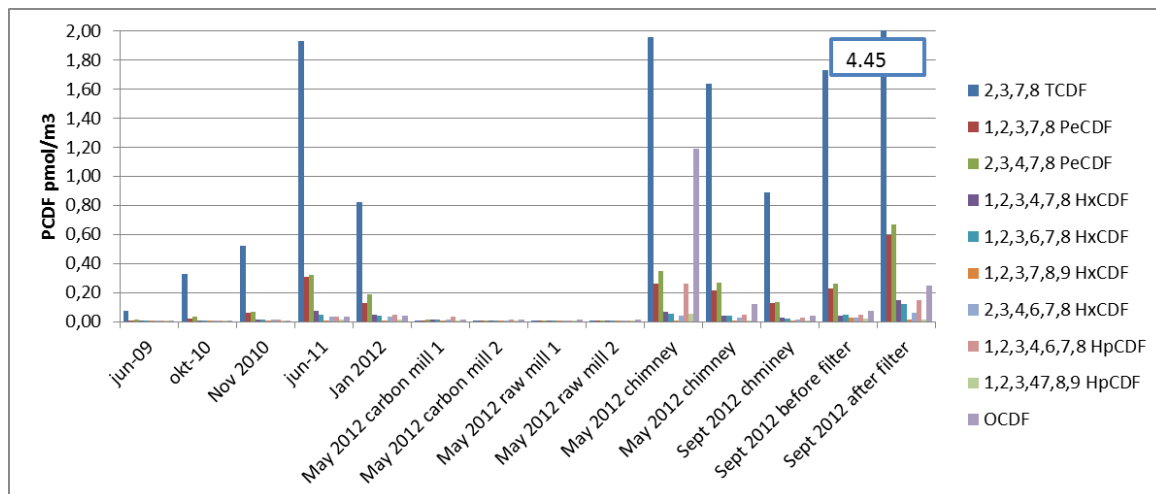


Figure 12 Congener distribution of PCDF at different sampling times

The TEQ of all the samples were calculated for both oven 3 and oven 4 shown in figure 13 a-13 b. The World health organization (WHO) standard for daily average value of dioxin emission from cement industries is set as 0.1 ng/m³ TEQ, the maximum permissible toxic level. This standard was used to assess the toxicity associated with all the samples analyzed.

In case of oven 3, all the samples have TEQ below 0.1 ng/m³, except May 2012 figure 13 (a). This is probably because in May 2012, the fuel used contained relatively high amount of KEO along with addition of RDF. RDF and KEO both are waste containing chlorine and hydrocarbons, so during combustion these materials are thought to form different precursors, which are responsible for the formation of dioxins in Cementa production plant or to increase the proportions of PCDD/F congeners with higher TEF values.

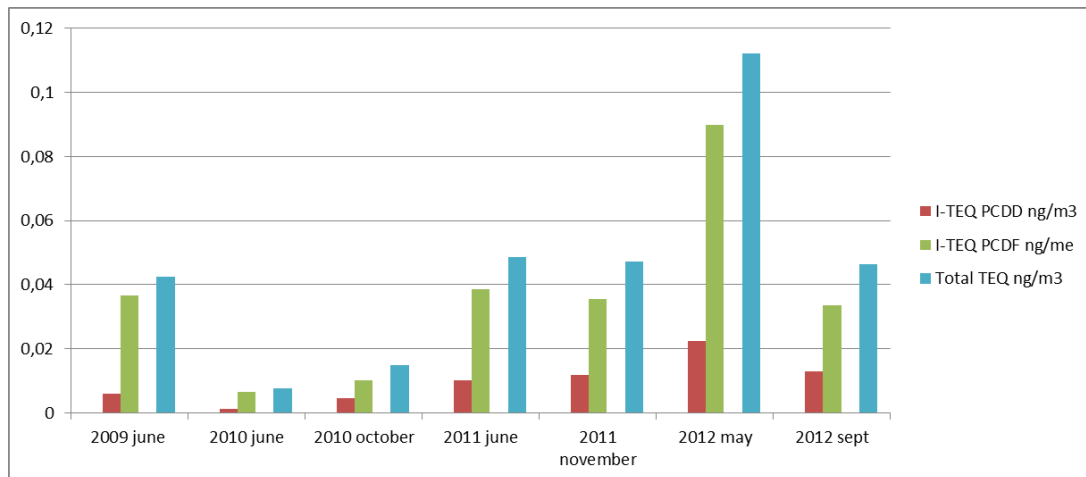


Figure 13 (a) WHO 2005 TEQ ng/m3 in Oven 3

Similarly for oven 4, the TEQ during June 2011, November 2011, May 2012 and September 2012 were found to exceed the toxic concentrations as shown in figure 13 (b). This increase in TEQ during these occasions may be attributed to the fuel used during these months. In June 2011, KEO and RDF were used as an additional alternative fuel along with other fuels. They will increase the proportions of congeners having higher TEF values as explained above. During November 2011, we did not find the fuel data so could not say anything about it. Moreover, in May and September 2012, RDF and SPA introduced as an additional fuel along with other fuels. These different mixes of fuels will give different types of precursors and therefore produce different types of congeners possessing different TEF values and as a result different toxicity observed during these different sampling occasions.

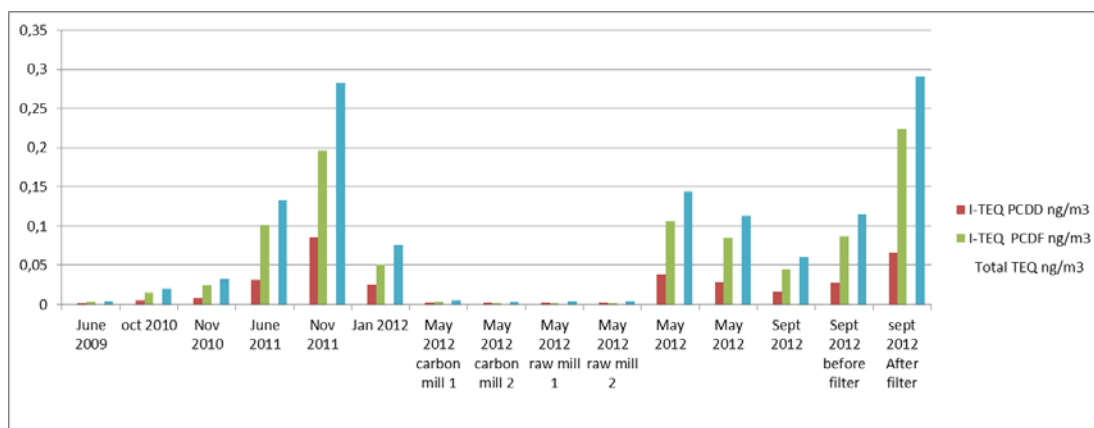


Figure 13 (b) WHO 2005 TEQ ng/m3 in Oven 4

8.1.1 Discussion

Dioxins emitted from cement kilns may originate from PCDD/Fs already present in the raw meal, organics and chlorine level in the raw meal and the fuel used. In the rotary kilns, there is very small chances for the dioxins to survive due to the very high temperature, long residence time and the excess of oxygen that would destroy all organic compounds. The organic compounds present in the raw meal volatilized in the preheater zone and become available as precursors for dioxins formation. According to Eduljee 1998 (48) chlorophenols and chlorobenzenes are formed as products of incomplete combustion in the preheater zone with chlorobenzene formation with preference to chlorophenols. A reaction mechanism in which

chlorobenzenes dominate would form higher chlorinated PCDDs at the expense of lower chlorinated PCDDs as observed during May and September 2012.

There is also another possibility that the residual carbon present in the flue gas deposited on the walls of APCD or adsorbed on the particulates. The temperature in the APCD facilitates the de novo mechanism in the presence of chlorine and oxygen for the formation of dioxins.

We can see clearly in figures 5-12 that concentrations of PCDFs are higher than PCDDs. Therefore, de novo mechanism might have occurred in these experiments. De novo synthesis requires carbonaceous material, oxygen, chlorine and metals as catalyst particularly Cu (35).

The oxygen required in de novo formation might be available in solid-state form present in the raw meal in the form of oxides. The oxygen may come from aluminum silicates and some metal oxides present in the raw meal. The chlorine used in the de novo synthesis found in solid phase or produced during the process in the form of HCl or Cl₂ (63). Vogg *et al.*, 1987 (77) has also proposed that alkali and alkaline earth metal chlorides could be a good source of chlorine for de novo formation. CuCl₂ and FeCl₃ has been identified the compounds in the waste in the incineration system with catalytic activity but CuCl₂ proved to be more efficient than FeCl₃ (78).

In the Cementa plant during May 2012 in oven 3, they started to introduce RDF and KEO along with other fuels and the concentration of dioxins produced is comparatively higher than other sampling occasions. The possible reason is that by using RDF and KEO, there will be higher chlorine and carbonaceous material produced in the system. Because RDF consists of combustible part of waste including plastic and found as a source of organic chlorine in the combustion system (76), and KEO is a used oil. These fuels would provide carbonaceous structures and chlorine more than other sampling occasions. The TEQ value in May 2012 in Oven 3 was exceeding the toxic level 0.1 ng/m³ set by the WHO. Therefore, we can say that during May 2012 in oven 3, congeners with high TEF values were produced more and contributed more to the TEQ value. Similarly, in case of Oven 4, in June 2011, November 2011, May and September 2012, the TEQ exceeding 0.1 ng/m³ but with varying in their values from each other. This is may be due to the reason that during these sampling occasions, Cementa used different fuel mixes that produced different precursors and as a result, different congeners are produced possessing different TEF values. Therefore, different TEQ values were measured on different sampling occasions in oven 4. During June 2011, KEO and RDF were introduced along with other alternative fuels, that will probably produce different precursors and different congeners will be formed as described above. We do not get information about fuels used during November 2011, so could not say anything about it, similarly during May and September 2012 Cementa introduced RDF and SPA along with other fuels. SPA is a kind of waste solvent and RDF waste containing plastics, these fuels would produce different precursors, and as a result, different congeners would be formed possessing different TEF values.

The dioxin formation in Cementa cement production plant can be related to the alternative fuel used in such a way that different mixes of different alternative fuels gave different congeners possessing different TEF values and as a result, different TEQ values were observed for different sampling occasions. Coal, RDF, SPA and KEO were used as alternative fuels with varying concentrations on different sampling occasion in part 1. Therefore, different kinds of precursors in different ratios are produced depending on the fuels used. It has previously proposed that homologue profile changes on changing fuels composition (51)- (50) and our results are consistent with these findings. Some studies show that PCDD/Fs formation depend not only of the fuel also on the trace organic contents of the raw meal (lime stone, sand shale clay and iron ore) and temperature of the flue gases as they pass through APCD (49).

From the above study, we found that in Cementa cement production plant with two similar ovens operated with different alternative fuel mixes produced different levels of dioxins. The oven 4 was found to be at more risk because dioxins emitted from oven 4 exceeded the TEQ 0.1 ng/m³ in more samples as compared with oven 3. In oven 3, only one sample has TEQ more than 0.1 ng/m³. Therefore, we decided to take more samples in oven 4 from different points during their production (figure 4), when they substituted alternative fuels to find out where the dioxins are actually formed.

8.2 Part 2 dioxin formation at different places in the Cementa production plant during cement manufacturing

The samples at raw mill, coal mill, before ESP, after ESP, Chimney O3 and Chimney O4 were gaseous, while others were solid samples. The concentrations of the dioxins for gaseous samples expressed in pmol/m³ and for solid samples expressed in pmol/g, normalized to 1 atm, 0°C, dry gas and 11% O₂. The TEQ values for gaseous samples were expressed in ng/m³ while for solid samples in ng/g.

Table 5 Amount of total PCDDs and PCDFs expressed in pmol/m³ for gaseous samples and pmol/g for solid samples, degree of chlorination and WHO 2005 TEQ expressed in ng/m³ for gaseous samples and ng/g for solid samples for all sampling points in oven 4 part 2.

Flue gases	Total PCDD (pmol/m ³)	Total PCDF (pmol/m ³)	# Cl PCDD	# Cl PCDF	WHO₂₀₀₅TEQ (ng/m ³)
Raw mill	1	6	4.95	4.37	0.02
Carbon mill	6	47	4.19	2.94	0.20
Before ESP	598	1319	4.03	2.36	2.74
After ESP	536	2339	2.18	3.31	3.06
Chimney O3	165	3023	3.51	3.29	2.06
Chimney O4	1097	3761	3.80	3.44	8.07
Solid samples	pmol/g	pmol/g			ng/g
Alox	0.5	1	3.41	3.10	0.00
Copper slag	0.1	1.2	3.07	2.40	0.00
Raw meal	0.5	3.3	4.09	3.05	0.01
Field A in ESP	0.3	0.4	3.77	3.18	0.00
Field B in ESP	3.2	24	4.41	3.25	0.08

The homologues of PCDDs and congener profiles for gaseous samples are shown in figure 14-15.

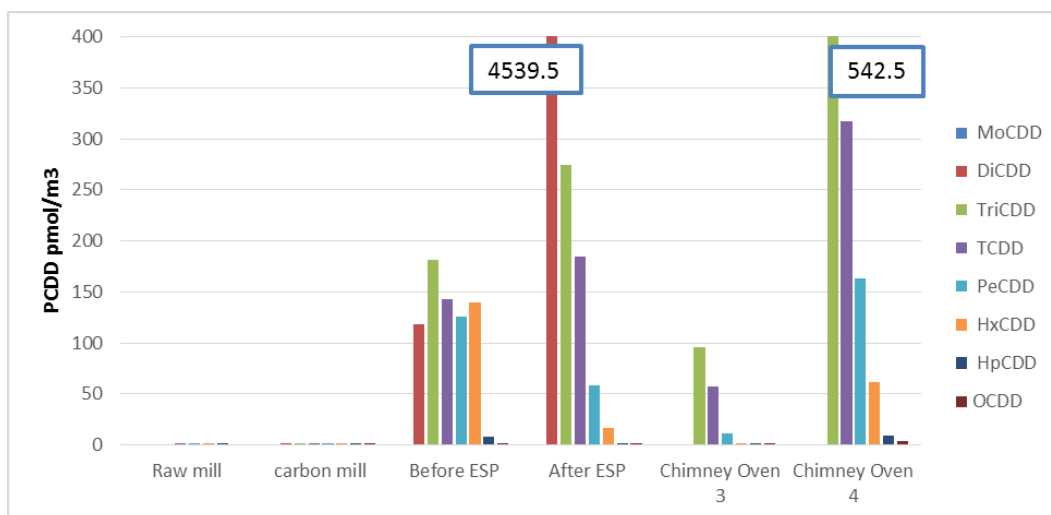


Figure 14 Homologue profile of mono to octa-chlorinated dibenzo-*p*-dioxins for gaseous samples during cement production

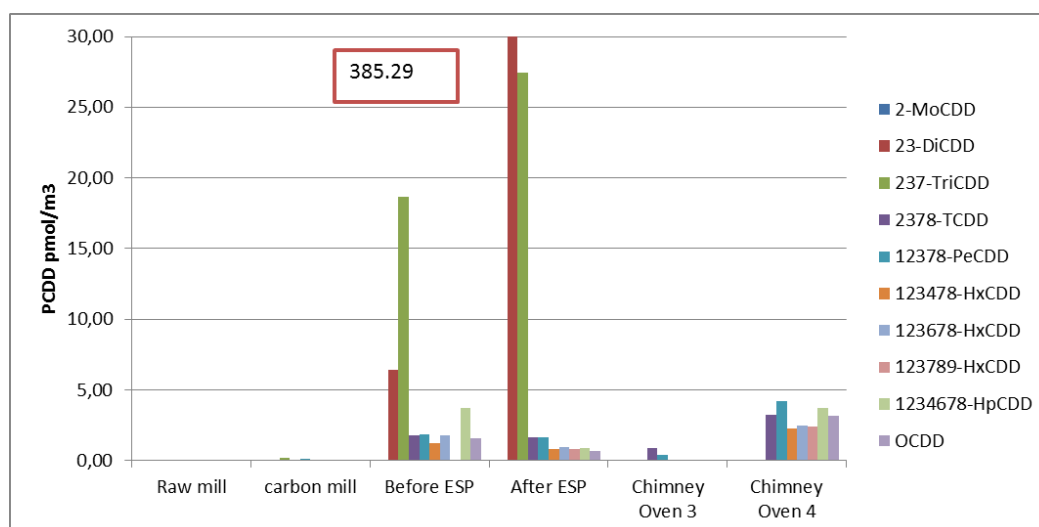


Figure 15 Congener profile of mono to octa-chlorinated dibenzo-*p*-dioxins for gaseous samples during cement production

The concentrations of PCDDs in raw mill and carbon mill were very low. Nevertheless, the TEQ associated with carbon mill exceeded the toxic level 0.1 ng/m^3 for dioxins. This increase in TEQ value could be related to PCDFs as can be seen in table 6 that PCDFs are formed more than PCDDs. The homologue profile of PCDDs before ESP (Figure 14) shows the increased proportions of di-hexa chlorinated dioxins with clear dominance of tri-chlorinated PCDDs, but this is not the case with congener profile in figure 15. In figure 15, we can see that tri-chlorinated is the most dominant congener and after that di, hepta and octa-chlorinated with decreasing order. Since we analyzed only 2378-substituted congeners, therefore the results show that there may be some other than 2378-substituted congeners formed before ESP that contribute to the homologues of PCDDs. This is because in the rotary kiln, different types of precursors are formed, so different congeners are formed depending on the precursors.

The dioxins formation before ESP may be attributed to the temperature that was $380\text{-}390^\circ\text{C}$, facilitating the heterogeneous formation of dioxins. The residual carbon and chlorine level in the flue gas may proceed through heterogeneous formation of dioxins (35).

The proportions of higher chlorinated (penta-octa chlorinated) PCDDs decreased after ESP as compared with before ESP. This effect can be explained that in ESP, particulate matter removed

by inducing the electrostatic force. The particles are charged and attracted towards opposite charged plates from where they were removed. The efficiency of ESP is a function of migration velocities of particles that is a function of particle size (79). Since higher chlorinated congeners possess less vapor pressure (80), therefore due to less vapor pressure, they have greater affinity with particles and can be trapped in the ESP and consequently less chlorinated congeners detected after ESP as shown in figure (14-15).

The homologue profile of PCDDs at chimney oven 4 shows the increase in relative proportions of all the species as compared to after ESP with tri-chlorinated PCDDs, the highest concentration and then tetra-octa chlorinated in a decreasing order (figure 14). The congener profile (figure 15) does not represent the pattern as in homologue. This explains the same reason that there may be some other than 2378-substituted congeners produced in the convector after ESP and before chimney oven 4. The homologue profile in chimney oven 4 could also be due to de-chlorination of highly chlorinated dioxins such as OCDD or OCDF to less chlorinated dioxins explained by weber *et al.* (2002) (81).

The homologue profile for chimney oven 3 shows the dominance of tri-chlorinated then tetra and penta chlorinated dioxins. We had only one sample from chimney oven 3, therefore it is not easy to say something about it because we do not have dioxin levels on other sampling points to compare with as we had in oven 4.

The homologue profile of PCDFs and congener pattern for gaseous samples are shown in figure 16-17.

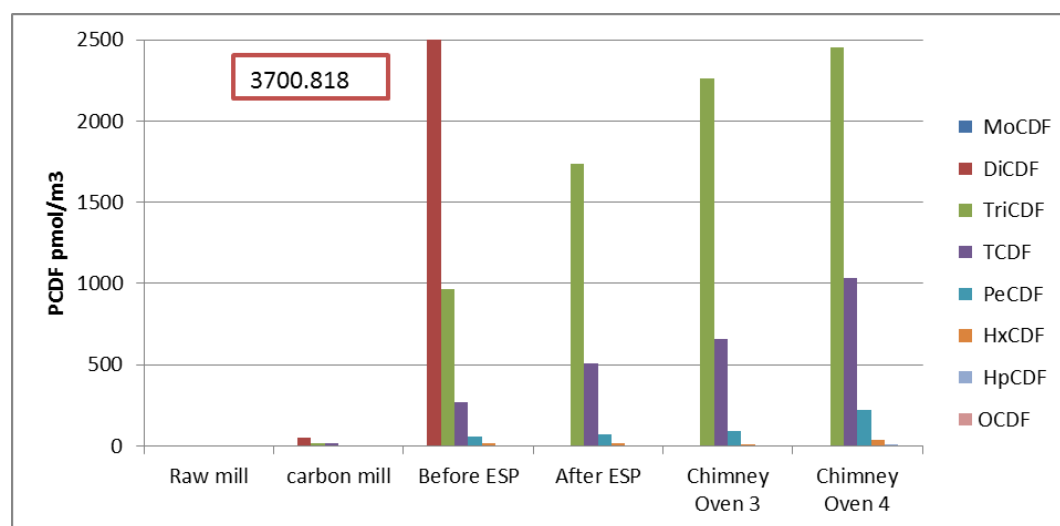


Figure 16 Homologue profile of mono to octa chlorinated dibenzo furans for gaseous samples during the cement production

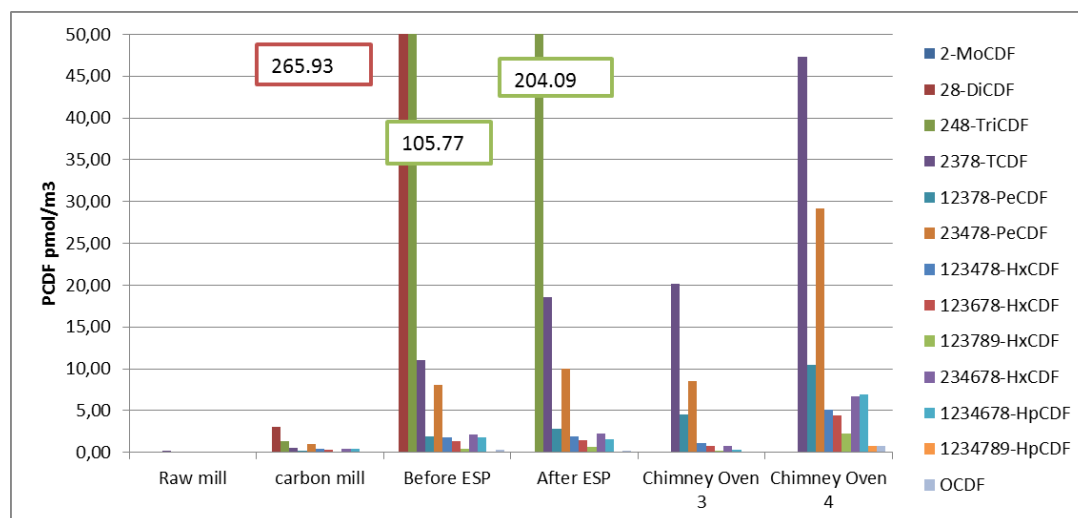


Figure 17 Congener pattern of mono to octa chlorinated dibenzo furans for gaseous samples during the cement production

The PCDF levels in raw mill and carbon were very low but in case of carbon mill, some PCDF congeners were measured having higher TEF values and contributed to the TEQ value, which goes higher than 0.1 ng/m³.

The homologue of PCDFs and congener profile in all samples were almost similar explaining there are not so much affected as of PCDDs. This is because of different formation mechanisms for these two compound groups. Wikström *et al.* (2003) proposed maximum formation rate for PCDDs between 300-400°C and 400-500°C for PCDFs (57). Since we analyzed dioxins below 400°C in Cementa plant, therefore we may say that during this temperature window PCDDs are more affected than PCDFs. In after ESP, the homologues of tri-hexa chlorinated furans increased but hepta and octa-chlorinated decreased. This is not very clear in figure 16 but can be seen in the appendix. This can be explained as, in the ESP, bigger particles due to less vapor pressure are trapped more than smaller particles as explained above therefore, drop in hepta and octa-chlorinated furans after ESP observed. The increased level of tri-hexa chlorinated furans could be due to the surface catalyzed reaction in the ESP. Similarly, the homologue profile of PCDFs during chimney oven 4 represents the increase in all individual species as compared with after ESP sample. However, the congener pattern in figure 17 does not show this type of pattern hence supporting the theory that there may be some other than 2378 substituted furans formed.

The PCDD homologue and congener profile of solid samples are shown in figure 18-19.

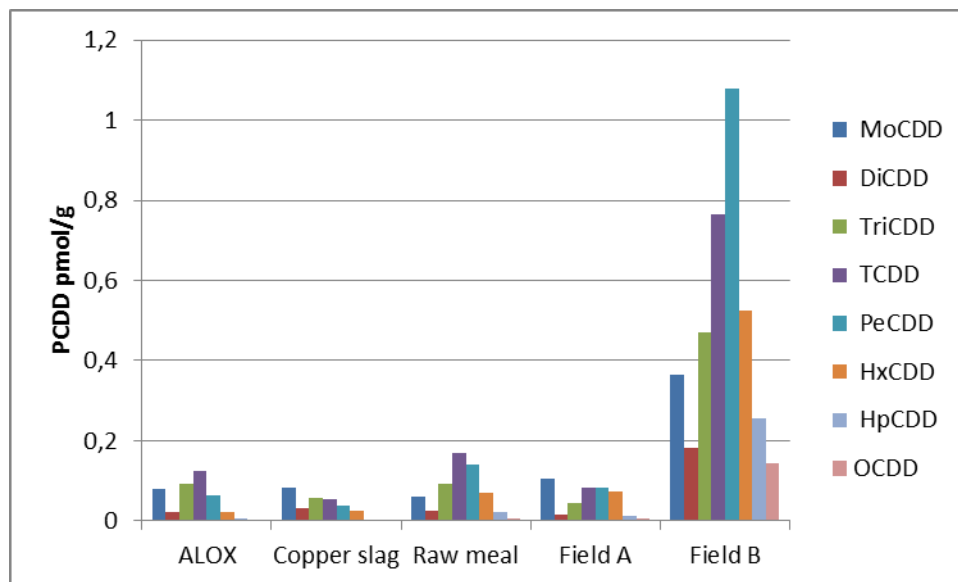


Figure 18 Homologue profile of PCDDs in solid samples during cement production

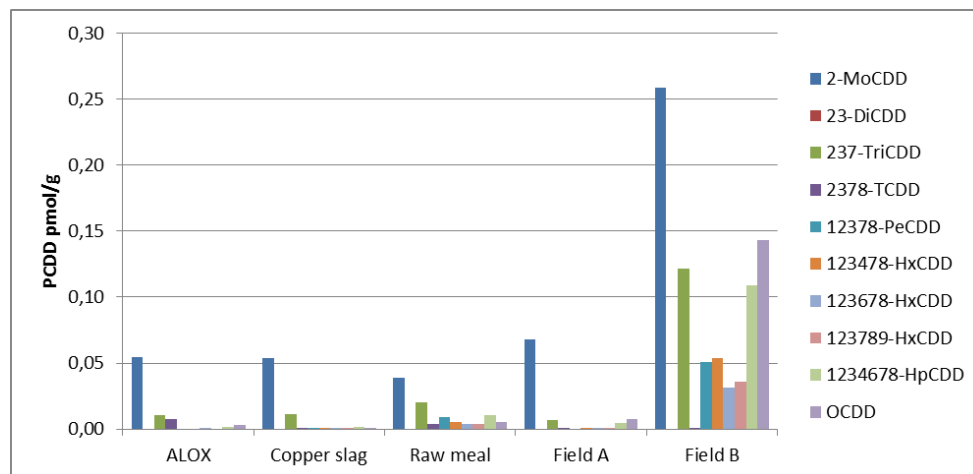


Figure 19 Congener pattern of PCDDs in solid samples during cement production

The PCDD levels in Alox, copper slag, raw meal and field A were very low with the highest in field B and the TEQ associated with these samples was also under the toxic level. Field A and B are the sampling points in ESP entering flue gas first in field A and then moved to B. The higher concentrations of dioxins in field B can be explained as larger particles trapped in field A, allowing smaller particles into field B. Since smaller particles provide the larger surface area in field B as compared with larger particles in field A, giving more dioxin formation in field B of higher surface area through surface catalyzed reaction in ESP.

The homologues for PCDF and congener profile of solid samples are shown in figure 20-21.

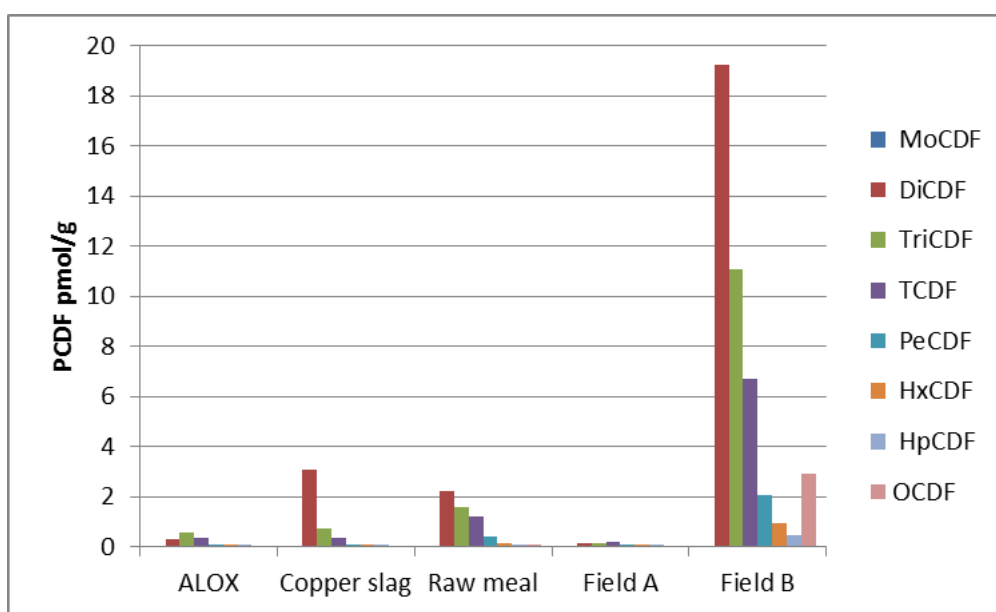


Figure 20 Homologue profile for PCDF of solid samples during cement production

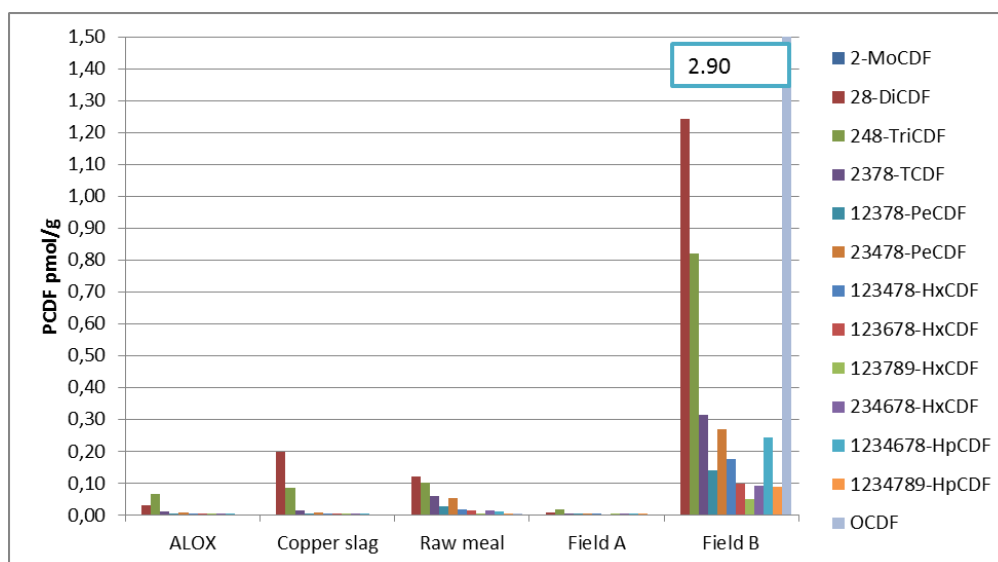


Figure 21 Congener profile for PCDF of solid samples during cement production

The furan levels in Alox, copper slag, raw meal; field A and field B were more than PCDDs but the TEQ associated with these samples were below the toxic level. The furan levels in field B are higher than field A and could be the same reason as explained for PCDDs. The homologue profile of PCDF in field B (figure 20) and congener profile (figure 21) showed that there might

be some other than 2378 substituted furans formed. This can also be due to the dechlorination of OCDF to less chlorinated furans as explained by Weber *at el.*, 2002 (81).

The TEQ value for all the gaseous samples expressed in ng/m³ and solid samples expressed in ng/g were calculated and presented in figure 22.

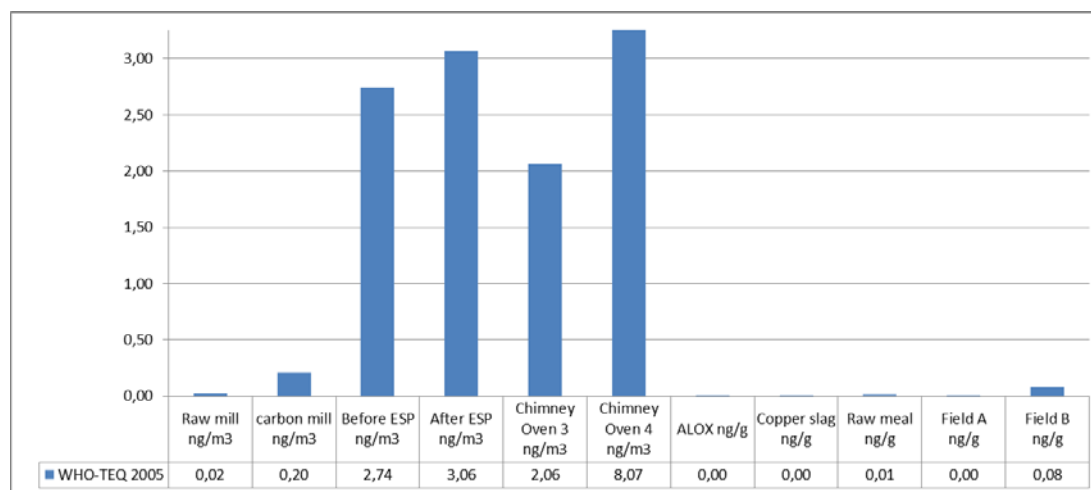


Figure 22 WHO 2005 TEQ concentrations during the cement production for different sampling points

In figure 22, the TEQ value associated with all samples represents that the TEQ value in carbon mill, before ESP, after ESP, chimney oven 3 and chimney oven 4 were above the toxic level 0.1 ng/m³ set by WHO. Therefore, we may say that at these sampling points the dioxin formed with congeners of high TEF values. In all solid samples, the TEQ value was below 0.1 ng/g making them non-risky but the sampling points for flue gas samples are at more risk.

8.2.1 Discussion

The amount of total PCDDs and PCDFs showed that PCDFs are higher than PCDDs shown in table 6. One explanation to this is that PCDFs can be formed through several routes whereas PCDDs formation routes are limited. PCDFs can be formed through many precursors such as biphenyls, phenols, chlorination of dibenzofurans or through de novo synthesis. It has also been shown to form through incorporation of oxygen and PAH (82). On the other hand, formation of PCDDs requires at least one ortho-substituted chlorophenols but in the raw gas of combustion system, there are 100 times more un-substituted phenols present. This explains the concentrations of PCDFs are higher than PCDDs in combustion system (83).

The dioxin concentrations in Alox, copper slag, raw meal, field A and B in ESP have very lower level of dioxins and the TEQ value below 0.1 ng/g. This effect may be explained in a way that not all the dioxins measured at these sampling occasions contribute to the TEQ; mostly less chlorinated dioxins contribute to TEQ values in gaseous samples.

Generally, dioxins are formed due to the organics and chlorine present in the raw meal and the fuel used. Moreover, some metals acting as catalyst may be present in the fuel and raw meal as well as the temperature of the APCD is very important in this regard. Therefore, we may say that in Cementa cement production plant, they used the raw meal with high contents of organics and chlorine with some catalysts in their raw meal or in the fuel. The organic compounds present in the raw meal volatilized and can act as precursors for gas phase reaction or adsorbed on the surface of particles in the flue gas and take part in the heterogeneous surface catalyzed reaction for the formation of dioxins. Moreover, during cement production using waste as alternative fuels may produce different types of precursors and those precursors combine to form dioxins.

The analysis of raw meal showed the presence of dioxins naturally occurring in the raw meal as shown in figure 18-21. These naturally occurring dioxins may desorb with the flue gas when flue

gas used to heat up the raw meal and come out in the flue gas. The decrease in highly chlorinated dioxins after ESP suggests the adsorption of higher chlorinated compounds in ESP.

The temperature of the APCD is important for controlling the dioxin formation. There was a study conducted on the formation of PCDD/Fs in cement kilns and tested the dioxins at two different temperatures 255°C and 400°C (56). The dioxins were maximum at higher temperature and minimum at lower temperature suggesting that the temperature of the APCD should be minimum in order to decrease the formation of dioxins.

Conclusion

From the above study, we come up with the conclusion that the formation of dioxins in the Cementa cement production facility depends on the alternative fuel used and the temperature of APCD. We observed different homologue profile for using different mixes of alternative fuels, because of production of different types of precursors.

To minimize the dioxins formation at Cementa cement production plants, raw meal and fuel used should contain minimum organic pollutants and chlorine contents. Sulfur contents in the raw meal have shown inhibitory effect, therefore to minimize the dioxins production there should be some inhibitory agents in the raw meal or raw gas. For the formation of dioxins temperature play a significant role, to minimize the dioxin emissions, temperature of the APCD should be minimum so that the raw gas cooled down quickly. To understand the exact relation between dioxin formations and alternative fuels in this study, the complete analysis of all the congeners and elemental analysis of the raw meal and the fuel is required.

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Appendix

Part 1 studies

The concentrations of PCDD congeners expressed in ng/m³ for oven 3.

	Jun-09	Jun-10	Oct-10	Jun-11	Nov 2011	May-12	Sept 2012
2,3,7,8 TCDD	0,004	0,001	0,001	0,006	0,006	0,009	0,002
1,2,3,7,8 PeCDD	0,001	0,000	0,002	0,003	0,005	0,010	0,006
1,2,3,4,7,8 HxCDD	0,001	0,000	0,002	0,002	0,002	0,007	0,008
1,2,3,6,7,8 HxCDD	0,001	0,001	0,003	0,002	0,002	0,013	0,015
1,2,3,7,8,9 HxCDD	0,001	0,000	0,003	0,002	0,002	0,009	0,008
1,2,3,4,6,7,8 HpCDD	0,014	0,003	0,020	0,006	0,008	0,063	0,097
OCDD	0,057	0,003	0,015	0,035	0,041	0,087	0,081

The concentrations of PCDF congeners expressed in ng/m³ for oven 3.

	June-09	June-10	Oct-10	June-11	Nov 2011	May-12	Sept 2012
2,3,7,8 TCDF	0,220	0,045	0,037	0,208	0,214	0,336	0,104
1,2,3,7,8 PeCDF	0,031	0,005	0,010	0,039	0,028	0,045	0,021
2,3,4,7,8 PeCDF	0,035	0,005	0,013	0,042	0,038	0,063	0,035
1,2,3,4,7,8 HxCDF	0,012	0,001	0,005	0,019	0,007	0,024	0,033
1,2,3,6,7,8 HxCDF	0,007	0,001	0,005	0,011	0,006	0,025	0,034
1,2,3,7,8,9 HxCDF	0,003	0,000	0,004	0,002	0,002	0,004	0,007
2,3,4,6,7,8 HxCDF	0,007	0,001	0,006	0,007	0,004	0,298	0,034
1,2,3,4,6,7,8 HpCDF	0,028	0,002	0,007	0,009	0,007	0,066	0,092
1,2,3,4,7,8,9 HpCDF	0,007	0,000	0,004	0,006	0,003	0,011	0,018
OCDF	0,047	0,002	0,008	0,051	0,017	0,103	0,046

Oven 4

The PCDDs congeners data expressed in ng/m³ for oven 4.

	Jun-09	Oct-10	Nov 2010	Jun-11	Nov-11	Jan 2012	May 2012 carbon mill 1	May 2012 carbon mill 2	May 2012 raw mill 1	May 2012 raw mill 2	May 2012 chimney	May 2012 chimney	Sept 2012 chimney	Sept 2012 before filter	Sept 2012 after filter
2,3,7,8 TCDD	0,001	0,003	0,004	0,022	0,028	0,013	0,001	0,001	0,001	0,001	0,026	0,020	0,011	0,017	0,048
1,2,3,7,8 PeCDD	0,000	0,002	0,003	0,009	0,054	0,010	0,001	0,001	0,001	0,001	0,011	0,007	0,005	0,007	0,016
1,2,3,4,7,8 HxCDD	0,000	0,001	0,001	0,002	0,016	0,007	0,002	0,002	0,002	0,002	0,003	0,003	0,001	0,011	0,003
1,2,3,6,7,8 HxCDD	0,000	0,001	0,002	0,002	0,016	0,008	0,002	0,002	0,002	0,002	0,004	0,003	0,002	0,011	0,005
1,2,3,7,8,9 HxCDD	0,000	0,001	0,001	0,002	0,010	0,005	0,002	0,002	0,002	0,002	0,003	0,003	0,001	0,011	0,002
1,2,3,4,6,7,8 HpCDD	0,001	0,009	0,008	0,011	0,016	0,043	0,007	0,003	0,002	0,002	0,029	0,009	0,017	0,013	0,109
OCDD	0,002	0,011	0,005	0,021	0,045	0,041	0,027	0,028	0,031	0,032	0,238	0,038	0,056	0,172	0,626

The PCDFs congeners data expressed in ng/m³ for oven 4.

	Jun-09	Oct-10	Nov 2010	Jun-11	Nov-11	Jan 2012	May 2012 carbon mill 1	May 2012 carbon mill 2	May 2012 raw mill 1	May 2012 raw mill 2	May 2012 chimney	May 2012 chimney	Sept 2012 chimney	Sept 2012 before filter	Sept 2012 after filter
2,3,7,8 TCDF	0,022	0,099	0,160	0,590	1,087	0,252	0,002	0,001	0,002	0,002	0,598	0,501	0,271	0,530	1,360
1,2,3,7,8 PeCDF	0,003	0,007	0,020	0,105	0,223	0,043	0,002	0,002	0,002	0,002	0,089	0,074	0,043	0,078	0,203
2,3,4,7,8 PeCDF	0,003	0,012	0,022	0,109	0,240	0,063	0,004	0,002	0,002	0,002	0,118	0,092	0,046	0,088	0,227
1,2,3,4,7,8 HxCDF	0,001	0,003	0,006	0,028	0,044	0,017	0,005	0,002	0,002	0,002	0,024	0,016	0,011	0,016	0,056
1,2,3,6,7,8 HxCDF	0,001	0,003	0,005	0,018	0,021	0,016	0,005	0,002	0,002	0,002	0,020	0,015	0,009	0,017	0,046
1,2,3,7,8,9 HxCDF	0,000	0,001	0,003	0,004	0,002	0,003	0,002	0,002	0,002	0,002	0,004	0,002	0,002	0,010	0,006
2,3,4,6,7,8 HxCDF	0,001	0,003	0,005	0,013	0,021	0,012	0,005	0,002	0,002	0,002	0,015	0,010	0,005	0,010	0,024
1,2,3,4,6,7,8 HpCDF	0,001	0,003	0,005	0,014	0,010	0,020	0,013	0,004	0,002	0,002	0,106	0,018	0,012	0,019	0,060
1,2,3,4,7,8,9 HpCDF	0,000	0,002	0,002	0,004	0,010	0,005	0,001	0,001	0,002	0,002	0,023	0,004	0,002	0,009	0,005
OCDF	0,001	0,003	0,004	0,015	0,012	0,017	0,007	0,005	0,006	0,006	0,527	0,053	0,016	0,033	0,110

Part II Studies

Dioxin formation ng/m³for gaseous samples and ng/g for solid samples at different points during the manufacturing of cement in Cementa production facility.

	Raw mill	carbon mill	Before ESP	After ESP	Chimney Oven 3	Chimney Oven 4	ALOX	Copper slag	Raw meal	Field A	Field B	Bland For gases	Blank for solids
2-MoCDD	0.00	0.00	0.00	0.00	0.00	0.00	0.012	0.012	0.009	0.015	0.057	0.24	0.02
23-DiCDD	0.00	0.00	1.61	97.51	0.00	0.00	0.000	0.000	0.000	0.000	0.000	0.01	0.00
237-TriCDD		0.05	5.37	7.89	0.00	0.00	0.003	0.003	0.006	0.002	0.035	0.02	0.00
2378-TCDD	0.00	0.01	0.56	0.52	0.28	1.04	0.003	0.000	0.001	0.000	0.000	0.00	0.00
12378-PeCDD	0.00	0.03	0.65	0.58	0.14	1.48	0.000	0.000	0.003	0.000	0.018	0.00	0.00
123478-HxCDD	0.00	0.02	0.47	0.30	0.02	0.88	0.000	0.000	0.002	0.000	0.021	0.00	0.00
123678-HxCDD	0.00	0.02	0.69	0.36	0.02	0.97	0.000	0.000	0.002	0.000	0.012	0.00	0.00
123789-HxCDD	0.00	0.02	0.01	0.31	0.01	0.94	0.000	0.000	0.002	0.000	0.014	0.00	0.00
1234678-HpCDD	0.01	0.03	1.58	0.38	0.02	1.58	0.001	0.001	0.005	0.002	0.046	0.00	0.01
OCDD	0.00	0.01	0.74	0.31	0.01	1.46	0.001	0.000	0.003	0.003	0.066	0.00	0.01

	Raw mill	carbon mill	Before ESP	After ESP	Chimney Oven 3	Chimney Oven 4	ALOX	Copper slag	Raw meal	Field A	Field B	Bland For gases	Blank for solids
2-MoCDF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28-DiCDF		0.71	63.05				0.007	0.047	0.029	0.001	0.295	0.21	
248-TriCDF		0.36	28.72	55.42			0.018	0.023	0.028	0.005	0.223	0.15	0.00
2378-TCDF	0.06	0.15	3.37	5.69	6.18	14.49	0.004	0.004	0.018	0.002	0.096	0.03	0.00
12378-PeCDF	0.01	0.07	0.66	0.98	1.53	3.58	0.001	0.001	0.009	0.001	0.048	0.00	0.00
23478-PeCDF	0.04	0.33	2.75	3.41	2.89	9.92	0.003	0.003	0.018	0.000	0.091	0.02	0.00
123478-HxCDF	0.01	0.14	0.69	0.72	0.41	1.90	0.000	0.001	0.007	0.000	0.065	0.00	0.00
123678-HxCDF	0.01	0.09	0.49	0.55	0.31	1.63	0.000	0.001	0.005	0.000	0.037	0.00	0.00
123789-HxCDF	0.00	0.04	0.16	0.25	0.07	0.84	0.000	0.000	0.001	0.000	0.018	0.00	0.00
234678-HxCDF	0.02	0.17	0.78	0.85	0.27	2.53	0.000	0.001	0.006	0.001	0.035	0.00	0.00
1234678-HpCDF	0.02	0.16	0.71	0.63	0.12	2.85	0.000	0.001	0.005	0.001	0.100	0.00	0.00
1234789-HpCDF	0.00	0.00	0.01	0.03	0.01	0.33	0.000	0.000	0.001	0.000	0.036	0.00	0.00
OCDF	0.00	0.02	0.13	0.09	0.01	0.32	0.000	0.000	0.001	0.000	1.287	0.00	0.00

The total contents of PCDDs and PCDFs expressed in ng/m³.

Total contents	Raw mill	carbon mill	Before ESP	After ESP	Chimney Oven 3	Chimney Oven 4	ALOX	Copper slag	Raw meal	Field A	Field B
PCDD	0.32	2.05	201.57	166.83	50.52	345.96	0.10	0.06	0.17	0.11	1.15
Tri D	0.00	0.37	52.17	78.80	27.56	156.00	0.03	0.02	0.03	0.01	0.14
Tetra-octa D	0.32	1.68	149.40	88.03	22.96	189.96	0.07	0.04	0.14	0.09	1.01
PCDF	1.89	14.22	373.67	660.08	851.05	1077.78	0.26	0.33	0.98	0.11	7.58
Tri Furans	0.00	5.17	262.77	470.67	613.36	666.87	0.15	0.20	0.43	0.04	3.00
Tetra-octa furans	1.89	9.06	110.90	189.40	237.69	410.91	0.12	0.13	0.56	0.06	4.58



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