Science of the Total Environment 485–486 (2014) 528–533

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Long-term sampling of dioxin-like substances from a clinker kiln stack using alternative fuels

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HIGHLIGHTS

- Results of PCDD/F and dl-PCB emissions in two clinker kilns were published.
- Long-term sampling approach enhanced possibilities for emissions behavior study.
- Emission factor was proposed for the studied clinker kiln.
- A regression model was proposed for dl-PCB emissions.

ARTICLE INFO

Article history:
Received 9 December 2013
Received in revised form 6 March 2014
Accepted 6 March 2014
Available online 16 April 2014

Editor: Adrian Covaci

Keywords:
Cement kiln
PCDD/F
PCB
Long-term sampling
Congener profile

ABSTRACT

The aim of this work is to characterize atmospheric emissions of polychlorinated dibenzo-p-dioxins (PCDDs)/polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) from a cement production plant where the existing clinker production line was completely replaced by a new state-of-the-art installation. The project started in April 2008 with the installation of a long-term sampling system in the stack of the clinker kiln that used petroleum coke as fuel; PCDD/PCDF and dl-PCB emissions were then evaluated for a two year period. To carry out the second part of the study, in 2010 the sampling system was moved to the new installation in which, apart from conventional fuel, recovered derived fuel (RDF) and WWTP sludge were used as alternative fuels. For both the old and new clinker kilns, PCDD/PCDF emission values were well below the limit established by the European Waste Incineration Directive 2000/76/CE (EWID) of 100 pg I-TEQ/Nm^3; values ranged from 0.43 to 2.02 and from 0.07 to 3.31 pg I-TEQ/Nm^3, respectively. dl-PCBs accounted for approximately 25% of the WHO-TEQ toxicity. These results prove that the installation is capable of reducing PCDD/PCDF and dl-PCB emissions when alternative fuels are integrated into the process.
In the case of PCDDs/PCDFs, the major contributions to total TEQ were usually from 2,3,7,8-TCDD (owing to its relative abundance) and 2,3,4,7,8-PeCDF (due to its high I-TEF of 0.5); while for dl-PCBs, the major contribution was from PCB-126. The slight shift in the congener profile between the old and new installations was characterized and a regression model was proposed for dl-PCB emissions depending on the RDF flow rate in the clinker.

1. Introduction

Industrial activities involving combustion processes release minor amounts of unwanted by-products into the atmosphere as a result of incomplete combustion or other chemical reactions. Among these pollutants, persistent organic pollutants (POPs) are of major concern not only due to their persistence in the environment, but also due to their capacity to bioaccumulate and biomagnify in biota combined with their toxic effects on human health (WHO, 2005). The Stockholm Convention on POPs requires the signatories to eliminate or reduce the release of 21 substances, consisting not only of pesticides and industrial chemicals but also of by-products such as hexachlorobenzene and the highly toxic polychlorinated dibenzo(p)dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs). Four main categories of sources are listed in the Annex of the Stockholm Convention as having the potential for comparatively high formation and release of these chemicals to the environment (UNEP, 2002). The list includes waste incineration plants, and co-incinerators of municipal, hazardous or medical waste, or of sewage sludge.

Clinker burning processes present many characteristics that optimize elimination of organic pollutants: very high temperatures and long residence times; high levels of turbulence and strong thermal currents; the fixation of trace pollutants in the clinker structure; and neutralization of acidic gases by active lime in the kiln load. This makes it possible to use

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http://dx.doi.org/10.1016/j.scitotenv.2014.03.021
0048-9697/

a wide variety of fuels, in particular different types of waste-derived fuels with calorific and material value; in case of fuels considered as biomass, this attenuates the environmental impact by reducing the use of non-renewable fossil fuels and the emission of greenhouse gases. Typical wastes used in clinker furnaces are paper, textiles, plastics, tires, animal meal and fat, recovered derived fuel (RDF) and municipal sewage sludge. The use of such derived fuels as an alternative to fossil fuels has become common in a number of countries and the overall substitution of conventional fuels by waste-derived fuels rose from 3% in 1990, to 17% in 2007 (European Commission, 2010). Particularly high increases have occurred in the use of RDF, animal meal and also sewage sludge, the management of which has been tightened over the last decade or so due to the strengthening of landfill and land use regulations.

Since the use of alternative fuels in clinker kilns may produce an impact on the composition of the emissions from the process, co-incineration has become a topic of major concern. Thus, several studies have assessed the environmental impact of alternative fuels in cement plants. In 2004, data from cement kilns in EU-27 countries showed that they mostly comply, independently of the thermal substitution rate, with the limit of 100 pg I-TEQ/Nm^3 set for incineration and co-incineration plants in the Directive 2000/76/EC (EWID, 2000). In Spain, measurements from 2000 to 2003 at 41 kilns using different waste fuels showed emission values in the range of 0.2 to 54 pg I-TEQ/Nm^3; comparable to the range for plants using only conventional fuel: 0.4–49 pg I-TEQ/Nm^3 (Fabrellas et al., 2004). Of 39 German rotary kilns reported in 2004, 26 had emissions of polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/Fs) in the clean gas below the limit of detection (LOD) of 5.1 pg I-TEQ/Nm^3 (European Commission, 2010). Several tests were conducted in two kilns at a Portland cement manufacturing plant with little effect on stack emissions reported when burning different supplementary waste fuels (Zemba et al., 2011). Conesa et al. (2011) reported values from a clinker kiln fired with RDF from municipal solid waste to be much lower (5 pg I-TEQ/Nm^3) than the limit set by EWID (100 pg I-TEQ/Nm^3), and no correlation was found between RDF rate and dioxin emission rate. Other studies of the effect of increasing the total thermal substitution rates with different alternative fuels or raw materials on the emissions of dioxin and furan reported no direct effect on emission levels when using tires and sewage sludge (Conesa et al., 2008) or meat meal and tires (Abad et al., 2004).

Nevertheless, all those studies were based on PCDD/F stack emission data obtained from analysis based on short-term manual sampling measurements, with sampling times ranging from 6 to 8 h, and therefore represent total stack process emissions only to a limited extent. Furthermore, it is known that PCDD/F emissions might vary significantly over time, with considerably higher values under unstable conditions such as plant start-up or shut-down (Wang et al., 2007; Tejima et al., 2007; Lothgren and Van Bavel, 2005). However, online determination on the stack for PCDD/Fs and dl-PCBs is not feasible with current technology. So, long-term continuous sampling on the stack and further analytical determination in the laboratory can fill the gap between short-term sampling and online monitoring. Such systems have been used for over ten years to gain a better understanding of air emissions, mainly in the field of municipal waste incinerators. In fact, those plants have been obliged by law to perform long-term sampling of their emissions since 2000 in Belgium (Reinmann et al., 2011) and since 2011 in France (Ministère de l'Ecologie, de l'énergie, du développement durable et de la mer, 2010).

Continuous sampling has many advantages over manual short-term sampling measurements. The most important is that the data obtained from continuous sampling of flue gas covering total operation periods, instead of 6 to 8 h, is more representative. Furthermore, as larger samples are involved in the analysis, lower LODs are achieved, thereby enhancing the capacity to characterize profile information. Dioxin profile determination of source emissions is valuable for further studies of the environmental impact on the surrounding area (Martínez et al., 2010).

In this paper, we report the long-term monitoring of PCDD/F and dl-PCB emissions in two different clinker kiln stacks at the same plant. The first year of the study focused on the characterization of the emissions from a kiln using conventional fuels. For the second part of the project, the continuous sampling system was installed in a new clinker kiln specially designed to make it possible to partially substitute conventional fuel with waste (RDF and sewage sludge).

2. Materials and methods

2.1. Case study

The monitoring of PCDD/F and dl-PCB emissions started in April 2008. After the installation of a long-term sampling device in the stack of one of the three clinker production lines (L1), emission samples were collected and sent to the laboratory for further analysis.

The 100 m rotary kiln was equipped with a 57-meter-high 4-stage cyclone pre-heater and fed with conventional fuels (carbon and petroleum coke) to produce 2600 Tm clinker/day. Flue gas treatment consisted of two electrostatic precipitators and wet scrubbers for the treatment of 280,000 Nm^3/h of flue gas that exits the stack at up to 140 °C and at a height of 63 m.

While the first part of the project was underway in L1, a completely new state-of-the-art clinker production line (L2) was built in order to replace the production of all three conventional lines. L2 was specifically designed to use alternative fuels and started operating at the end of 2011. In order to continue with the characterization of PCDD/F and dl-PCB emissions, the long-term sampling system was re-installed in the new stack.

L2 consists of a 50 m rotary clinker kiln fed with pet-coke and waste municipal sewage sludge, equipped with a 125-meter-high 5-stage cyclone pre-heater and a precalciner fed with pet-coke and RDF to produce 4100 Tm clinker/day. Flue gas treatment consists of filter bags for the treatment of 473,000 Nm^3/h of flue gas that exits the stack at up to 120 °C and at a height of 150 m.

2.2. Sampling campaigns

Ten sampling episodes (S1 to S10) were carried out from April 2008 to January 2010 in the first clinker kiln (L1) where only conventional fuels were used. Afterwards, eight sampling episodes (S11 to S18) were carried out in L2 with different amounts of fuels (Table 1) fed to the precalciner (pet-coke and RDF) and to the furnace in the high-temperature combustion zone (pet-coke and sludge).

Sampling campaigns were generally based on 30-day sampling periods, nevertheless different sampling times were assessed (Table 1). An automatic long-term sampling device DioxinMonitoringSystem® (MonitoringSystems, Bad Voeslau, Austria) was used according to the dilution method described in EN-1948 part 1. The system has been described previously (Steiner, 2003) and allows (in contrast to 6-to-8-hour manual spot-sampling methods) the continuous isokinetic sampling of flue gas for periods of up to several weeks. At the end of each sampling period, the cartridge containing the adsorbent media (a corrugated particle filter, polyurethane foam and a 20 g layer of XAD-2) was sent to the laboratory for further analysis together with the sampling data including average filter temperature, relative flue gas humidity, oxygen content and sampling volumes. The total content of pollutants in the sample along with sampling volume information resulted in the mean emission values of PCDD/Fs and dl-PCBs for each run. In order not to sample when the plant was off, the sampling system was configured to automatically stop if the flue gas was below 70 °C for 4 min. The system commenced sampling again once this value had been above 70 °C for 15 min.

The whole sampling process was controlled by the addition before sampling to the adsorbent media (over the XAD-2 between the filter and PUFs) of a mixture of the standard solutions EN-1948SS and P48-SS (Wellington Laboratories, Canada) containing: 400 pg of both ^{13}C-1,2,3,7,8-PeCDF and ^{13}C-1,2,3,7,8,9-HxCDF, and 800 pg of