Emissions of polybrominated dibenzo-\(p\)-dioxins and dibenzofurans (PBDD/Fs) and polycyclic aromatic hydrocarbons (PAHs) from a cement kiln using a continuous monitoring system

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The aim of the present study was to assess the emission of different persistent organic pollutants from a cement plant over a period of one year, under normal operating conditions. In this way, a Dioxin Monitoring System (a long-term sampling device manufactured by Monitoring Systems) was installed in the clinker kiln stack of the cement plant, located in the vicinity of the University of Alicante. The factory has a production capacity of 150 t/h of clinker and uses petroleum coke as primary fuel, but also alternative fuels such as SRF (solid recovered fuel), ASR (automotive shredder residue), sewage sludge, waste tires, and meat and bone meal wastes, with an energy substitution level of about 40%.

The study consisted of a total of 13 samples, namely:
- Ten samples collected in 3-4 week periods, for the determination of brominated dioxins and furans (PBDD/Fs).
- Three samples collected during one-week periods, for the determination of polycyclic aromatic hydrocarbons (PAHs).

The analytical procedure (sampling, extraction, cleanup, fractionation and analysis) met the minimum requirements described in the European dioxin monitoring standard for emissions from stationary sources (EN 1948:1,2,3,4). Quantification of PBDD/Fs was performed using the isotopic dilution method, while for the analysis of PAHs, deuterated analogues were used as internal standards.

For every sampling period, PBDD/F emission values were at least three orders of magnitude below the limit established by the European Directive 2010/75/EU for their chlorinated analogues (0.1 ng ITEQ/Nm\(^3\)). Total PBDD/F emission values ranged from 0.01 to 0.44 pg ITEQ/Nm\(^3\) which, considering an estimated average emission factor of 2094 Nm\(^3\)/ton clinker, are equivalent to 0.02 and 0.92 ng/ton clinker, respectively. The PBDD/F congener patterns were similar for all the samples, with octabrominated dibenzofuran as the most abundant congener and a furan/dioxin ratio higher than one, as it has been observed in incineration processes.

Regarding the 16 US EPA priority PAHs analyzed (from two to six aromatic rings), in all cases naphthalene was the most abundant (6.10 - 9.77 µg/Nm\(^3\)), followed by phenanthrene (2.33 - 4.86 µg/Nm\(^3\)) and acenaphthylene (0.37 - 0.92 µg/Nm\(^3\)). No PAHs of 5 or 6 aromatic rings were detected. With respect to the 6 PAHs considered as carcinogenic compounds by the WHO, only 0.4 ng/Nm\(^3\) benzo(a)anthracene were detected in one sample. In addition, no correlation was observed between the emission of any of the pollutants measured and the degree of substitution with alternative fuels.

ACKNOWLEDGEMENTS:
Support for this work was provided by the following projects:
- Ministry of Science and Innovation (Spain): CTQ2011-23618.
- Ministry of Economy and Competitiveness (Spain): CTQ2013-41006-R.
- Valencian Community Government (Spain): PROMETEOII/2014/007.