

Polychlorinated dibenzo(*p*)dioxin and furan (PCDD/F) congener profiles in cement kiln emissions and impacts

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ARTICLE INFO

Article history:

Received 7 August 2011

Received in revised form 26 December 2011

Accepted 27 December 2011

Available online 26 January 2012

Keywords:

Cement kilns

Hazardous waste incineration

PCDD/F congeners

Dioxins

Emission profiles

ABSTRACT

Cement kilns are known to emit polychlorinated dibenzo(*p*)dioxins and furans (PCDD/Fs; “dioxins”), but estimates of the amounts and patterns of these emissions vary widely. These variations may stem from a combination of factors, including the design and operating conditions of the kiln, and the fuels and raw materials fed into the kiln. The goal of this study was to examine the patterns of dioxin emissions in a large set of stack-tests at two Portland cement kilns in Portugal that use a variety of fuels. A total of 152 stack-tests provided data on PCDD/F congener concentrations during which the kilns combusted a varied mix of fuels, including petroleum coke, coal, various “special” supplemental fuels, and refinery distillation ends, which are classified as hazardous wastes. The use of coal to fuel the kilns was found to generate significantly different emission-profiles relative to the use of petroleum coke, but the addition of hazardous wastes as a supplemental fuel did not significantly alter profiles. All of the kiln emission profiles were found to differ markedly from profiles in ambient air. However, the small absolute dioxin emission rates from the kilns suggested that kiln impacts would not be detectable *via* ambient air monitoring, even in rural settings.

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1. Introduction

Combustion of organic material generates, among other things, myriad products of incomplete combustion (PICs). In 1977, Olie et al. (1977) discovered that among these PICs are polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo-*p*-furans (PCDD/Fs; “dioxins”). These chemicals were, and remain, of interest because of the extremely high toxicity of the congener 2,3,7,8 tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), and the demonstrated or estimated high toxicity of 16 other dioxin congeners (reviewed in van den Berg et al., 1998, and recently examined in detail in US EPA, 2010).

Since the late 1970s, combustion chemists and others have studied the many interacting factors that appear to govern the extent and pattern of PCDD/F emissions from combustion sources and industrial processes. The relative amounts of various PCDD/F congeners

emitted from a given source (the source’s congener profile or congener “fingerprint”) are of interest for two primary reasons. First, the pattern of congeners emitted from a source might provide insight into the processes that lead to PCDD/F formation. Second, the fingerprints generated from various sources or source types, when compared with the profiles found in air or other environmental media, might allow identification and apportionment of the sources affecting specific locations.

PCDD/F emission data have been published for a number of cement manufacturing facilities (see Zemba et al., 2011), but few studies have focused on PCDD/F congener profiles. Based on limited data, Abad et al. (2004) found no marked differences in PCDD/F emissions or congener profiles in a facility using tires and meat meal as alternative fuels. Cleverly et al. (1997) presented an analysis of PCDD/F congener profiles for anthropogenic sources based on the US EPA’s compilation of PCDD/F emission data. These data seemed to indicate marked differences in the congener distributions between cement kilns burning hazardous wastes and those not burning hazardous wastes. However, the emission-data were generated from several different kilns, tested under different (and often incompletely specified) operating conditions, so that the reasons for these differences could not be readily determined or generalized. In particular, some of the tests were intentionally conducted under “stressed” operating conditions, at worst-case temperatures and

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combustion efficiencies, especially in cases where hazardous waste was being burned and regulatory limits were being established. Moreover, hazardous wastes vary tremendously in their chlorine content and numerous other potentially determinative factors.

In this paper, we present a study of PCDD/F congener profiles in the exhaust-stack emissions from two Portland cement kilns, tested under normal operating conditions and using a variety of fuels, including fuels designated as hazardous waste. The cement kilns, located in Outão, Portugal, are owned and operated by Companhia Geral de Cal e Cimento S.A. (Secil). More than 150 individual stack tests were conducted while these kilns burned a variety of primary, special, and hazardous waste fuels. This unusually large data set affords an opportunity to characterize the variabilities in the kiln's congener profiles relative to the use of different fuels under normal operating conditions. Variabilities in the magnitudes of the emissions (rather than variabilities in the profiles) are presented in detail elsewhere (Zemba et al., 2011). Overall PCDD/F congener concentration summary data for the stack gases at the two kilns are presented in Table 1.

We also analyze data on PCDD/F congener levels and profiles that have been measured in ambient air at various locations in Portugal (Coutinho et al., 2007). Combining the kilns' emission data with atmospheric dispersion modeling results allows an assessment of whether the Secil kiln impacts could be detectable by employing congener-specific sampling of ambient air.

2. Materials and methods

2.1. Secil kilns

Portland cement is primarily made of cement clinker which largely comprised calcium silicates (Ca_3SiO_5 and Ca_2SiO_4). Clinker is made by: (1) grinding a mixture of limestone (containing calcium carbonate, CaCO_3), and clay or shale to make a fine "rawmix", (2) heating the rawmix in a high-temperature (up to 1450 °C), counter-flow, rotary kiln, and (3) grinding the resulting clinker to make cement. Processes in the kiln include the decomposition of calcium carbonate (CaCO_3) into calcium oxide CaO and carbon dioxide CO_2 , and the reaction of calcium carbonate (CaCO_3) and calcium oxide to form the calcium silicate clinker nodules. The two similar Portland cement kilns operated by Secil in Outão, Portugal are designated Kiln 8 and Kiln 9 (detailed schematic diagrams of the kilns are provided in the Supplemental material). Kiln 8 is a rotary kiln, 5 m in diameter and 80 m long, fitted with a preheating tower with four levels of cyclones and ten Unax coolers. Kiln 8 has a nominal clinker production capacity of 2150 tons per day. Kiln 9 is a

rotary kiln, 5.25 m in diameter and 83 m long, fitted with preheating tower with four levels of cyclones and nine Unax coolers. Kiln 9 has a nominal clinker production capacity of 3500 tons per day. Both kilns use GRECO-type burners. One substantial difference between the kilns is that following the preheater tower, Kiln 8 uses a suspended preheater, while Kiln 9 uses in-line extra air calciner which obtains more complete initial decarbonization (conversion of CaCO_3 into CaO) than does the Kiln 8 preheater. Both kilns process the same aggregate feeds and use similar mixes of fuels. The primary fuel used to fire the kilns is petroleum coke, although occasionally coal has been used. Special supplemental fuels include wood, animal flour, refuse-derived fuel, auto shredder fluff, and tires. The kilns also use refinery distillation ends as a special supplemental fuel. This supplemental fuel potentially contains toxic metals such as cadmium, mercury, and lead as well as toxic and environmentally persistent organic compounds, and is designated as hazardous waste in Portugal. To ensure that the kilns meet the exhaust gas concentration limits of European Union (EU) Directive 2000/76/EC, the Secil Outão facilities each has electrostatic precipitators and a baghouse that operate in series.

2.2. Determination of PCDD/F concentrations and emissions

Kiln 8 underwent 65 individual stack test runs for PCDD/F emissions from April 2005 through November 2008; Kiln 9 underwent 87 individual stack test runs for PCDD/F emissions from February 2002 through December 2008. Sampling and analytical determination of PCDD/F levels in the Secil kilns' exhaust gases were performed in accordance with EN 1948 (2006). Flue gas (including dust) was extracted isokinetically from the exhaust stack via a titanium enclosed water-cooled glass probe, which rapidly cooled the sample before it entered the collection system. This collection system consisted of a condensate flask in an ice bath (receiving condensate and a part of the dust), and two collection cartridges. The first cartridge contained a flat filter and the second one a polyurethane foam (PUF) sorbent with proven efficiency for the separation of organic substances. The PUF was installed on both sides of a flat high-efficiency filter. The filters were followed by a gas drying tower, gas pump, gas volume meter, temperature and pressure meters. A sampling standard (C13-labeled 1,2,3,7,8-Penta-CDF, 1,2,3,7,8,9-Hexa-CDF, 1,2,3,4,7,8,9-Hepta-CDF, in a toluene carrier solvent) was added to the condensate flask before sampling. Samples were solvent-extracted from the condensate, PUF, flat filters, and (if necessary) the glass sampling tube (which was cut into pieces), and the extracts were combined for analysis. Clean-up on multicolumn systems used carbon-on-glass fiber or carbon-on-celite filters. HRGC/HRMS measurements used a VG-AutoSpec or Finnigan MAT

Table 1

Overall summary data for PCDD/F congener stack concentrations for Secil Kilns 8 and 9. Concentrations are in units of pictograms per normal cubic meter (pg/Nm^3) adjusted to 10% O_2 .

Congener	Kiln 8				Kiln 9			
	Mean	Std. dev.	Max.	Det. %	Mean	Std. dev.	Max.	Det. %
2,3,7,8-TCDD	0.7	1.1	6.5	28%	0.3	0.5	4.3	11%
1,2,3,7,8-PCDD	0.7	1.3	10.0	17%	0.2	0.3	1.5	10%
1,2,3,4,7,8-HxCDD	0.8	1.0	6.5	12%	0.3	0.2	1.0	9%
1,2,3,6,7,8-HxCDD	0.8	1.0	5.8	15%	0.3	0.2	1.3	9%
1,2,3,7,8,9-HxCDD	0.7	0.9	4.7	9%	0.3	0.2	1.0	8%
1,2,3,4,6,7,8-HpCDD	2.1	2.7	17.0	52%	1.3	2.2	18.0	46%
OCDD	5.3	6.6	41.0	62%	6.8	21.0	190.0	57%
2,3,7,8-TCDF	72.2	106.8	538.0	92%	11.4	43.8	371.0	84%
1,2,3,7,8-PCDF	7.4	12.4	71.0	58%	1.5	4.6	33.0	38%
2,3,4,7,8-PCDF	7.8	11.2	48.0	65%	1.7	6.9	62.0	34%
1,2,3,4,7,8-HxCDF	2.2	4.6	30.0	45%	0.6	1.0	7.2	25%
1,2,3,6,7,8-HxCDF	1.3	2.3	13.7	34%	0.4	0.7	4.2	17%
1,2,3,7,8,9-HxCDF	0.8	1.3	9.4	14%	0.3	0.2	1.2	11%
2,3,4,6,7,8-HxCDF	1.3	2.3	13.3	29%	0.4	0.8	5.0	18%
1,2,3,4,6,7,8-HpCDF	2.3	3.5	20.6	68%	0.9	1.0	4.2	66%
1,2,3,4,7,8,9-HpCDF	1.1	2.5	16.0	12%	0.5	0.7	5.5	17%
OCDF	3.3	5.1	34.0	37%	1.7	1.8	9.1	37%

95 with SP2331 and/or DB-5 capillary columns. For each substance two isotope masses were measured. Quantification was carried out using internal/external standard mixtures. Quantitative determinations of PCDD/Fs were made using the isotope dilution method with 2,3,7,8-substituted ¹³C-UL internal standards. Recoveries of the sample standards averaged 70–80%, but were not used to correct measured values. Sample detection limits varied by congener and over the course of the study, but in general were two to three times lower than necessary to meet the EN 1948 standards (e.g., 0.5 pg/m³ for the 2,3,7,8-TCDD congener).

2.3. Congener profile determination and statistical analysis

For purposes of profile construction, PCDD/F congeners that were not detected in any given test-run were presumed to be present at one-half of the lower limit of detection. Within each test-run, each congener's profile level was calculated as the quotient of the congener's concentration divided by the sum of the concentrations of the seventeen 2,3,7,8-substituted congeners. This normalization was chosen to equally weight profiles among tests with varying levels of total PCDD/F emissions. To determine the overall congener profile for a specific set of facility operating conditions (e.g., Kiln 8 burning coal only), each congener's profile level from the tests under the defined condition was averaged.

Comparisons between pairs of congener profiles were performed by applying a maximum log-likelihood analysis. Given a set of mean measured profile levels $m_{i,j}$ for congeners i and facility/fuel j , with standard errors $s_{i,j}$, n samples, and true (yet unknown) congener profile levels $\mu_{i,j}$, the probability distribution function of the likelihood that the measured mean levels are from the true but unknown levels follows a Student's t distribution with $n - 1$ degrees of freedom. The overall sum of the log-likelihoods that two sets of measured profile levels are from two underlying, yet unknown, sets for profile levels is given by Eq. (1):

$$\text{overall log-likelihood} = \sum_{j=1,2} \sum_{i=1}^{17} -\frac{n_{i,j}}{2} \ln \left[1 + \left(\frac{m_{i,j} - \mu_{i,j}}{s_{i,j}} \right)^2 / (n_{i,j} - 1) \right]. \quad (1)$$

If it is assumed that the two sets of measured profile levels are from two separate underlying profiles, then the maximum overall log-likelihood is identically zero; this occurs when the values of $\mu_{i,j}$ are set equal to the values of $m_{i,j}$. The test for whether the measured profiles from two test conditions are from the same underlying profile was performed by first assuming identical values of $\mu_{i,j}$ for both measured profile sets, and then maximizing the overall log-likelihood by varying the values of the true profile levels $\mu_{i,j}$ under the constraints that profile levels are non-negative, and that the sums of the 17 levels for a given facility and operating condition are equal to one. The maximizing was done using the solver tool in Microsoft Excel. The test for a statistically significant difference between two profiles was based on application of a χ^2 (chi-squared) test of two times (for a two sided test) the difference between the maximum overall log-likelihoods for the profiles under the two assumptions about the values of $\mu_{i,j}$ (i.e., that they are either independent, or identical), with 16 degrees of freedom. Because the maximum log-likelihoods of the independent μ 's, are identically zero, the test was essentially done on twice the negative of the maximum log-likelihood for the case of identical μ 's. Two measured profiles were deemed to be from the same underlying profile if the result of the χ^2 test (the p value) was less than 0.05.

2.4. Atmospheric dispersion modeling

Off-site, ground-level, incremental ambient air concentrations of the seventeen PCDD/F congeners due to emissions from both of the

Secil kilns were estimated using the U.S. EPA AERMOD air dispersion modeling system (US EPA, 2004). Model inputs included average measured emission rates and stack exhaust gas parameters, one year of site-specific meteorological data, and local topographic and land-use data. Each congener was modeled separately in both the vapor and surface adsorbed particle-phase. The partitioning of each congener between these phases was based on data from the U.S. EPA's Human Health Risk Assessment Protocol for hazardous waste combustion facilities (US EPA, 2005). Vapor phase modeling included congener-specific data for diffusivity in air and water, Henry's Law constants, and resistance to cuticular uptake as recommended by U.S. EPA (Wesely et al., 2002). Off-site air concentrations were determined over a polar grid of receptors centered on the Secil property, with an angular receptor spacing of 10°, and a radial spacing of 100 m out to 3 km from the site center, and 500 m out to 10 km from the site center.

3. Results and discussion

3.1. Congener profiles

Fig. 1 displays the PCDD/F and congener profiles for each Secil kiln as distinguished by primary fuel (coke or coal), and by whether supplemental hazardous fuels were used in conjunction with the use of coke. The height of the bars indicates the fraction of each congener's concentration relative to the total concentration of all seventeen listed congeners, averaged among the tests; the error bars indicate one standard deviation of the percentages among the tests. As shown, there are substantial congener level variabilities within tests of the same kiln and the same fuel. This variability remained when the data were weighted by total congener levels for each test, or when the data were censored by eliminating tests with either low numbers of detected congeners or low total concentrations.

Overall, the profiles for the two Secil kilns are similar, with two PCDD/F congeners, namely 2,3,7,8-TCDF and OCDD, almost always being measured at the highest concentrations. The overall profile shapes also generally match those based on data compiled by the U.S. EPA and reported by Cleverly et al. (1997). Visually, the profiles for the two kilns appear different with Kiln 8's emissions having a more pronounced enrichment in 2,3,7,8-TCDF, while Kiln 9's emissions have a more even split between this congener and OCDD. Also, it is interesting that some of the fuel-specific patterns in the profiles (notably the levels for 2,3,7,8-TCDF) appear similar for the two kilns.

However, statistically significant differences between profiles (as determined by the test described above) were found for only some of kiln/fuel comparisons. None of the kiln-to-kiln profile comparisons (for a specific fuel) found significant differences (the greatest p value among the tests for the measured profiles being from identical true profiles was 0.044 for the inter-kiln comparison of tests with coke-plus-hazardous waste fuel). Among the single kiln, fuel-to-fuel comparisons, the use of coal as a fuel produced significantly different profiles than when petroleum coke was used either with or without supplemental hazardous waste fuels. The overall finding that there were only few statistically significant differences between profiles is perhaps attributable to the large variabilities in the profiles among otherwise similar tests as evidenced by the sizable standard deviations shown in Fig. 1. Additional comparisons of profiles (not shown) resulted in no significant differences between profiles for coke combustion with and without the use of special-but-not-hazardous fuels, and for test data censored for either low numbers of detected congeners or low total concentrations.

Our results comport with those reported by Karstensen (2008), both in terms of absolute stack-gas concentrations (Table 1) and emission rates (Zemba et al., 2011), and also with respect to the independence of the concentrations and rates relative to whether hazardous waste or nonhazardous waste is used as fuel for cement clinker production. Examination of the kiln-specific data (US EPA, 2001, 2006) analyzed by

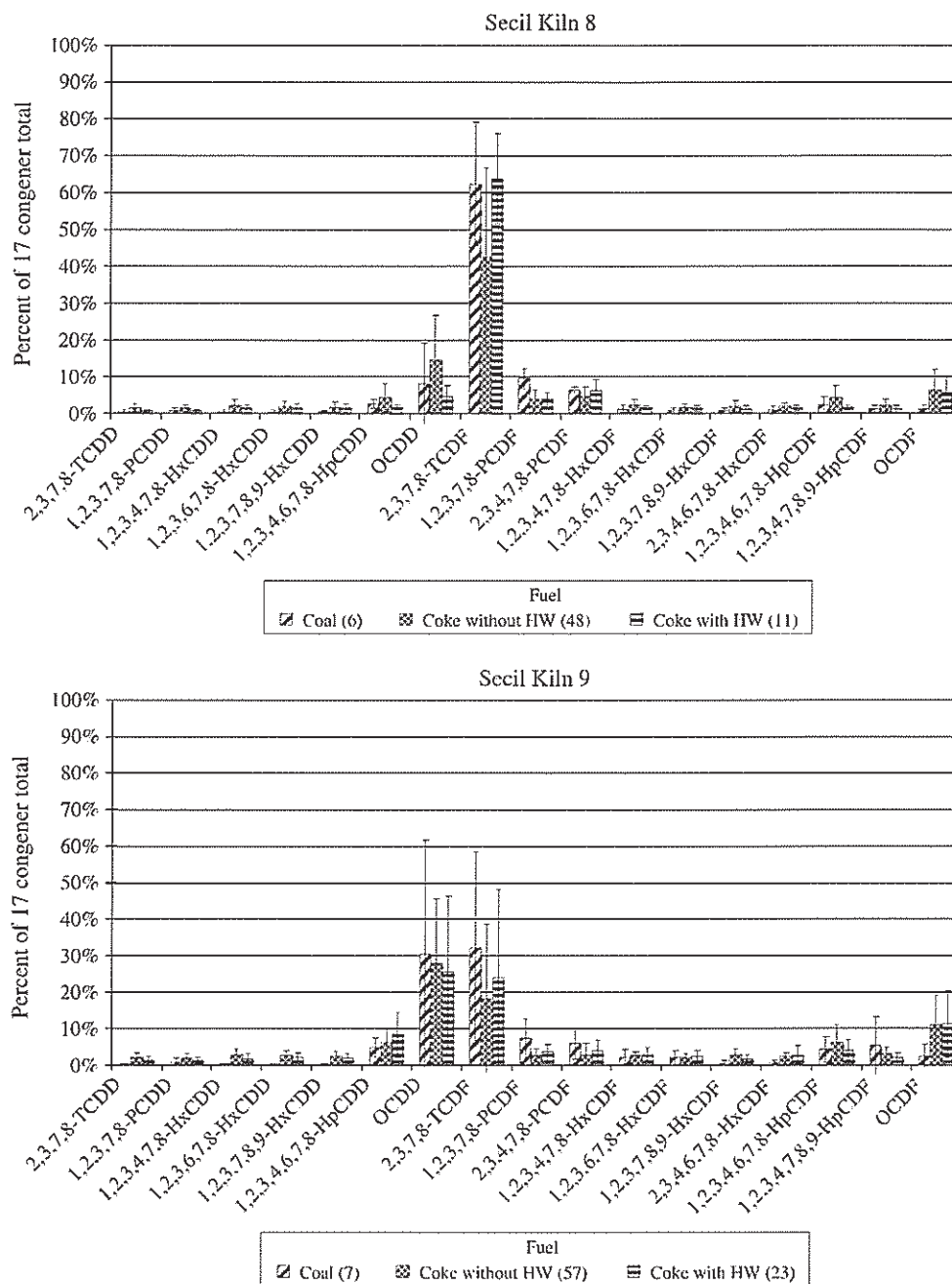


Fig. 1. PCDD/F congener profiles for the two cement kilns (Kiln 8 above, Kiln 9 below) at Outão when burning different fuels. Bars indicate the fraction of each congener relative to the total of all 17 listed congeners, averaged among tests. Error bars indicate one arithmetic standard deviation of the values among the tests; numbers in parentheses indicate number of tests.

Cleverly et al. (1997) indicates that PCDD/F profiles differ among facilities but are similar among tests at individual kilns (within the range of normal measurement variability). Profiles do not systematically differ based on hazardous waste combustion, but appear to reflect individual facility characteristics. The OCDD and 2,3,7,8-TCDF are most frequently the peak congeners for facilities that both use and do not use hazardous waste (Table 2).

More broadly, destruction of fuel-contaminants in cement kilns depends on several factors, including high production temperatures, long residence times, surplus oxygen during and after combustion, and inherent dry scrubbing by the alkaline nature of limestone (Karstensen, 2008). Tests performed two decades ago on various cement kilns in the U.S. had indicated relatively high emission rates of PCDD/Fs, including facilities combusting hazardous waste, but, as noted above, these earlier

tests had been intentionally conducted under sub-optimal combustion conditions (Cleverly et al., 1997; Brzuzy and Hites, 1996). Elevated emissions were found to be associated with *de novo* PCDD/F formation in particulate control systems (electrostatic precipitators and baghouses) operating at temperatures above 450 K, irrespective of hazardous waste utilization.

Recent investigations indicate that PCDD/F formation-rates typically depend not on the fuel, but instead on the trace organic chemical content of the raw materials (limestone, sand, shale, clay, and iron ore), and the temperature of flue gases as they pass through air pollution control devices (Karstensen, 2008; Constans, 1996). Because the gas and raw materials in the cement manufacturing process flow in opposite directions, there is significant potential for semi-volatile components to build up in a recycle loop in the back end of the

Table 2

Congeners with the highest average concentration for Portland cement kilns included in the US EPA (2001) PCDD/F emissions database.

Congener	Number of facilities for which congener concentration is highest	
	Hazardous waste used as supplemental fuel	No use of hazardous waste
1,2,3,7,8,9-HxCDD	1	–
1,2,3,4,6,7,8-HpCDD	4	–
OCDD	3	8
2,3,7,8-TCDF	6	4
1,2,3,7,8-PCDF	1	–
2,3,4,7,8-PCDF	1	–
2,3,4,6,7,8-HxCDF	1	–
OCDF	1	1

process. It is likely that the more chemically stable PCDDs exit the process without being altered from how they were formed, or they are present in the raw materials, in which the fully chlorinated OCDD dominates. With regard to the PCDFs, in contrast, the higher molecular weight congeners likely condense onto particulates and recycle back through the process, where these less thermodynamically stable compounds are converted to more volatile, lesser chlorinated congeners. These are then emitted without the opportunity for condensation and recycling back through the process.

3.2. Cement kiln fingerprints and air impacts

PCDD/F congener profiles are of interest in part because, if robust and unique profiles can be established for specific types of PCDD/F sources, it might be possible to identify and apportion source contributions to ambient total PCDD/F concentrations or TEQ levels (Gullett and Wikström, 2000; Abad et al, 2004; Pleil and Lorber, 2007; Kim et al., 2007; Rivera-Austrui et al., 2011; Schuhmacher et al., 2009). Thus we have examined the possibility of using congener profiles to identify the impacts of emissions from the Secil cement kilns on near-field ambient air concentrations. To do this we compare relative profiles and absolute concentrations of PCDD/F congeners between the maximum modeled

ambient air impacts from the kilns' emissions with background ambient air data measured at sites that are not significantly impacted by the kilns' emissions.

Atmospheric emissions from the Secil Outão facilities were the subject of a recent multi-pathway human health risk assessment (Intertox, 2007). This assessment included detailed air quality modeling of the PCDD/F congener emissions from Kilns 8 and 9 to estimate incremental atmospheric concentrations at maximally affected locations under worst-case meteorological conditions. The maximum PCDD/F impacts from the kilns' emissions were approximately 1 km from the facility center (a fairly typical distance from such a source for the maximum impact location). The congener profile of these maximum, modeled, annual-average ambient air impacts is plotted in Fig. 2 beside profiles derived from recent measurements of PCDD/F congeners in ambient air (Coutinho et al., 2007). The first two background profiles are based on data collected near Portugal's two largest cities, Porto which is approximately 300 km to the north of Outão, and Lisbon which is approximately 30 km to the northwest of Outão. The third profile is based on data collected on the remote island of Madeira, which is approximately 1000 km southwest of the Portuguese mainland and 500 km west of the coast of Morocco. The fourth profile is based on a worldwide average of ambient air data. The most notable difference between the Secil impact profiles and the background profiles is that the Secil profile level of 2,3,7,8-TCDF, at the point of the kilns' maximum modeled ambient impact is an order of magnitude greater than in any of the ambient air samples, while the profile levels of 1,2,3,4,6,7,8-HpCDD and OCDD are much lower than the background air data (Fig. 2). This is not unexpected, given that the background profiles are mixtures from a wide range of dioxin sources with different profiles than the Secil kilns (see Cleverly et al., 1997), and that the background profiles are for dioxins which have environmentally 'aged' in the atmosphere, where different congeners are degraded and deposited from the air at different rates (US EPA, 2005).

At first glance one might expect that these profile differences, especially the high 2,3,7,8-TCDF profile levels in the Secil emissions could be used as a marker for detecting the kilns' impacts via ambient air monitoring. However, for a signature profile or marker to be useful in practice, the absolute impacts must be sufficiently large to be observable above the variability in the background levels. As shown in Fig. 3, the modeled,

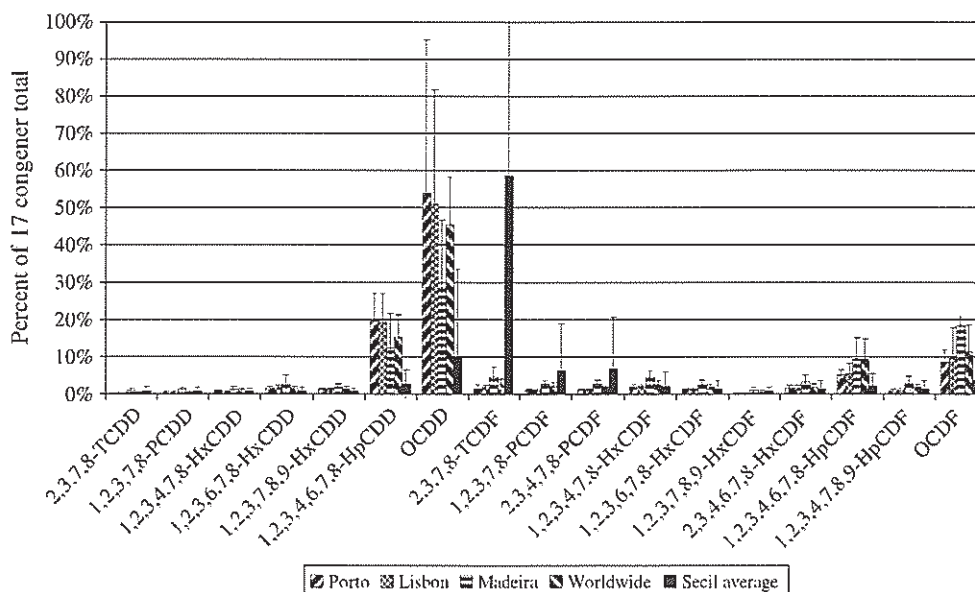


Fig. 2. Measured congener profiles in ambient air at three Portuguese locations, in a worldwide atmospheric average, and for modeled average atmospheric impacts from the Secil Outão facilities. Bars indicate the fraction of each congener relative to the total of all 17 listed congeners, averaged among tests. Error bars indicate one arithmetic standard deviation of the values among the data.

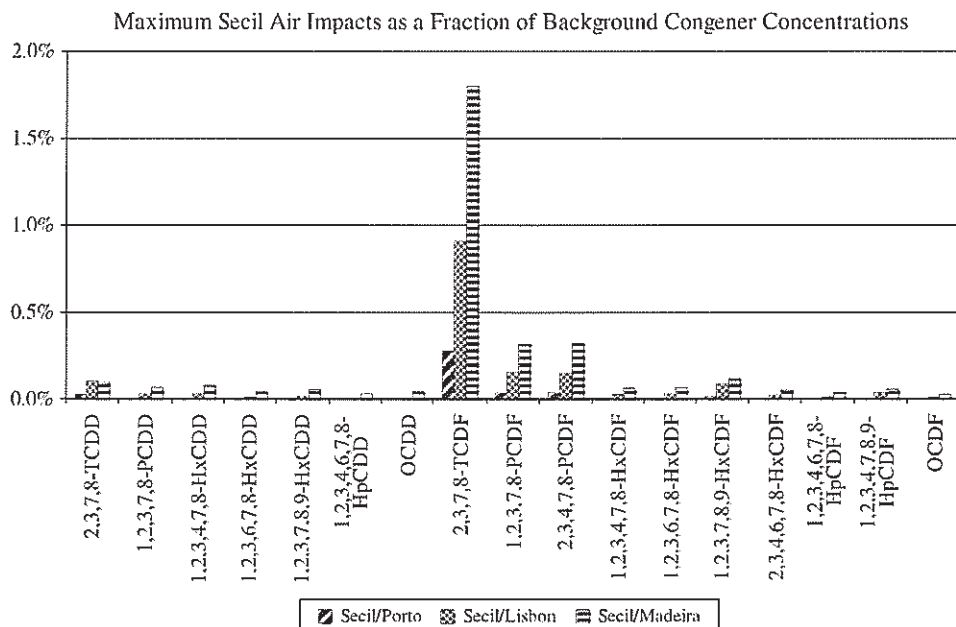


Fig. 3. Maximum, modeled, incremental atmospheric concentrations of PCDD/F congeners due to emissions from the Secil facilities in Outão as percentages of measured concentrations at three locations.

maximum impact of 2,3,7,8-TCDF from kiln emissions is less than 2% of the background measured in Madeira air, and less than 1% of background concentrations in the urban settings. Thus, even were the kilns' maximum impact superimposed on the relatively clean background air of Madeira, the presence of 2,3,7,8-TCDF in the kilns' emissions would likely be indistinguishable from the background air without the kilns' impacts. Simply put, the signal-to-noise ratios of the kilns' impacts over the background variabilities are too weak to be observable.

4. Conclusions

Overall, then, extensive testing of PCDD/F emissions from two cement kilns found considerable variability in congener profiles from test to test (even among tests conducted under nominally similar conditions), but general similarities among various average profiles. Congener profiles when coal was used as a primary fuel were found to be significantly different than when petroleum coke was used as a primary fuel, but the addition of supplemental hazardous waste fuels did not produce significantly different profiles, in contrast to the findings of previous profile analyses (Cleverly et al., 1997). Moreover, although congener profiles in the kiln-emissions are notably different than those measured in ambient air, the absolute magnitude of emissions from well-controlled kilns renders their impacts too small to be distinguishable from background.

5. Acknowledgments

This work was sponsored in part by Secil Companhia Geral de Cal Cimento S.A. Stack test sampling and analyses were performed by Eurofins/Ergo. Atmospheric dispersion modeling of PCDD/F emissions from the Secil kilns was performed by UVW and Professor Nelson Barros of University of Fernando Pessoa, Porto, Portugal.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.scitotenv.2011.12.062.

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Handwritten notes and stamps in the top right corner, including a circular stamp with the text "US-2-17-13" and "M. Ames" and a signature.