



Emissions of metals and polychlorinated dibenzo(*p*)dioxins and furans (PCDD/Fs) from Portland cement manufacturing plants: Inter-kiln variability and dependence on fuel-types

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ABSTRACT

Emissions from Portland cement manufacturing facilities may increase health risks in nearby populations and are thus subject to stringent regulations. Direct testing of pollutant concentrations in exhaust gases provides the best basis for assessing the extent of these risks. However, these tests (i) are often conducted under stressed, rather than typical, operating conditions, (ii) may be limited in number and duration, and (iii) may be influenced by specific fuel-types and attributes of individual kilns. We report here on the results of more than 150 emissions-tests conducted of two kilns at a Portland cement manufacturing plant in Portugal. The tests measured various regulated metals and polychlorinated dibenzo(*p*)dioxins and furans (PCDD/Fs). Stack-gas concentrations of pollutants were found to be highly variable, with standard deviations on the order of mean values. Emission rates of many pollutants were higher when coal was used as the main kiln fuel (instead of petroleum coke). Use of various supplemental fuels, however, had little effect on stack emissions, and few statistically significant differences were observed when hazardous waste was included in the fuel mix. Significant differences in emissions for some pollutants were observed between the two kilns despite their similar designs and uses of similar fuels. All measured values were found to be within applicable regulatory limits.

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1. Introduction

Like all processes that involve combustion, the production of Portland cement results in emissions of air pollutants. Among these are trace quantities of “air toxics” including metals, such as mercury, cadmium, and lead, and numerous organic compounds, including polychlorinated dibenzo(*p*)dioxins and furans (PCDD/Fs). Because of the very high temperatures and long residence times required to manufacture cement clinker, destruction of incoming organic compounds during combustion

is essentially complete. Because of this combustion efficiency, cement kilns are considered to be ideal environments in which to simultaneously recover heat from and dispose of various organic wastes with high BTU-content. Thus, although primary fuels for cement manufacturing include coal and petroleum coke, various supplemental, waste-based fuels are often used as well. The latter may include wood wastes, refuse-derived fuel (RDF) and other forms of municipal solid waste, auto shredder fluff, tires, sewage sludge, and various hazardous wastes, such as spent industrial solvents and refinery distillation ends. The question thus arises as to whether and under what conditions the use of these supplemental and/or hazardous fuels influences the types and/or amounts of pollutants emitted from cement kilns.

Some studies of cement kiln emissions at facilities using supplemental fuels have been published, although data sets have tended to be limited. Emission inventory approaches emphasize categorical distinctions (distinguishing facilities that burn hazardous waste from those that do not), but individual facility-specific data are rarely provided (US EPA, 2006; UNEP, 1999). Further, early inventory estimates of PCDD/F

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emissions from hazardous waste combustion in cement kilns have been found to be significantly overestimated due to great variability among individual facilities unrelated to hazardous waste combustion (Cudahy and Rigo, 1998). Studies thus focused on the performance of individual kilns in response to their use of supplemental fuels. An early study in a Norwegian cement kiln found that the use of hazardous wastes as supplemental fuels did not increase emissions of PCDD/Fs (Benestad, 1989). Several recent studies have examined the use of municipal solid waste as a supplemental fuel. Conesa et al. (2011) report that emissions of PCDD/Fs and metals are lower than EU limits when co-firing MSW-derived solid recovered fuel, and found that emissions do not correlate with waste feed rate. Genon and Brizio (2008) found that the addition of RDF to petroleum coke increased emissions of mercury and other metals, but decreased such emissions when added to coal. Rovira et al. (2010) report slightly but not significantly greater emissions of some metals from a kiln using RDF for 15% of its fuel energy. Zabaniotou and Theofilou (2008) report metal and PCDD/F emissions during the use of supplemental sewage sludge to be well below standards, but provide no comparative data to examine the incremental effects (if any) of the sludge. Limited testing of PCDD/Fs at three cement kilns using meat meals and tires as special fuels found no apparent difference in PCDD/F emissions compared with literature data, but the authors note a dearth of published comparative data for individual facilities (Abad et al., 2004). Sidhu et al. (2001) identified chemical mechanisms of PCDD/F formation in raw meal combustion in a kiln environment. Carrasco et al. (2002) found increased metals emissions when co-firing scrap tires, but decreased PCDD/F emissions. On the other hand, Conesa et al. (2008) report increased PCDD/F with tire combustion, and no effect of sewage sludge. The potential influences of tire firing methods and procedures are cited as potential factors in both cases.

This paper analyzes an extensive database of air toxics emission tests conducted by the Portland cement manufacturer Secil at its facility in Outão, Portugal. Secil has undertaken a comprehensive program to make frequent measurements of stack emissions under typical operating conditions (as opposed to stressed conditions, which are frequently tested at facilities in the U.S. to examine conditions most conducive to pollutant emissions). More than 150 individual stack tests were conducted over a seven year period to examine variability in emission rates and the effects of burning different primary fuels and supplemental waste-derived fuels. This large data set affords a unique opportunity to characterize emission variability and to examine issues such as whether the co-incineration of hazardous waste and other special wastes leads to increased emissions of pollutants such as mercury and PCDD/Fs.

2. Methods

2.1. Facility description

The two similar Portland cement kilns operated by Secil in Outão, Portugal are designated Kiln 8 and Kiln 9. 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 production capacity of 2150 ton clinker 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 production capacity of 3500 ton of clinker per day. Both kilns use GRECO-type burners. One substantial difference following the preheater tower is Kiln 8's use of a suspended pre-heater vs. Kiln 9's in-line extra air calciner. 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 also been used. Special supplemental fuels include wood, animal flour, refuse-derived fuel, auto shredder fluff, and tires. The kilns have also recently added refinery distillation ends as a special fuel that is designated as hazardous waste in Portugal. To insure that the kilns meet the exhaust gas concentration limits of European Union (EU)

Directive 2000/76/EC, the Secil Outão facilities each have electrostatic precipitators and a baghouse that operate in series.

2.2. Sampling

Over the period of 1997 to 2008, Kilns 8 and 9 underwent 66 and 91 individual stack test runs respectively for metals and PCDD/Fs (>90% conducted from 2005 to 2008). Sampling and analytical determination of concentrations of specific elements in the Secil kilns' exhaust gases was performed in accordance with EN 14385 (2004). Flue gas (including dust) was extracted isokinetically from the flue gas duct via a titanium enclosed glass probe. Particulate matter in the sampled gas volume was collected on a heated quartz fiber filter (Munktell MK 360) in a titanium holder to avoid contamination, in accordance with EN 13211 (2001). Following the filter, the gas stream was passed through a series of three impingers cooled in an ice bath to collect condensable material. The impingers contained 75 ml of 4.5% nitric acid and 1.7% hydrogen peroxide. The filters, including the collected dust, were completely dissolved by acidic reagents (HNO₃, HF, HCl). The digestion mixture was heated in a Teflon vessel following a specific temperature program. No preparation before analysis was normally necessary for the absorption liquid. If the absorption liquid contains particles they were dissolved following the procedure for filters. Analysis was carried out by graphite furnace atomic absorption spectrometry (GF-AAS) with Zeeman background compensation. Calibration was done with at least five calibration solutions using commercial elemental standards, quality-checked by additional quantification of a reference material. The detection limits (DL) for the elements antimony, arsenic, cadmium, chromium, cobalt, copper, lead, manganese, nickel thallium, and vanadium were (with some exceptions) significantly below 1 µg/m³ for each element and a typical sampling volume of 1 m³. Detection limits were calculated by the blank value method described in VDI Guideline 2449 Part 1 (1995) for a statistical probability of 95%.

Methods for mercury sampling and analysis were consistent with the draft European Standard. Flue gas was collected using a similar sampling train to the one used for metals sampling, but with the addition of a final permanganate/nitric acid condensate impinger. Before analysis, mercury in the permanganate solution was reduced by hydroxide peroxide or hydroxyl-ammonium chloride. Mercury was analyzed using cold vapor atomic absorption spectrometry (CVAAS) after being reduced to elementary form using tin (II).

Sampling and analytical determination of PCDD/F levels in the Secil kilns' exhaust gases was performed in accordance with EN 1948 (sampling: part 1, analysis: parts 2 and 3, 2006). Flue gas (including dust) was extracted isokinetically from the flue gas duct via a titanium enclosed water-cooled glass probe which rapidly cooled the sample before it entered the collection system. The collection system consisted of a condensate flask in an ice bath that receives the accumulating condensate and a part of the dust, and which is followed by two cartridges. The first cartridge contains a flat filter and the second one contains two polyurethane foams (PUF), a special 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 are followed by an equipment group consisting of 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) 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. Clean-up on multicolumn systems used carbon-on-glass fiber or carbon-on-celite filters. HRGC/HRMS measurements used a VG-Auto-Spec or Finnigan MAT 95 with SP2331 and/or DB-5 capillary columns. For each substance 2 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 13 C-UL internal standards.

2.3. Data analysis

Pollutant exhaust gas concentrations were measured while using a variety of combinations of primary fuel (petroleum coke or coal) and special waste-derived fuels. 88% of the Kiln 8 tests contained one or more supplemental fuels, accounting (when burned) for an average of 26% of total fuel by mass (range: 7–68%). Similarly, 81% of the Kiln 9 tests contained one or more supplemental fuels, accounting (when burned) for an average of 30% of total fuel by mass (range: 4–62%). Hazardous waste was burned in 18% and 26% of the tests of Kilns 8 and 9, respectively, at average rates accounting for 11% (3–17%) and 15% (6–34%) of fuel mass respectively. Initial examination of data found minor differences in measured stack-gas concentrations among tests in which petroleum coke (the main fuel) was burned alone or in conjunction with various special wastes. As such, petroleum coke was considered as a single class with or without the use of supplemental special fuels, with the exception of hazardous waste, which was segregated for specific examination related to the fact that its use triggers special regulatory requirements. Data were segregated into three groups:

- **Coke:** Tests in which petroleum coke was used in conjunction with up to five special wastes as supplemental fuel (wood, meat bone, RDF, fluff, and tires);
- **Coke&HW:** Tests in which petroleum coke was supplemented with hazardous waste and up to five special wastes; and
- **Coal:** Tests in which coal, and not petroleum coke, was used as the main fuel, in conjunction with up to five special wastes.

Statistical analyses of the stack test results were conducted within an MS Excel spreadsheet environment. The principal contrasts examined are the burning of different primary fuels (*Coke* vs. *Coal*) and the burning

of hazardous waste in conjunction with the normal fuel mix (*Coke* vs. *Coke&HW*) for two kilns. Inferential t-tests were conducted for each pollutant to identify potentially significant differences in emissions.

Multiple regression analysis was used to investigate the effects of both primary and supplemental fuels on emissions. A linear regression equation (Eq. (1)) was tested for each pollutant in which the stack-gas concentration (S_i) for a pollutant i is modeled as a constant (C_i intercept) plus the sum of the products of fuel j mass flow rates (m_j) and pollutant/fuel-specific coefficients μ_{ij} :

$$S_i = C_i + \sum_j \mu_{ij} m_j \quad (1)$$

In addition, kiln-specific emission factors were compared with those provided in US EPA's Compilation of Air pollution Emission Factors, known as AP42.

3. Results

3.1. Overall emission and compliance with EU standards

Because it burns various wastes, Secil conducts stack testing to demonstrate compliance with European Union (EU) Directive 2000/76/EC, which sets limits on the stack-gas effluent concentrations of mercury (Hg, 0.05 mg/m³); cadmium and thallium (Cd + Tl, 0.05 mg/m³ combined); antimony, arsenic, lead, chromium, cobalt, copper, manganese, nickel, and vanadium (Sb to V, 0.5 mg/m³ combined); and PCDD/Fs (0.1 ng/m³ combined toxic equivalents to 2,3,7,8-tetrachlorodibenzo(p)dioxin), at standard temperature (273 K) and pressure (101.3 kPa) and 10% oxygen (dry gas basis). Under its risk management and community involvement policy, Secil

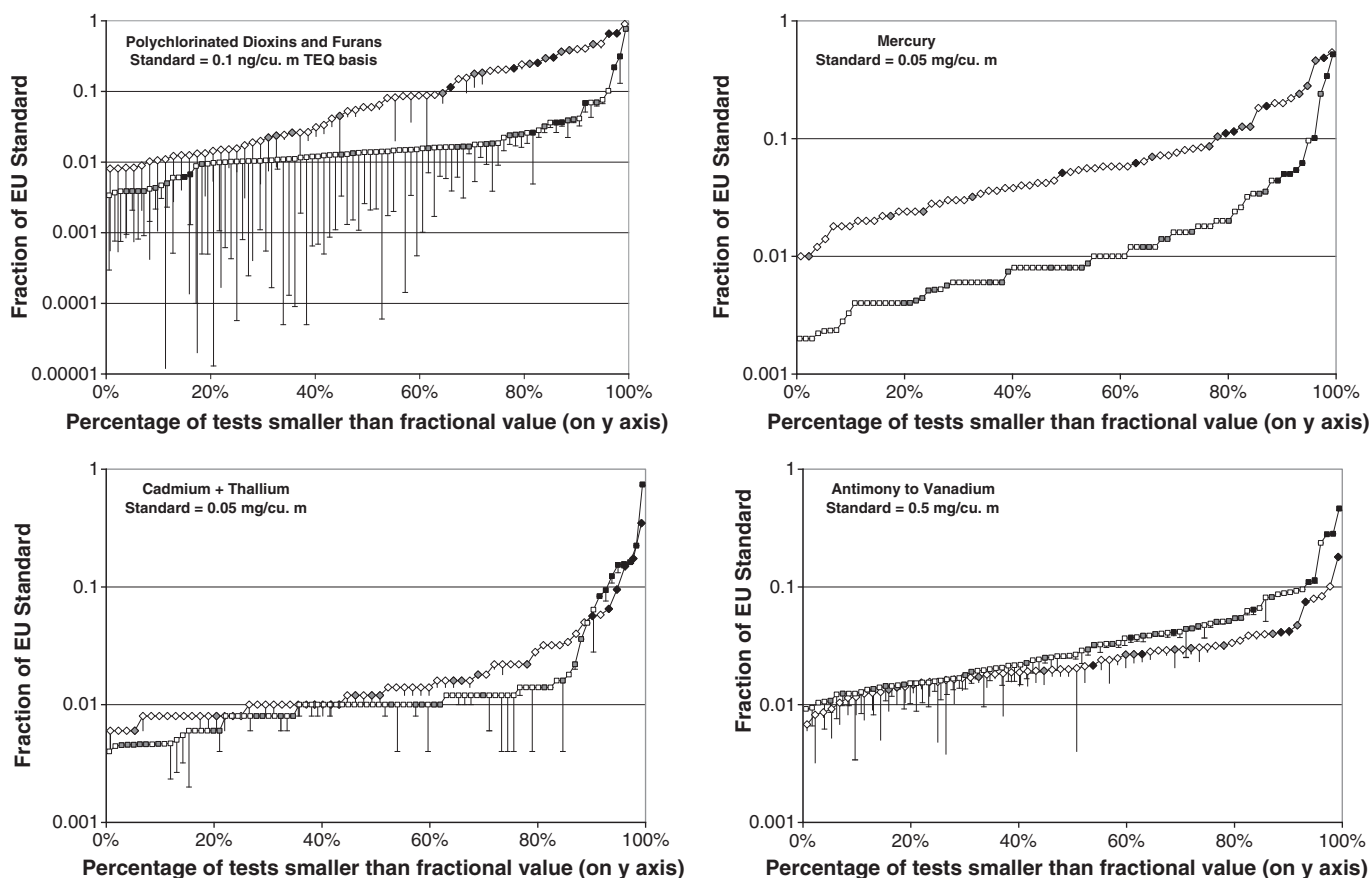


Fig. 1. Ratios of measured stack-gas concentrations to EU Directive 2000/76/EC limits. Distributions of test results for Kiln 8 (◇) and Kiln 9 (□). Black-filled symbols indicate runs with coal as primary fuel, and gray symbols indicate hazardous waste combustion. Non-detects plotted at detection limits, with error bars indicating zero values.

has conducted more than one hundred and fifty stack tests for these parameters at its Kilns 8 and 9 at the Outão site (a number far greater than required by regulation). Frequent testing was designed to evaluate special fuel use compared with baseline. Most of the stack tests have been conducted under typical operating conditions. Petroleum coke was the primary fuel during most tests, supplemented in many cases with one or more special fuels (including hazardous waste). Fig. 1 shows the overall results of the stack-gas sampling program, normalized by the applicable EU limits. The limits have not been exceeded in any of the tests. Moreover, the bulk of the test results have been far below the limits. About 83% of PCDD/F, 88% of Hg, 93% of Cd + Tl, and 95% of Sb to V stack test results are more than a factor of ten smaller than their respective limits. Median test results are 2% (Hg), 1% (Cd + Tl), 2.4% (Sb to V), and 1.6% (PCDD/Fs) of the EU emissions limit values.

3.2. Influence of kilns and fuel types

Visually, the Fig. 1 plots suggest differences in stack-gas concentrations between the two kilns, especially for mercury and PCDD/Fs, where clear separation is indicated in the distributions, especially when the effects of non-detects are considered for PCDD/Fs. Some fuel-dependent differences in emission levels (discussed below) are also shown Fig. 1. Tables 1–3 provide statistical summaries of stack effluent concentrations of metals and PCDD/F congeners, organized by the three groupings. Each table separates data for Kilns 8 and 9. It should be noted that the number of tests in the various groupings are unequal. The smaller number of tests in the *Coke&HW* and (particularly) the *Coal* groupings limits the power of inferential statistical methods to establish whether significant differences exist among the data (to be discussed later). Many of the pollutants have low frequencies of detection, a consequence of the facility's effective pollution control program.

Interestingly, one of the pollutants detected at a high frequency in all three groupings is mercury, partly because of consistently lower detection limits relative to some other metals, but also likely due to its partial presence in elemental vapor form, which form is very difficult to capture by the pollution control devices employed at the kilns. Lead, a relatively volatile metal at combustion temperatures, also has a relatively high frequency of detection. Other frequently detected metals include chromium, copper, and manganese, probably because of their generally higher presence in the raw materials. Metals such as antimony, arsenic, cadmium, and cobalt are detected at relatively low frequencies when the kilns burn petroleum coke (Tables 1 and 2). Burning coal (Table 3) leads to higher levels of detection for most pollutants, with markedly higher mean concentrations in many cases. The generally higher test results using coal as the main fuel are also apparent in Fig. 1.

In Tables 1–3, non-detected chemicals are presumed to be present at the lower limit of detection. This approach likely overestimates the means. An indicator of the sensitivity of the mean concentrations to the convention for handling of non-detects is included in Tables 1–3 by the use of underlined estimates to indicate cases for which the mean decreases by 10% or less if non-detects are treated as zeros. These underlined estimates are not sensitive to the convention used for non-detects. Conversely, italicized mean values indicate cases for which mean concentrations would decrease by 50% or more if non-detects were treated as zeroes. As expected, there is a general inverse relationship between the frequency of detection and the effect of non-detects on the mean. At the limits, there is no effect on the mean if there are no non-detects, and if all values are non-detects, the mean is wholly determined by the non-detect convention (ranging between zero and the average detection limit). For cases in between, the effect on the mean can vary substantially. For example, at a frequency of

Table 1

Stack effluent concentrations of metals and polychlorinated dibenzo(p)dioxin and furan (PCDD/F) congeners from two cement kilns operated by Secil in Outão, Portugal. Main fuel petroleum coke, supplemented by up to five special wastes (not including hazardous waste). Concentrations of metals in units of $\mu\text{g}/\text{dscm}$ and PCDD/F congeners in pg/dscm (all at 10% O_2). Mean concentrations include non-detects (NDs) at full detection limits; underlined means vary by less than 10% if NDs are assumed at zero, while italicized means vary by more than 50%. Shaded pollutant cell names indicate a statistically significant difference in the mean values between Kiln 8 and Kiln 9 ($p = 0.05$). Group *Coke*.

Pollutant	Kiln 8					Kiln 8 to Kiln 9 ratio	Kiln 9				
	Frequency of detection	Mean	SD	Range of detects	Range ND detection limits		Frequency of detection	Mean	SD	Range of detects	Range ND detection limits
Mercury (Hg)	47 of 48	<u>3.23</u>	4.27	0.5–27	1–1	5.7	50 of 56	<u>0.57</u>	0.71	0.1–4.8	0.12–0.26
Cadmium (Cd)	6 of 48	<i>0.15</i>	0.15	0.2–1	0.1–0.2	0.93	18 of 57	<i>0.16</i>	0.18	0.1–1.4	0.10–0.12
Thallium (Tl)	31 of 48	0.66	0.54	0.2–2.8	0.2–0.8	1.7	23 of 57	0.38	0.24	0.12–0.6	0.1–1.8
Antimony (Sb)	8 of 48	0.69	0.73	0.4–0.7	0.3–4.3	1.3	10 of 57	0.55	0.38	0.33–0.7	0.17–3.1
Arsenic (As)	10 of 48	0.41	0.17	0.3–1	0.2–0.9	0.74	14 of 57	0.55	0.60	0.12–4.1	0.12–2.2
Lead (Pb)	40 of 48	<u>1.71</u>	1.38	0.3–6.9	0.4–1.1	0.87	48 of 57	<u>1.96</u>	1.55	0.4–8.8	0.3–0.9
Chromium (Cr)	32 of 48	1.50	1.96	0.4–13.6	0.4–1.8	0.48	43 of 57	<u>3.11</u>	11.1	0.5–83	0.3–4.4
Cobalt (Co)	9 of 48	0.17	0.13	0.1–0.7	0.1–0.6	0.82	18 of 57	<i>0.20</i>	0.17	0.1–0.7	0.1–0.9
Copper (Cu)	43 of 48	<u>2.85</u>	2.93	0.4–17	0.4–2.9	0.60	55 of 57	<u>4.71</u>	7.17	0.4–37	0.3–0.4
Manganese (Mn)	38 of 48	<u>3.33</u>	6.41	0.7–44	0.6–2.3	1.2	45 of 57	<u>2.68</u>	2.50	0.1–13	0.5–4.6
Nickel (Ni)	26 of 48	1.29	1.51	0.3–8.1	0.3–0.7	0.45	38 of 57	2.89	4.47	0.6–25	0.4–2.2
Vanadium (V)	30 of 48	0.50	0.28	0.2–1.2	0.2–0.8	1.1	27 of 57	0.45	0.46	0.17–3.4	0.11–0.8
2,3,7,8-TCDD	10 of 48	0.76	0.97	0.5–6.5	0.3–2.3	2.0	7 of 57	<i>0.37</i>	0.16	0.15–0.9	0.11–0.9
1,2,3,7,8-PCDD	5 of 48	0.72	0.76	0.6–3.8	0.2–2.3	1.9	4 of 57	<i>0.37</i>	0.17	0.17–1.1	0.11–1
1,2,3,4,7,8-HxCDD	2 of 48	1.12	1.25	0.8–2.0	0.4–4.6	2.0	4 of 57	0.55	0.26	0.1–0.6	0.11–1.9
1,2,3,6,7,8-HxCDD	4 of 48	1.08	1.27	0.6–2.1	0.3–4.6	2.1	3 of 57	0.51	0.27	0.2–1.1	0.1–1.9
1,2,3,7,8,9-HxCDD	1 of 48	1.02	1.29	1.7–1.7	0.3–4.6	2.1	3 of 57	0.49	0.26	0.3–0.6	0.1–1.9
1,2,3,4,6,7,8-HpCDD	27 of 48	1.74	1.73	0.6–8.6	0.4–3.3	1.9	25 of 57	0.91	0.46	0.38–2.1	0.4–1.8
OCDD	33 of 48	4.77	4.14	1.2–17	1.1–9.2	1.1	36 of 57	4.29	6.86	1–52	1–11
2,3,7,8-TCDF	43 of 48	<u>47.0</u>	91.6	0.4–538	0.4–0.6	11.5	44 of 57	<u>4.10</u>	10.1	0.21–69	0.3–0.5
1,2,3,7,8-PCDF	25 of 48	<u>4.64</u>	8.24	0.3–34.7	0.2–4.2	8.1	17 of 57	0.57	0.75	0.16–4	0.11–0.6
2,3,4,7,8-PCDF	28 of 48	<u>5.37</u>	9.54	0.4–48	0.1–3.6	7.8	14 of 57	0.69	1.16	0.16–7	0.1–0.6
1,2,3,4,7,8-HxCDF	20 of 48	2.19	4.90	0.5–30	0.3–3.8	4.6	8 of 57	0.48	0.22	0.14–0.9	0.1–1.6
1,2,3,6,7,8-HxCDF	14 of 48	1.37	2.30	0.3–13.7	0.2–7.5	3.2	5 of 57	0.42	0.24	0.12–1	0.1–1.6
1,2,3,7,8,9-HxCDF	3 of 48	1.03	1.07	0.5–3.2	0.4–3.8	1.9	5 of 57	0.53	0.22	0.12–0.8	0.11–1.6
2,3,4,6,7,8-HxCDF	12 of 48	1.35	2.13	0.5–13.3	0.2–3.8	3.0	5 of 57	0.45	0.24	0.13–1.1	0.1–1.6
1,2,3,4,6,7,8-HpCDF	35 of 48	2.08	3.31	0.4–20.6	0.3–3.7	2.8	38 of 57	0.73	0.45	0.27–2.3	0.3–1.5
1,2,3,4,7,8,9-HpCDF	5 of 48	1.26	2.36	0.6–16	0.4–3.7	2.3	5 of 57	0.55	0.21	0.13–0.5	0.11–1.5
OCDF	20 of 48	4.25	6.70	0.7–34	0.5–18	2.3	21 of 57	1.85	1.51	0.50–7.2	0.5–7.5

Table 2

Stack effluent concentrations of metals and polychlorinated dibenzo(p)dioxin and furan (PCDD/F) congeners from two cement kilns operated by Secil in Outão, Portugal. Main fuel petroleum coke, supplemented by hazardous waste and up to five special wastes. Concentrations of metals in units of $\mu\text{g}/\text{dscm}$ and PCDD/F congeners in pg/dscm (all at 10% O_2). Mean concentrations include non-detects (NDs) at full detection limits; underlined means vary by less than 10% if NDs are assumed at zero, while *italicized means* vary by more than 50%. Shaded pollutant cell names indicate a statistically significant difference in the mean values between Kiln 8 and Kiln 9 ($p=0.05$). Boxed highlighting indicates a statistically significant difference of the mean value compared with the mean for the *Coke* baseline group without hazardous waste combustion (Table 1) for the same kiln; cell shading indicates the mean is lower than baseline, and a superimposed "X" indicates less than 50% detection frequency in both means. Group *Coke&HW*.

Pollutant	Kiln 8					Kiln 8 to Kiln 9 ratio	Kiln 9				
	Frequency of detection	Mean	SD	Range of detects	Range ND detection limits		Frequency of detection	Mean	SD	Range of detects	Range ND detection limits
Mercury (Hg)	11 of 12	<u>6.58</u>	6.68	0.5–23	1.1–1.1	6.3	23 of 23	<u>1.05</u>	2.43	0.2–12	–
Cadmium (Cd)	3 of 12	<u>0.15</u>	0.10	0.2–0.4	0.1–0.1	0.77	5 of 22	<u>0.19</u>	0.32	0.2–1.6	0.1–0.1
Thallium (Tl)	9 of 12	0.48	0.16	0.3–0.7	0.2–0.4	1.6	8 of 22	<u>0.31</u>	0.22	0.2–1	0.1–0.6
Antimony (Sb)	3 of 12	0.99	0.97	0.7–3.1	0.3–1.3	2.7	0 of 22	<u>0.37</u>	0.16	–	0.2–0.7
Arsenic (As)	0 of 12	<u>0.36</u>	0.067	–	0.2–0.4	1.2	3 of 22	<u>0.29</u>	0.13	0.2–0.5	0.1–0.5
Lead (Pb)	9 of 12	1.65	0.77	1–2.8	0.6–0.9	0.81	21 of 22	<u>2.03</u>	0.78	0.5–3.4	0.2–0.2
Chromium (Cr)	7 of 12	1.10	0.59	0.5–2.1	0.3–1.8	0.44	15 of 22	<u>2.51</u>	2.26	1.0–8.7	0.3–6
Cobalt (Co)	0 of 12	<u>0.18</u>	0.072	–	0.1–0.3	0.86	4 of 22	<u>0.21</u>	0.34	0.1–0.2	0.1–1.7
Copper (Cu)	11 of 12	<u>1.98</u>	1.09	0.6–4.4	1–1	0.32	21 of 22	<u>6.17</u>	7.39	0.7–27	0.5–0.5
Manganese (Mn)	12 of 12	<u>5.05</u>	4.24	1.4–16	–	1.8	22 of 22	<u>2.78</u>	3.39	0.6–16	–
Nickel (Ni)	7 of 12	1.04	0.66	0.8–2.5	0.3–0.7	0.45	14 of 22	<u>2.31</u>	2.63	0.7–11	0.3–1.1
Vanadium (V)	10 of 12	0.59	0.11	0.4–0.7	0.5–0.6	1.6	7 of 22	<u>0.38</u>	0.20	0.3–0.6	0.11–0.7
2,3,7,8-TCDD	5 of 12	1.02	0.62	0.7–2.1	0.3–1.8	2.2	3 of 23	<u>0.47</u>	0.85	0.1–4.3	0.11–0.5
1,2,3,7,8-PCDD	3 of 12	<u>1.14</u>	0.79	0.9–1	0.4–2.5	2.9	4 of 23	<u>0.39</u>	0.31	0.1–1.5	0.11–0.6
1,2,3,4,7,8-HxCDD	3 of 12	<u>2.01</u>	1.75	0.6–0.9	0.8–5.1	3.9	4 of 23	<u>0.51</u>	0.31	0.1–0.8	0.11–1.3
1,2,3,6,7,8-HxCDD	3 of 12	<u>2.23</u>	1.63	1.3–2.2	0.8–5.1	3.7	5 of 23	<u>0.59</u>	0.35	0.2–1.3	0.11–1.3
1,2,3,7,8,9-HxCDD	2 of 12	<u>1.97</u>	1.78	0.6–0.7	0.53–5.1	3.7	4 of 23	<u>0.54</u>	0.31	0.1–0.9	0.11–1.3
1,2,3,4,6,7,8-HpCDD	4 of 12	<u>2.79</u>	1.79	4–6	0.6–4	1.3	13 of 23	<u>2.13</u>	1.96	0.8–6.8	0.4–2.9
OCDD	4 of 12	<u>6.26</u>	4.03	3–15	1.7–10	0.98	12 of 23	<u>6.38</u>	5.45	1.5–23	1.0–10
2,3,7,8-TCDF	11 of 12	<u>104</u>	94	8–253	11–11	5.0	23 of 23	<u>21</u>	77	0.2–371	–
1,2,3,7,8-PCDF	7 of 12	<u>7.28</u>	6.65	3–18	0.8–4.4	3.3	12 of 23	<u>2.18</u>	6.75	0.4–33	0.11–0.7
2,3,4,7,8-PCDF	8 of 12	<u>11.1</u>	11.3	4.7–39	0.8–1.6	3.1	12 of 23	<u>3.5</u>	12.8	0.4–62	0.11–0.9
1,2,3,4,7,8-HxCDF	5 of 12	<u>2.72</u>	1.61	2.6–5	0.7–4	2.6	11 of 23	<u>1.06</u>	1.59	0.1–7.2	0.11–1.1
1,2,3,6,7,8-HxCDF	4 of 12	<u>2.13</u>	1.27	1.4–3	0.7–4.2	2.6	7 of 23	<u>0.82</u>	1.00	0.1–4.2	0.11–1.1
1,2,3,7,8,9-HxCDF	3 of 12	<u>1.68</u>	1.42	0.6–0.9	0.7–4.2	3.3	4 of 23	<u>0.51</u>	0.31	0.2–1.2	0.11–1.1
2,3,4,6,7,8-HxCDF	4 of 12	<u>2.17</u>	1.26	1.8–3	0.7–4.2	2.3	9 of 23	<u>0.95</u>	1.30	0.2–5	0.11–1.1
1,2,3,4,6,7,8-HpCDF	4 of 12	<u>2.53</u>	1.31	2.8–4	0.7–4	2.4	16 of 23	<u>1.04</u>	1.03	0.4–4.2	0.3–0.5
1,2,3,4,7,8,9-HpCDF	0 of 12	<u>1.58</u>	1.38	–	0.5–4	2.5	7 of 23	<u>0.62</u>	0.51	0.1–2.0	0.11–1
OCDF	1 of 12	<u>7.88</u>	7.16	7.9–7.9	1–20	2.6	9 of 23	<u>2.99</u>	2.33	1.1–9.1	0.3–5.1

detection of the order of 50%, non-detects can account for a fraction of the mean ranging from only a few percent up to more than half the value. Detection limits varied among samples during the data collection period. In some cases, the average detection limit of the non-detects exceeded the average detected value. Thus, as is often the case when pollutants are intermittently at measureable levels, care must be taken in interpreting the results of pollutants that are detected at low frequencies.

Despite the uncertainties, mean pollutant stack-gas concentrations suggest potential systematic differences in kiln emission levels. Pollutant names with shaded cells in Tables 1–3 indicate statistically significant differences in mean stack-gas concentrations between Kilns 8 and 9 (as determined by the inferential Student *t* test at $p=0.05$). For convenience, Tables 1–3 also include the ratio of the means for the two kilns. In many cases, the means often differ by a factor of two or more, despite the technological similarities of the kilns. Kiln 8 has higher concentrations of mercury and all but one PCDD/F congener irrespective of fuel grouping, while Kiln 9 exhibits higher concentrations of cadmium, chromium, cobalt, copper, lead, and nickel. Additionally, Kiln 8 has higher concentrations of antimony, manganese, thallium, and vanadium if the two coke-burning groups (which make up the majority of the stack test runs) are considered. A consistent relationship was not found between PCDD/F and hydrogen chloride concentrations in stack-gas among the kiln and fuel groupings. As discussed below, patterns in the stack-gas concentrations of various metals may be related to differences in the mix of special fuels used in Kilns 8 and 9, but also may be the result of

differences in production capacity, kiln dust capture and recycling systems, and preheater design.

Tables 2 and 3 also indicate pollutants for which inferential *t*-tests ($p=0.05$) suggest statistically different means between the fuel groupings *Coal* vs. *Coke* and *Coke&HW* vs. *Coke*. These cases are indicated by highlighted borders on the cells containing the significantly different means, with shading used to indicate a lower mean value in the *Coal* or *Coke&HW* case (compared with the baseline *Coke* group). The statistically significant results indicated in Tables 2 and 3 are qualified by a superimposed "X" if both of the mean values are based on distributions in which more than 50% of the individual samples are non-detects, since these inferences are necessarily uncertain. However, the *t*-tests were also conducted for distributions based on treating non-detects at both full and half detection limits, and predicted results were found to be similar.

In all cases, the unqualified statistically significant findings suggest higher mean pollutant concentrations when burning *Coal* or *Coke&HW* vs. the baseline *Coke* grouping. More significant differences are found for the case of *Coal* vs. *Coke*, for which cadmium and five PCDD/F congeners are found to be higher for the *Coal* test vs. the *Coke* test in Kiln 8 (Table 3). In the case of *Coke&HW* vs. *Coke*, a single PCDD/F congener (1,2,3,4,6,7,8- HpCDD) for Kiln 9 is the only unqualified significant difference. This suggests no robust indication of higher emissions when burning hazardous waste, although the majority (72%) of the pollutant mean concentrations in the *Coke&HW* group (Table 2) do exceed their *Coke* group counterparts (Table 1).

Table 4 provides summary information on fuel use for the combined *Coke* and *Coke&HW* groups used for the regression analyses.

Table 3

Stack effluent concentrations of metals and polychlorinated dibenzo(p)dioxin and furan (PCDD/F) congeners from two cement kilns operated by Secil in Outão, Portugal. Main fuel coal, supplemented by up to five special wastes (not including hazardous waste). Concentrations of metals in units of $\mu\text{g}/\text{dscm}$ and PCDD/F congeners in pg/dscm (all at 10% O_2). Mean concentrations include non-detects (NDs) at full detection limits; underlined means vary by less than 10% if NDs are assumed at zero, while italicized means vary by more than 50%. Shaded pollutant cell names indicate a statistically significant difference in the mean values between Kiln 8 and Kiln 9 ($p = 0.05$). Boxed highlighting indicates a statistically significant difference of the mean value compared with the mean for the Coke baseline group without hazardous waste combustion (Table 1) for the same kiln; cell shading indicates the mean is lower than baseline, and a superimposed "X" indicates less than 50% detection frequency in both means. Group Coal.

Pollutant	Kiln 8					Kiln 8 to Kiln 9 ratio	Kiln 9				
	Frequency of detection	Mean	SD	Range of detects	Range ND detection limits		Frequency of detection	Mean	SD	Range of detects	Range ND detection limits
Mercury (Hg)	6 of 6	8.44	8.12	2.56–24.3	–	1.1	8 of 8	7.63	8.94	2.2–26	–
Cadmium (Cd)	6 of 6	6.94	5.39	2.6–17	–	0.68	8 of 8	10.23	10.86	3.8–37	–
Thallium (Tl)	4 of 6	0.46	0.22	0.23–0.61	0.49–0.81	0.74	3 of 8	0.63	0.31	0.21–0.80	0.51–1.1
Antimony (Sb)	1 of 6	0.77	0.10	0.9–0.9	0.66–0.83	0.86	1 of 8	0.89	0.16	1–1	0.73–1.2
Arsenic (As)	2 of 6	0.56	0.11	0.5–0.65	0.50–0.74	0.85	2 of 8	0.67	0.20	0.5–0.66	0.47–1
Lead (Pb)	6 of 6	4.74	5.47	1.27–15.5	–	0.19	8 of 8	24.70	28.76	3.8–88	–
Chromium (Cr)	6 of 6	1.66	1.09	0.18–3.52	–	0.48	8 of 8	3.46	1.49	1.55–6.5	–
Cobalt (Co)	4 of 6	0.35	0.28	0.08–0.79	0.21–0.26	0.13	6 of 8	2.68	6.60	0.14–19	0.18–0.22
Copper (Cu)	6 of 6	2.17	0.63	1.45–3.15	–	0.32	7 of 8	6.83	6.10	2.2–21	5.4–5.4
Manganese (Mn)	6 of 6	19.1	28.1	3.6–76	–	0.52	7 of 7	36.4	76.7	4.6–210	–
Nickel (Ni)	6 of 6	2.31	1.31	0.54–4.5	–	0.22	8 of 8	10.61	14.39	1.45–44	–
Vanadium (V)	5 of 6	0.54	0.16	0.38–0.61	0.83–0.83	0.10	5 of 8	5.29	10.34	0.37–30	0.72–0.94
2,3,7,8-TCDD	3 of 6	1.52	2.30	1.2–6.1	0.08–0.43	2.2	0 of 8	0.68	1.62	–	0.06–4.7
1,2,3,7,8-PCDD	3 of 6	2.46	3.78	1.2–10	0.25–0.57	3.4	1 of 8	0.72	0.96	0.26–0.26	0.24–2.9
1,2,3,4,7,8-HxCDD	3 of 6	1.73	2.37	1.2–6.5	0.25–0.71	6.0	0 of 8	0.29	0.05	–	0.24–0.38
1,2,3,6,7,8-HxCDD	3 of 6	1.56	2.13	1.2–5.8	0.17–0.71	6.8	0 of 8	0.23	0.07	–	0.12–0.29
1,2,3,7,8,9-HxCDD	3 of 6	1.45	1.64	1.2–4.7	0.25–0.86	5.0	0 of 8	0.29	0.05	–	0.24–0.38
1,2,3,4,6,7,8-HpCDD	3 of 6	9.65	4.52	5–17	8.7–12	1.7	2 of 8	5.78	4.95	4.4–18	3.5–4.2
OCDD	3 of 6	19.5	12.6	17–41	2.9–16	0.48	2 of 8	40.8	60.9	21–190	10–32
2,3,7,8-TCDF	6 of 6	201	142	54–460	–	5.7	6 of 8	35	53	1.2–130	0.12–0.13
1,2,3,7,8-PCDF	6 of 6	30.5	22.5	11–71	–	3.5	4 of 8	8.8	12.3	2.6–23	0.24–33
2,3,4,7,8-PCDF	6 of 6	20.6	13.4	9.1–40	–	3.3	4 of 8	6.3	7.7	2.5–17	0.24–20
1,2,3,4,7,8-HxCDF	4 of 6	5.12	5.60	2.4–16	0.5–5.7	2.6	3 of 8	1.96	1.55	1.3–3.8	0.36–4.4
1,2,3,6,7,8-HxCDF	4 of 6	3.25	4.36	1.2–12	0.5–1.0	2.0	3 of 8	1.61	1.03	1.3–2.9	0.36–2.7
1,2,3,7,8,9-HxCDF	3 of 6	2.61	3.46	2.4–9.4	0.25–0.86	4.0	1 of 8	0.65	0.51	0.29–0.29	0.24–1.3
2,3,4,6,7,8-HxCDF	3 of 6	3.53	4.73	2.4–13	0.5–1.2	3.8	2 of 8	0.94	0.88	0.14–1.3	0.13–2.7
1,2,3,4,6,7,8-HpCDF	5 of 6	6.28	5.83	2.5–17	1.4–1.4	1.6	3 of 8	3.96	2.82	2.9–3.8	0.36–7.4
1,2,3,4,7,8,9-HpCDF	3 of 6	4.02	4.60	3.3–13	0.37–2.9	1.7	3 of 8	2.51	1.80	0.43–5.5	0.4–2.7
OCDF	3 of 6	4.13	4.67	3.7–13	0.33–2.9	1.2	2 of 8	3.48	3.51	0.43–4.4	0.24–7.8

Petroleum coke was used in conjunction with one or more special fuels in 87% and 79% of the tests for Kilns 8 and 9, respectively. Special fuels (when used) constituted (by mass) from 7% to 49% of the Kiln 8 fuel and from 5% to 62% of the Kiln 9 fuel, averaging 26% and 30%, respectively, for Kilns 8 and 9.

Regression analysis results, presented in Table 5 for pollutants detected in at least 60% of stack tests, indicate some weak potential relationships between emissions and various fuels amidst a larger degree of noise. The low r^2 values indicate that the regressions have limited ability to explain the overall variability in the measured stack-gas concentrations. The intercept variable (C_i) is indicative of no dependence on fuel mix. It is predicted as a significant variable in a number of cases, and the positive values might reflect some limited

dependence of emissions on aggregate composition (as the source) or some other non-fuel related factor. Hazardous waste fuel is identified as an explanatory variable for the same pollutants having significantly greater mean concentrations per the t -test analyses (that is, 1,2,3,4,6,7,8-HpCDF in Kiln 9, unqualified results in Table 2). However, consistent trends across specific kiln/fuel combinations are not apparent. Of the twelve pollutants included in Table 5, there are no cases for which a particular fuel is predicted as a significant explanatory variable in the same direction for both kilns. There are even several examples for which a fuel is predicted to increase pollutant levels in one kiln, but decrease the same pollutant levels in the other kiln. For example, the petroleum coke is indicated as an explanatory variable for 2,3,7,8-TCDF and the pentachlorinated furans, but the signs of the coefficients differ between Kiln 8 (a negative predicted effect) and Kiln 9 (a positive predicted effect). The overall implication of the regression analyses is that special fuel combustion generally affects pollutant emissions at a level well below the inherent variability in stack-gas measurements.

3.3. Emission factors

The U.S. EPA AP42 emission factor database provides values for some metals for Portland cement plants, and they are compared with normalized Secil emissions in Fig. 2. Interestingly, Secil emissions are not uniformly lower than the AP42 values, despite the fact that the AP42 values reflect older data from a period when emission controls were generally less advanced. This suggests that for cement kilns, aggregate materials, kiln design, and in some cases fuels may be of greater importance in determining emissions than the use of modern

Table 4

Fuel use in the combined Coke and Coke&HW groups.

Average rates, ranges of rates, and frequencies of fuel use during emission tests Rates in ton/h (during tests when fuel is used) Percentages indicate frequency of tests during which fuel is used							
	Coke	Wood	Bone meal	Refuse-derived fuel	Fluff	Tires	Hazardous waste
Kiln 8	9.0	1.1	2.2	0.6	0.2	1.0	1.5
	4.8–11.8	0.1–2.1	0.1–4.6	0.1–2.2	0.1–0.3	0.2–2.0	0.9–2.1
	100%	45%	57%	40%	15%	53%	20%
	(13% alone)						
Kiln 9	12.7	2.1	2.7	1.1	0.3	1.6	2.7
	6.9–17.0	0.6–4.5	0.6–5.0	0.3–2.0	0.1–1.2	0.1–4.6	1.0–6.0
	100%	46%	45%	42%	33%	47%	28%
	(21% alone)						

Table 5

Potentially significant variables indicated by multiple regression analyses of emissions by fuel type (minimum frequency of detection = 60% in at least one of the kilns).

Pollutant	Kiln 8			Kiln 9		
	f.o.d.	r ²	Explanatory variables	f.o.d.	r ²	Explanatory variables
Mercury (Hg)	97%	0.16	+ HW**	92%	0.19	+ IN* - CK* - WD**
Thallium (Tl)	67%	0.24	- IN* + CK**	39%	0.15	+ IN* + BM* - HW**
Lead (Pb)	82%	0.16	+ CK** + BM**	87%	0.11	+ IN* - TI**
Chromium (Cr)	65%	0.12	+ TI**	73%	0.07	+ IN* - CK**
Copper (Cu)	90%	0.26	+ TI**	96%	0.25	- WD* + HW**
Manganese (Mn)	83%	0.09		85%	0.09	+ HW*
Nickel (Ni)	55%	0.08	+ BM*	66%	0.07	- RD*
Vanadium (V)	67%	0.19	+ IN** - CK* + TI**	43%	0.21	- TI** - HW*
OCDD	62%	0.07		60%	0.17	+ HW**
2,3,7,8-TCDF	90%	0.23	- IN* + CK** + BM** + HW**	84%	0.27	+ IN* - CK** - WD**
2,3,4,7,8-PCDF	60%	0.23	+ CK** + BM** - TI* + HW**	33%	0.25	+ IN* - CK* - WD**
1,2,3,4,6,7,8-HpCDF	65%	0.05		68%	0.12	+ BM* + HW**

Notes f.o.d = frequency of detection in stack-gas measurements.

- indicates a negative coefficient, + indicates a positive coefficient.

Italicized results differ for regression analyses based on full and half detection limits for non-detects (the more significant result is presented, but may not be robust).

Key to variables: IN – Intercept; CK – Coke; WD – Wood; BM – Bone meal; RD – Refuse-Derived Fuel; FL – Fluff; TI – Tires; HW – Hazardous Waste.

** $p = 0.05$ –5% chance the null hypothesis (no explanatory value) is false.* $p = 0.1$ –10% chance the null hypothesis (no explanatory value) is false.

air pollution controls. Note that for cadmium, for example, emission rates are lowest for coke, highest for coal, and intermediate for the fuel-types and kilns represented in AP42.

4. Discussion and conclusions

Pollutant emissions to the atmosphere are a critical measure of a Portland cement manufacturing facility's performance. Predictions of emission rates based either on design specifications, before a facility is built, or on limited stack-gas testing, once the facility is built, may be uncertain, given the many factors that determine average emission rates over the long term. The rich Secil database provides insights into the uncertainties involved in estimating emission rates of toxic air pollutants, although the high frequency of non-detects for many of the analytes in the database hampers statistical characterizations in several cases. Note also that, although emission rates varied by one or two orders of magnitude for each pollutant over the 150 tests (Fig. 1), all rates were within EU emission limit standards.

The two dry process kilns at the Secil-Outão facility are similar in most aspects of their design and operation. They produce the same type of cement from the same aggregate materials, burn similar mixes of fuels, and utilize similar air pollution controls. It is thus, at first glance, surprising to find notable differences in emissions between the two kilns. Trends of higher emissions are mostly consistent across

fuel groups, *i.e.*, many pollutants tend to be higher in one kiln than the other for each of the *Coke*, *Coke&HW*, and *Coal* groupings. Stack-gas concentrations of mercury and most PCDD/F congeners are higher in Kiln 8, whereas metals such as chromium, copper, and nickel are at greater concentrations in Kiln 9. Conjecturally, these differences may be the result from differences in (i) kiln size (Kiln 9 is larger and has roughly 1.5 times more capacity), (ii) aggregate preheater design (both kilns have four cyclone stages with 2 strings, but in Kiln 8 these are followed by a suspended pre-heater, whereas Kiln 9 has an in-line calciner), or (iii) cement kiln dust collection and recycling systems (to be investigated in future work). For mercury and PCDD/F, we hypothesize that the inter-kiln differences stem from differences in the temperatures experienced by the aggregate materials and exhaust gases downstream of the kiln (the aggregate being the likely source of both mercury and PCDD/F) (Karstensen, 2008; Senior et al., 2010). Thus, although all of the emission rates were below applicable regulatory limits, the fact that rates of some pollutants were notably smaller from one kiln relative to the other suggests that these rates depend on many factors, not all of which could be predicted *a priori*.

These test results suggest that the primary fuel used can affect emissions of many pollutants, but that the use of various special fuels, including hazardous waste, has only minor influences. Emissions for some pollutants were found to be higher when coal was used as the main kiln fuel rather than petroleum coke (Table 3), although this

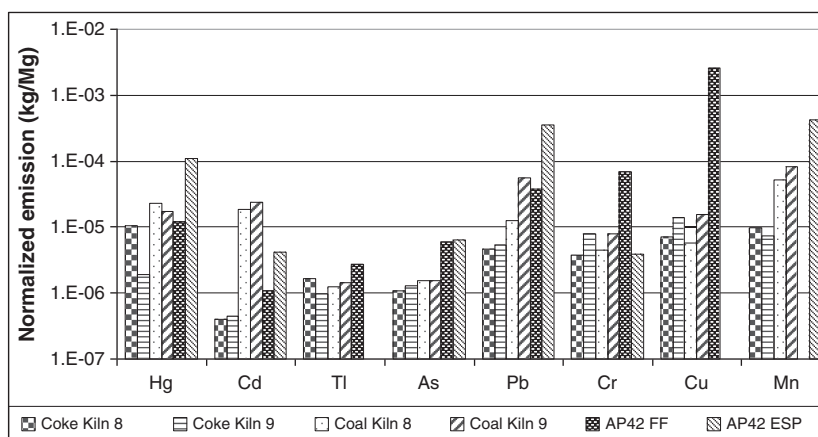


Fig. 2. Normalized emission factors for Secil Kilns 8 and 9 compared with U.S. EPA emission factors. U.S. AP42 differentiated by particle control device (FF=fabric filter, ESP=electrostatic precipitator).

finding may be due to factors not yet investigated (such as those described above). In particular, emissions of cadmium, as well as a number of PCDD/F congeners (including 2,3,7,8-TCDF, which is the most prominent congener) were significantly higher in both kilns when coal was burned — a robust finding given the limited number of stack tests in the *Coal* groupings (which limits inferential power). In contrast, various supplemental fuels (used in lesser amounts, Table 4) appeared to have little overall effect on stack emissions. Multiple regression analyses suggest a small portion of the variability of some pollutant's emission rates are related to the use of some specific fuels (Table 5), including the combustion of hazardous waste, which appears to result in higher emissions of mercury in one kiln. However, significant influences of special fuels were not consistent between the two kilns (Table 5). Overall, the effects of supplemental fuels (including hazardous waste) on pollutant stack-gas concentrations appear to be well within the variability of the overall data.

In other settings, differences in aggregate materials, basic control technologies, and design characteristics may also be important determinants of pollutant emissions. The U.S. EPA's Compilation of Emission Factors (AP42; US EPA, 1995) is a commonly used resource for predicting emission rates, but the relevance and robustness of these factors can vary substantially. For example, the AP42 emission factors for mercury, lead, and many other air toxics for Portland cement manufacturing are based on only one or two stack tests, and the available values exhibit order of magnitude variability (US EPA, 1994). Moreover, industry-wide emission databases could easily be improved through the gathering of the significant amount of data that has been generated through stack testing, but this type of cross-sectional data does not necessarily reflect the variability and uncertainty of emissions from a specific facility.

In summary, the extensive testing of the Secil kilns demonstrated the ability of the facility to repeatedly meet regulatory emission limits over time. Test results indicated higher emissions of many metals and PCDD/Fs when coal was used as a primary fuel, but relatively minor differences for most special fuels (including hazardous waste). Inter-kiln differences in Hg and PCDD/F measurements suggested relatively small differences in kiln design and operating practices can substantially affect emissions.

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