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# Supercritical Water Oxidation of Dioxins and Furans in Waste Incinerator Flyash, Sewage Sludge and Industrial Soil

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## ABSTRACT

Three environmental samples containing dioxins and furans have been oxidised in the presence of hydrogen peroxide under supercritical water oxidation conditions. The samples consisted of a waste incinerator flyash, sewage sludge and contaminated industrial soil. The reactor system was a batch, autoclave reactor operated at temperatures of between 350 °C to 450 °C, corresponding to pressures of ~20 MPa to 33.5 MPa and with hydrogen peroxide concentrations from 0.0 to 11.25 vol.%. Hydrogen peroxide concentration and temperature/pressure had a strong positive effect on the oxidation of dioxins and furans. At the highest temperatures and pressure of supercritical water oxidation of 450 °C and 33.5 MPa and with 11.25 vol.% of hydrogen peroxide, the destruction efficiencies of the individual PCDD/PCDF isomers were between 90 and 99%. There did not appear to be any significant differences in the PCDD/PCDF destruction efficiencies in relation to the different sample matrices of the waste incinerator flyash, sewage sludge and contaminated industrial soil.

**Keywords:** Supercritical water oxidation; Dioxin; PCDD; Flyash; Sewage sludge; Soil

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## **1. Introduction**

Polychlorinated dibenzo-*p*-dioxins (PCDD, i.e. 'dioxins') and the closely related polychlorinated dibenzofurans (PCDF, i.e. 'furans') constitute a group of chemicals that have been demonstrated to occur ubiquitously in the environment [1]. They have been detected in soils and sediments, rivers and lakes, chemical formulations and wastes, herbicides, hazardous waste site samples, landfill sludges and leachates [1,2]. PCDD and PCDF have a number of recognised sources, among which are their formation as by-products of chemical processes such as the manufacture of wood preservatives and herbicides, the smelting of copper and scrap metal, the recovery of plastic coated wire, combustion of municipal waste, coal, wood and industrial waste and natural combustion such as forest fires [2-4].

In relation to the research reported here, PCDD/PCDF are also found in waste incinerator flyash, sewage sludge and contaminated industrial soils. Waste incinerator flyash and air pollution control system residues represent a major emission of PCDD/PCDF to land [5-7]. It is estimated that more than 1 million tonnes of hazardous flyash and air pollution control residues are generated in Europe each year from the incineration of municipal solid waste, much of which is landfilled [7,8]. In addition, PCDD/PCDF have been detected in sewage sludge and reported in several studies [6,9-14]. Certain types of contaminated industrial soils are also reported to contain significant concentrations of PCDD/PCDF [15-17]. Therefore, waste incinerator flyash, sewage sludge and contaminated industrial soil represent significant environmental samples which require processes of remediation.

There is considerable concern over the presence of PCDD/PCDF in the environment due to their high toxicity. The remediation of environmental samples contaminated with PCDD/PCDF represents a significant challenge, as the

concentrations are very low, but their toxicity is high [18]. Supercritical water has been suggested as a novel and effective treatment process to completely destroy organic pollutants [19-21]. The treatment process involves the complete oxidation of the organic contaminants in a water environment at high temperature and pressure at conditions that exceed the critical point of water (temperature of 374 °C and pressure of 22.1 MPa). The properties of water under these conditions are markedly different from that of ambient water. It has unique features with respect to its density, dielectric constant, ionic product, viscosity, diffusivity, electric conductance and solvent ability. An oxidant in the form of oxygen or hydrogen peroxide is required and oxidises the organic material to mainly carbon dioxide and water. At supercritical water conditions the vapour and liquid phases become indistinguishable and the water behaves as a dense fluid such that organic compounds become highly soluble and the oxidant is completely miscible with the fluid, thus minimising mass transfer resistances and providing rapid reaction rates. There is thus interest in investigating the use of supercritical water as a treatment option for the oxidation of PCDD/PCDF.

There are few studies in the literature on the use of supercritical water oxidation to destroy PCDD/PCDF in complex environmental matrices. In this paper, the destruction of PCDD/PCDF in three contaminated environmental samples, waste incinerator flyash, sewage sludge and industrial soil using supercritical water oxidation has been investigated. The influence of the process conditions of temperature/pressure and oxidant concentration on PCDD/PCDF oxidation were investigated.

## **2. Materials and methods**

### ***2.1 PCDD/PCDF samples***

The three environmental samples contaminated with PCDD/PCDF were, reference fly ash from a municipal solid waste incinerator (BCR-490) reference sewage sludge (BCR-677) and reference industrial sandy soil (BCR-529). The samples were obtained from the European Commission Joint Research Centre Institute for Reference Materials and Measurements (IRMM), Geel, Belgium. Tables 1, 2 and 3 show the certified concentrations of the reference PCDD/PCDF samples. In addition, the tables also show analyses of the main Toxic Equivalent PCDD/PCDF which were present in the samples and analysed by our laboratory, but were not certified in the standard reference materials. Although the total number of possible PCDD isomers is 75 and total possible furan isomers is 135, to ease the analytical process, only the most toxic PCDD/PCDF are analysed in the form of the toxic equivalent (TEQ) standard scheme. The TEQ or Toxic Equivalent scheme is based on the available toxicological and biological data to generate a set of weighting factors, each of which expresses the toxicity of a particular PCDD or PCDF in terms of the most toxic PCDD, i.e. 2,3,7,8 TCDD. Toxicity depends on the number and position of the chlorine substituents. The most toxic isomers belong to the 2,3,7,8 group and hence the 17 isomers selected for the TEQ scheme include such isomers. The three environmental PCDD/PCDF reference samples were used as received.

## ***2.2 Experimental reactor***

The supercritical water reactor was made from Inconel, with a volume capacity of 75 ml and the internal length, and diameter were 15 cm and 2.5 cm, respectively. The reactor was manufactured by the Parr Instrument Co. IL, USA. External heating was via an electrical furnace with full temperature and heating rate control (Figure 1). The

PCDD/PCDF contaminated sample (2.0 g) was placed in the reactor with 20 ml of water containing hydrogen peroxide as the oxidant at concentrations from 0.0 to 11.25 vol.%. The reactor was sealed and heated at a heating rate of  $\sim 10\text{ }^{\circ}\text{C min}^{-1}$  to the final temperature of 350  $^{\circ}\text{C}$ , 400  $^{\circ}\text{C}$  or 450  $^{\circ}\text{C}$ , since the reactor was a sealed system, heating resulted in corresponding pressures of  $20 \pm 2\text{ MPa}$ ,  $27 \pm 2\text{ MPa}$  and  $33.5 \pm 2\text{ MPa}$ . The temperature and pressure of 350  $^{\circ}\text{C}/20 \pm 2\text{ MPa}$  and 400  $^{\circ}\text{C}/27 \pm 2\text{ MPa}$  corresponding to sub-critical water conditions and 450  $^{\circ}\text{C}$  and  $33.5 \pm 2\text{ MPa}$  corresponding to supercritical water conditions. Once the desired temperature was reached, the reactor was held at that temperature for one hour and then the heating was stopped and the reactor was removed from the heater and cooled to room temperature by an air cooling system. Therefore, the residence time of the reactants in the reactor ranged from  $\sim 95$  minutes at 350  $^{\circ}\text{C}$  to  $\sim 105$  minutes at 450  $^{\circ}\text{C}$ .

After each experiment the solid samples were separated from the water by vacuum filtration before being dried overnight at a temperature of 105 $^{\circ}\text{C}$  in a vacuum oven and then stored prior to analysis.

### ***2.3 Analysis of PCDD/PCDF***

US-EPA method 1613 was applied for the analysis of PCDD/PCDF in solid matrices [22]. The entire analytical procedure, including sample digestion, extraction and isolation of the PCDD/PCDF from solid samples through to the instrumental analysis with the GC-TQ/MS, was validated using the BCR-490, BCR-529 and BCR-677 reference materials. In addition, samples of PCDD/PCDF-free analytical sand spiked with two different concentrations of precision and recovery standard (PAR) solution were analysed through the entire procedure. The PAR solution contained only native PCDD/PCDF but the labelled homologues were added just before extraction.

The dried solid environmental samples obtained after reaction were spiked with 10 $\mu$ l of  $^{13}\text{C}_{12}$ -labelled 2,3,7,8-chloro substituted PCDD/PCDF standard prior to the whole analytical procedure to determine the percentage analytical recovery of the analytical procedure. The solid samples were extracted using a Dionex ASE-100 (Thermo Fisher UK Ltd.) accelerated solvent extraction system and toluene as solvent to extract the organic compounds from the sample matrix. The system was set at a temperature and pressure of 200°C and 1500 psi and purged with nitrogen gas. For fractionation and isolation of the PCDD/PCDF from the extracted organic fraction an automated liquid chromatography multicolumn Power Prep/Dioxin System from Fluid Management Systems (FMS), Inc., U.S.A was used. The system is based on a sequence of acidic-basic multilayer silica, basic alumina and activated carbon adsorbents, pre-packed in a disposable Teflon column and hermetically sealed [23].

The isolated and concentrated PCDD/PCDF fraction was analysed using a gas chromatograph coupled to a triple quadrupole mass spectrometer (GC-TQ/MS). The gas chromatograph was a Varian model 450-GC with a Varian 8400 auto-sampler, coupled to a Varian 320-TQ/MS. The acquisition of data was carried out with a Varian MS Workstation Version 6.9.2. Helium was used as a carrier gas at a constant flow-rate of 1ml min<sup>-1</sup>. The gas chromatograph capillary column was a Varian CP-Sil 88 with column length 50 m, internal diameter 0.25 mm, and 0.25  $\mu$ m film thickness. 2  $\mu$ l of PCDD/PCDF fraction sample volume was injected into the gas chromatograph in split/splitless injection mode at 270 °C. The column oven temperature was programmed at 140°C as an initial temperature and held for 2 minutes, before heating at 45 °C min<sup>-1</sup> to 190 °C with no holding time, and finally heating at 5°C min<sup>-1</sup> to 240 °C held for 31.89 minutes giving the total GC programme time of 45 minutes. Details

of the analytical system, procedure and method validation have been reported elsewhere [6].

### **3. Results and discussion**

#### ***3.1 Analytical recovery***

The accuracy of the analytical procedure was verified by comparison with the certified values of the IRMM reference samples BCR-490, BCR-677 and BCR-529 for incinerator flyash, sewage sludge and industrial sandy soil respectively. The results are shown in Tables 1, 2 and 3. The percentage recoveries were in a satisfactory range from 80 – 120 %. There did not appear to be any significant differences in the analytical recoveries of the PCDD/PCDF isomers from each of the different sample matrices of flyash, sludge and soil. Holscher et al [24] investigated the presence of PCDD/PCDF in a wide range of sample matrices, including incinerator flyash, soil and food samples and reported recoveries in the range of 50-120%.

#### ***3.2 Oxidation of PCDD/PCDF contaminated samples in supercritical water***

Figure 2 shows the individual isomers of PCDD/PCDF in the flyash sample after treatment by supercritical water oxidation at 450 °C and  $33.5 \pm 2$  MPa in relation to increased concentration of hydrogen peroxide concentration from 0.00% to 11.25%. All of the isomers consistently decreased in concentration in the waste incinerator flyash samples with increasing hydrogen peroxide concentration. Three of the isomers (1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF and 1,2,3,7,8,9-HxCDF) were identified as showing high oxidation rates of more than 96% and for congeners 2,3,7,8-TCDD and

2,3,7,8-TCDF the oxidation achieved, were above 93% and 91% respectively at the maximum, 11.25% hydrogen peroxide concentration. Figure 3 illustrates the effect of hydrogen peroxide, oxidation temperature and pressure on the oxidation rate of the 2,3,4,8-TCDD and TCDF isomers. The highest oxidation rates achieved reduced the TCDD from 185.67 ng kg<sup>-1</sup> to 11.68 ng kg<sup>-1</sup> and reduced the TCDF from 794.81 ng kg<sup>-1</sup> to 69.74 ng kg<sup>-1</sup>, which were reductions up to 93% and 91% respectively at 450 °C and with 7.5% of hydrogen peroxide. Generally, all PCDD/PCDF concentrations in the waste incinerator flyash were significantly decreased when hydrogen peroxide concentration, temperature/pressure were increased. However, at the lower temperature of 350 °C, for 2,3,7,8-TCDD there was little oxidation, even with increasing concentration of hydrogen peroxide. Even at 400 °C, oxidation was only effective at the higher concentrations of hydrogen peroxide.

Figure 4 shows the influence of hydrogen peroxide concentration from 0.0% to 7.5% on the supercritical water oxidation of PCDD/PCDF in sewage sludge at 450 °C and 33.5 ± 2 MPa. All of the PCDD/PCDF isomer concentrations were found to have decreased, by more than 50%, even in the absence of hydrogen peroxide, however, in the presence of hydrogen peroxide there was a marked decrease in PCDD/PCDF isomer concentration. For several PCDD/PCDF isomers, namely 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD and 1,2,3,4,7,8,9-HpCDF, complete (100%) oxidation occurred at only 3.75% hydrogen peroxide concentration. Additionally, five isomers (1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDF, 1,2,3,4,7,8-HxCDD, 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8,9-HpCDF) were 100% oxidised when the concentration of hydrogen peroxide was increased to 7.50%. Figure 5 shows the supercritical water oxidation rate of 2,3,7,8-TCDD and 2,3,7,8-TCDF in sewage sludge in relation to temperature (and pressure) and hydrogen peroxide concentration. At the lower oxidation

temperature of 350 °C, there was only a modest reduction in PCDD/PCDF concentration. The small increase in 2,3,7,8-PCDF concentration at 350 °C was within the experimental/analytical errors of the experiments. At the higher temperature of 450 °C, the 2,3,7,8-TCDD and 2,3,7,8-TCDF concentration was found to be significantly reduced from 1.44 ng/kg to 0.011 ng/kg and 47.49 ng/kg to 0.16 ng/kg, respectively. The low concentration of 2,3,7,8-TCDD in the original sewage sludge standard sample should be noted.

The supercritical water oxidation of PCDD/PCDF in contaminated industrial soil at 450°C and  $33.5 \pm 2$  MPa in relation to hydrogen peroxide concentration 0.0% to 7.5% is shown in Figure 6. The results obtained for all isomers were found to consistently decrease when hydrogen peroxide concentration was increased. The highest rate of oxidation was obtained with isomer 1,2,3,7,8,9-HxCDF which was 100%. Other PCDD/PCDF isomers, namely, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDF and OCDF were found to have a 99% removal rate compared with the reference sample. The supercritical water oxidation of the most toxic isomers i.e 2,3,7,8-TCDD and 2,3,7,8-TCDF in the industrial contaminated solid sample is shown in Figure 7. The oxidation of both isomers resulted in a decrease in concentration in the resultant soil sample. At 450 °C temperature, pressure  $33.5 \pm 2$  MPa and 7.5% hydrogen peroxide concentration the 2,3,7,8-TCDD concentration decreased from 4017 ng kg<sup>-1</sup> to 12 ng kg<sup>-1</sup>, representing a 99.7% reduction. For the 2,3,7,8-TCDF isomer, the reduction was from 65 ng kg<sup>-1</sup> to 6 ng kg<sup>-1</sup> a 90.7% reduction in concentration. These reductions compare with only 60.7% for 2,3,7,8-TCDD and 67.1% for 2,3,7,8-TCDF at 0.00% hydrogen peroxide, indicates the importance of the oxidant in PCDD/PCDF oxidative destruction in

supercritical water. Meanwhile at the oxidation conditions of 350 °C and  $20 \pm 2$  MPa, the concentration of TCDD and TCDF isomers were reduced from 4017 ng kg<sup>-1</sup> to 2500 ng kg<sup>-1</sup> and from 65 ng kg<sup>-1</sup> to 37 ng kg<sup>-1</sup> respectively, when the concentration of hydrogen peroxide was increased to 7.5%.

The supercritical water oxidation of the PCDD/PCDF contaminated waste incinerator flyash, sewage sludge and industrial soil has been shown to be effective, with reductions of over 90% and in some cases, 100% removal. There did not appear to be any significant differences in the destruction efficiencies of the PCDD/PCDF in relation to the different sample matrices of the flyash, sludge and soil. Although the sewage sludge and contaminated soil would have higher organic content compared to the flyash, there was no discernable difference in their PCDD/PCDF destruction efficiencies.

At subcritical water conditions the efficiency of the oxidation process decreased. Greater destruction efficiencies of organic compounds can be achieved at higher temperatures, in the temperature range 600 °C to 650 °C [25]. There have been very few studies on the use of supercritical water oxidation of dioxins, mostly from studies in Japan [26-29]. Kawajiri et al [27] used supercritical carbon dioxide to extract dioxins from waste incinerator flyash, where extraction efficiencies of over 99% were reported. The extracted fraction containing dioxins was then subject to oxidation in subcritical and supercritical water. They reported that high destruction efficiencies of the dioxins in the flyash were obtained at high temperature hydrothermal conditions (10 MPa, 15 MPa pressures and 600 °C temperature) and also at supercritical water oxidation conditions (25 MPa pressure and temperatures of 500 and 600 °C). Kawasaki et al [28] investigated the use of supercritical water oxidation to destroy polychlorinated biphenyls in high concentrations together with

experiments with dioxins. The dioxins was in the form of the octa-PCDD as a standard solution. Experiments were carried out in a continuous flow reactor with residence times between 21 and 33 seconds at temperatures between 560 and 600 °C and pressures of 23.5 MPa. They found that high levels of destruction efficiency were obtained for the dioxins from 99.794% to 99.999% depending on process conditions and dioxin concentration. They also reported that the supercritical water oxidation of high concentrations of chlorinated wastes would generate significant concentrations of corrosive hydrogen chloride. They therefore suggested that corrosive resistant titanium-palladium metal alloys would be required for the reactor construction at temperatures above 380 °C. Chen et al [30] investigated the hydrothermal processing of waste incinerator flyash for the decomposition of PCDD/PCDF. They investigated the influence of, addition of iron to the flyash, reaction time and cooling procedure after reaction on the decomposition of PCDD/PCDF. They found a reaction time of one hour was satisfactory for PCDD/PCDF decomposition. However, a major influence of iron addition was shown, where they reported a 46.17% (TEQ) decomposition rate for PCDD/PCDF on the flyash, but when iron was added, the decomposition rate increased to 90.33%. Okajima et al. [29] reported on a dioxin treatment process involving extraction of dioxins from waste incinerator flyash and adsorption onto activated carbon. The activated carbon was then treated by supercritical water oxidation to destroy the dioxins at 20 MPa and 500 °C. However, the oxidation treatment also oxidised the activated carbon. The decomposition efficiency of dioxins was more than 99%.

In this present study, the maximum conditions of supercritical water oxidation was 450 °C and 33.5 MPa and with the highest hydrogen peroxide concentration which gave destruction efficiencies of the individual PCDD/PCDF isomers of mostly

between 90 and 99%. However, at lower temperatures and lower hydrogen peroxide concentrations, PCDD/PCDF isomer oxidation was much lower. This is in contrast to the results reported by others where high destruction efficiencies of PCDD/PCDF were reported [27-29]. However, in the work of Kawajiri et al [27] and Okajima et al. [29] the PCDD/PCDF treatment process involved extraction of the PCDD/PCDF from the sample matrix as a first step, followed by oxidation under supercritical water conditions. Similarly, Kawasaki et al [28] examined supercritical water oxidation of PCDD/PCDF in the form of a standard solution of the octa-PCDD. In our work, the supercritical water oxidation was undertaken directly on the solid PCDD/PCDF contaminated environmental samples. Consequently, matrix effects, such as strong adsorption of the PCDD/PCDF onto the sample and/or the ease of access of the reactants to the PCDD/PCDF which may be in the pores of the solid matrix are likely to influence the oxidation process. In addition, others have used higher temperatures of reaction, of up to 600 °C [27, 28] to produce the very high destruction efficiencies for PCDD/PCDF compared to the conditions used in this work. The literature data suggests that to achieve the high destruction efficiencies of 99.9999% for PCDD/PCDF, high supercritical water oxidation conditions are required at temperatures of above 550 °C.

#### **4. Conclusions**

In this research, waste incinerator flyash, sewage sludge and contaminated industrial soil containing dioxins and furans have been processed under supercritical water oxidation conditions. The hydrothermal processing conditions were in relation to temperatures of between 350 °C to 450 °C, corresponding to pressures of ~20 MPa to

33.5 MPa and with H<sub>2</sub>O<sub>2</sub> concentrations from 0.0 to 11.25 vol.%. The destruction efficiencies at subcritical water conditions (the lower temperatures and pressures) were not satisfactory in reducing the PCDD/PCDF concentration. However, supercritical water oxidation of 450 °C and 33.5 MPa and with 11.25 vol.% H<sub>2</sub>O<sub>2</sub> produced destruction efficiencies of the individual PCDD/PCDF isomers of between 90 and 99%. The destruction efficiencies were independent of the different types of sample matrices. The results suggest that for the almost complete destruction of PCDD/PCDF, high temperatures and pressure, well into the supercritical water oxidation conditions are required to achieve the high destruction efficiencies of 99.9999%.

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**Table 1.** Percentage recovery of PCDD/PCDF from the analysis of the standard waste incinerator flyash compared to the certified value (BCR-490)

<b>Compounds</b>	<b>Result (ng/kg)</b>	<b>Cert. Value (ng/kg)</b>	<b>Recovery %</b>
2,3,7,8 TCDD	185.67	169.00	109.86
2,3,7,8 TCDF	794.81	900.00	88.31
2,3,4,7,8 PeCDF	1698.94	1850.00	91.83
1,2,3,7,8 PeCDD	748.90	670.00	111.78
1,2,3,4,7,8 HxCDF	2154.23	2370.00	90.90
1,2,3,6,7,8 HxCDF	2425.75	2640.00	91.88
1,2,3,7,8 PeCDF	1487.96	1710.00	87.02
1,2,3,4,7,8 HxCDD	786.02	950.00	82.74
1,2,3,6,7,8 HxCDD	447.37	480.00	93.20
1,2,3,7,8,9 HxCDD	2437.43	2840.00	85.83
1,2,3,4,6,7,8 HpCDF	6267.24		
1,2,3,7,8,9 HxCDF	366.89	340.00	107.91
2,3,4,6,7,8 HxCDF	2335.59	2470.00	94.56
1,2,3,4,6,7,8 HpCDD	3005.25		
1,2,3,4,7,8,9 HpCDF	2544.67		
OCDF	5537.59		
OCDD	6002.23		

**Table 2** Percentage recovery of PCDD/PCDF from the analysis of the standard sewage sludge compared to the certified value (BCR-677)

<b>Compounds</b>	<b>Result (ng/kg)</b>	<b>Cert. Value (ng/kg)</b>	<b>Recovery %</b>
2,3,7,8 TCDD	1.440	1.510	95.36
2,3,7,8 TCDF	47.490	45.000	105.53
2,3,4,7,8 PeCDF	14.161	16.900	83.79
1,2,3,7,8 PeCDD	3.527	4.100	86.02
1,2,3,4,7,8 HxCDF	15.390	14.500	106.14
1,2,3,6,7,8 HxCDF	5.840	6.100	95.74
1,2,3,7,8 PeCDF	26.070	24.800	105.12
1,2,3,6,7,8 HxCDD	244.890	235.000	104.21
1,2,3,7,8,9 HxCDD	68.350	79.000	86.52
1,2,3,4,6,7,8 HpCDF	57.950	61.600	94.08
1,2,3,7,8,9 HxCDF	0.740	0.840	88.10
2,3,4,6,7,8 HxCDF	4.930	5.600	88.04
1,2,3,4,6,7,8 HpCDD	2.950	3.500	84.29
1,2,3,4,7,8,9 HpCDF	7.010	6.300	111.27
OCDF	204.270	177.000	115.41
OCDD	13.870	12.700	109.21

**Table 3** Percentage recovery of PCDD/PCDF from the analysis of the standard industrial sandy soil compared to the certified value (BCR-529)

<b>Compounds</b>	<b>Result (ng/kg)</b>	<b>Cert. Value (ng/kg)</b>	<b>Recovery %</b>
2,3,7,8 TCDD	4017.00	4500.00	89.27
2,3,7,8 TCDF	64.93	80.00	81.16
2,3,4,7,8 PeCDF	296.61	360.00	82.39
1,2,3,7,8 PeCDD	362.76	440.00	82.45
1,2,3,4,7,8 HxCDF	2892.30	3400.00	85.07
1,2,3,6,7,8 HxCDF	895.44	1090.00	82.15
1,2,3,7,8 PeCDF	168.07	150.00	112.05
1,2,3,4,7,8 HxCDD	1150.08	1220.00	94.27
1,2,3,6,7,8 HxCDD	4506.69	5400.00	83.46
1,2,3,7,8,9 HxCDD	2460.29	3000.00	82.01
1,2,3,4,6,7,8 HpCDF	2271.68		
1,2,3,7,8,9 HxCDF	17.65	20.00	88.25
2,3,4,6,7,8 HxCDF	300.11	370.00	81.11
1,2,3,4,6,7,8 HpCDD	7686.50		
1,2,3,4,7,8,9 HpCDF	3074.19		
OCDF	3583.87		
OCDD	4821.00		

## Figure Captions

Figure 1. Schematic diagram of the supercritical water oxidation reactor.

Figure 2. Total oxidation of individual isomers of PCDD/PCDF without and with the presence of various concentrations of  $H_2O_2$  at a temperature  $450^\circ C$  and pressure of  $33.5 \pm 2$  MPa for fly ash.

Figure 3. Reduction of 2,3,7,8-TCDD and 2,3,7,8-TCDF at different temperature, pressure and  $H_2O_2$  concentration for fly ash

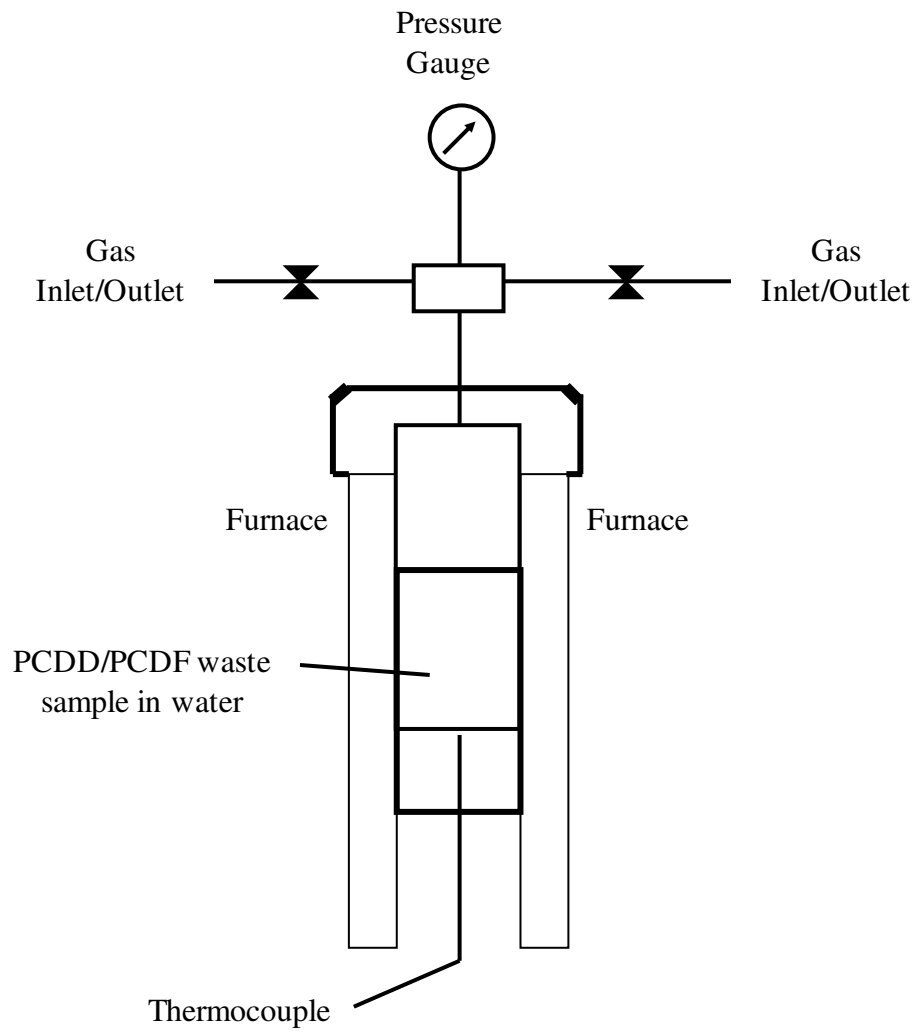
Figure 4. Total oxidation of individual isomers of PCDD/PCDF without and with the presence of various concentrations of  $H_2O_2$  at a temperature  $450^\circ C$  and pressure  $33.5 \pm 2$  MPa for sewage sludge.

Figure 5. Reduction of 2,3,7,8-TCDD and 2,3,7,8-TCDF at different temperature, pressure and  $H_2O_2$  concentration for sewage sludge

Figure 6. Total oxidation of individual isomers of PCDD/PCDF with and without the presence of various concentrations of  $H_2O_2$  at a temperature  $450^\circ C$  and pressure  $33.5 \pm 2$  MPa for industrial soil

Figure 7. Reduction of 2,3,7,8-TCDD and 2,3,7,8-TCDF at different temperature, pressure and  $H_2O_2$  concentration for industrial soil

Figure1. Schematic diagram of the supercritical water oxidation reactor.



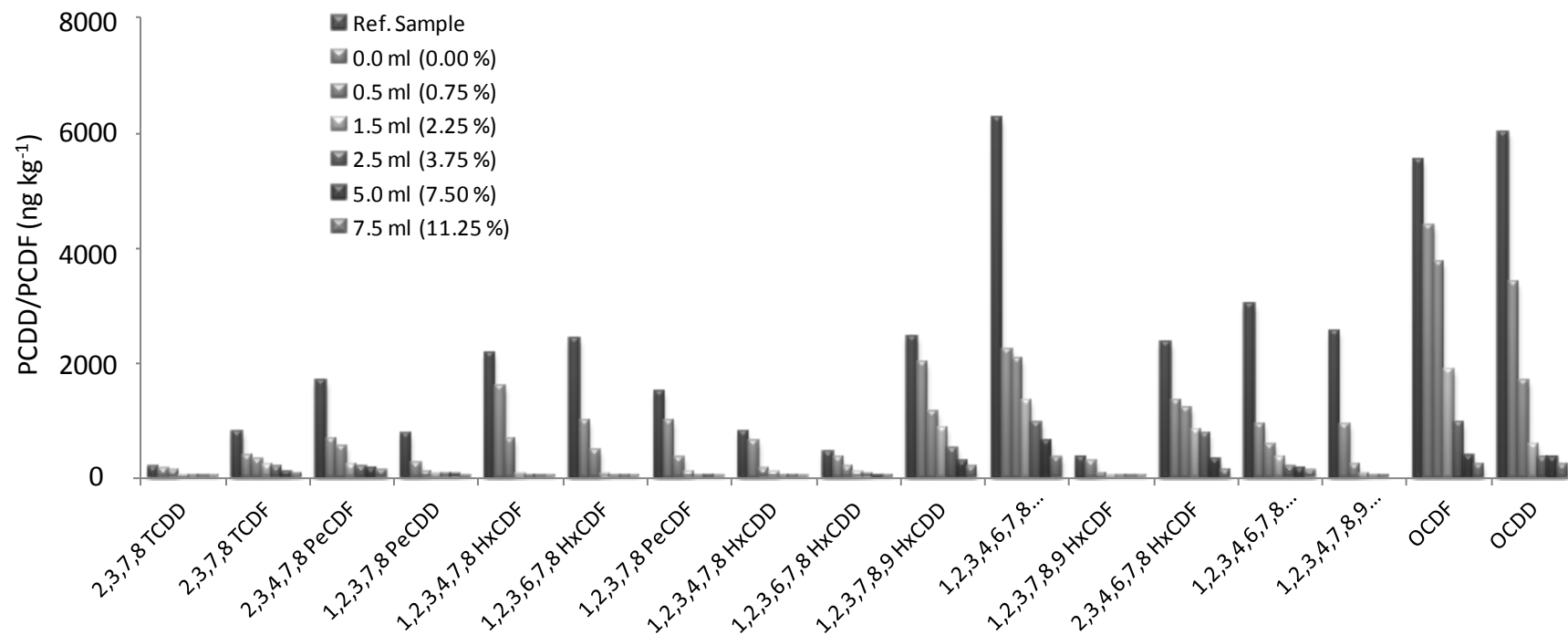
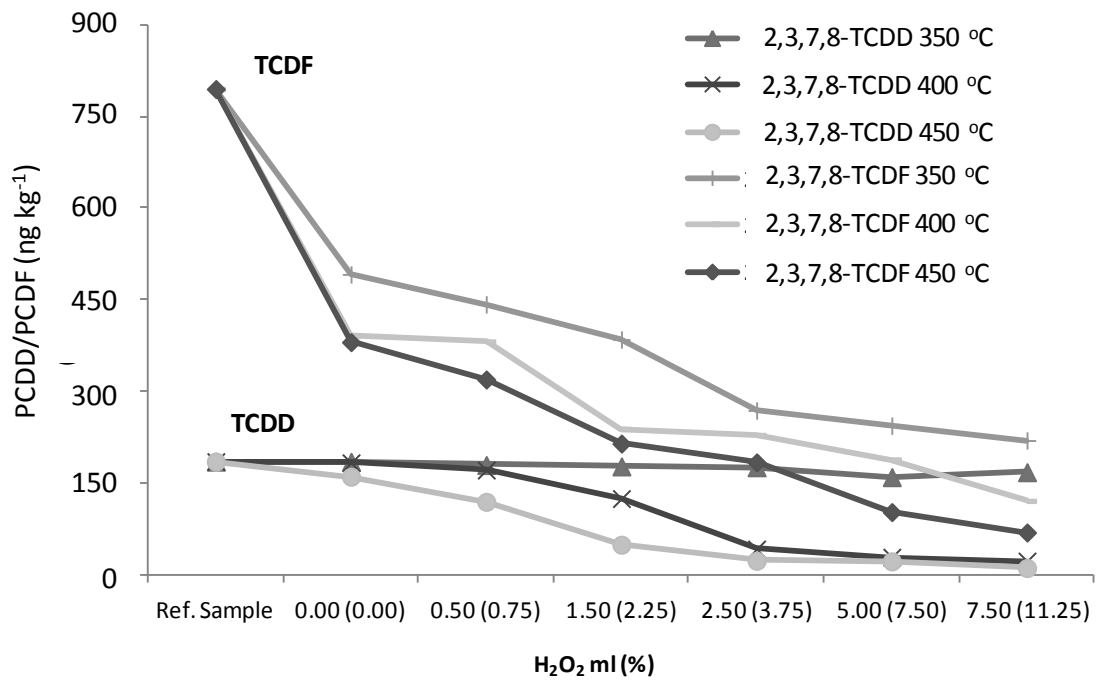


Figure 2. Total oxidation of individual isomers of PCDD/PCDF without and with the presence of various concentrations of H<sub>2</sub>O<sub>2</sub> at a temperature 450°C and pressure of 33.5 ± 2 MPa for fly ash

Figure 3. Reduction of 2,3,7,8-TCDD and 2,3,7,8-TCDF at different temperature, pressure and H<sub>2</sub>O<sub>2</sub> concentration for fly ash



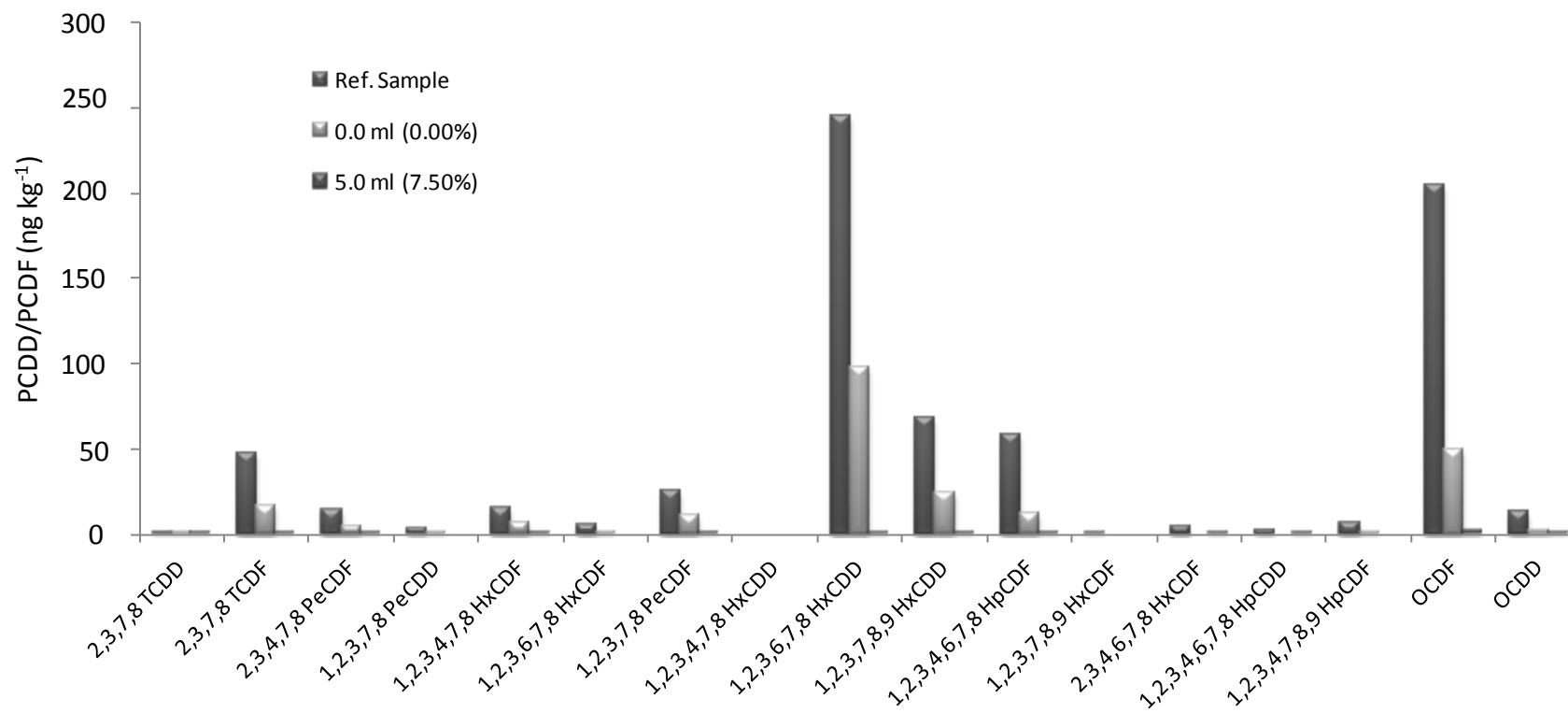
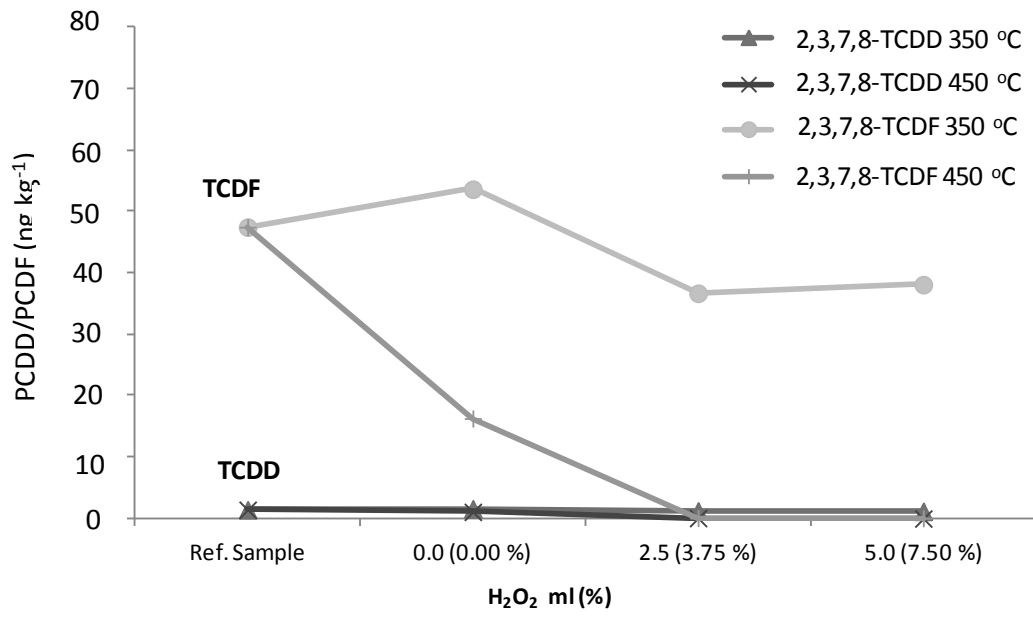


Figure 4. Total oxidation of individual isomers of PCDD/PCDF without and with the presence of various concentrations of H<sub>2</sub>O<sub>2</sub> at a temperature 450°C and pressure 33.5 ± 2 MPa for sewage sludge

Figure 5. Reduction of 2,3,7,8-TCDD and 2,3,7,8-TCDF at different temperature, pressure and H<sub>2</sub>O<sub>2</sub> concentration for sewage sludge



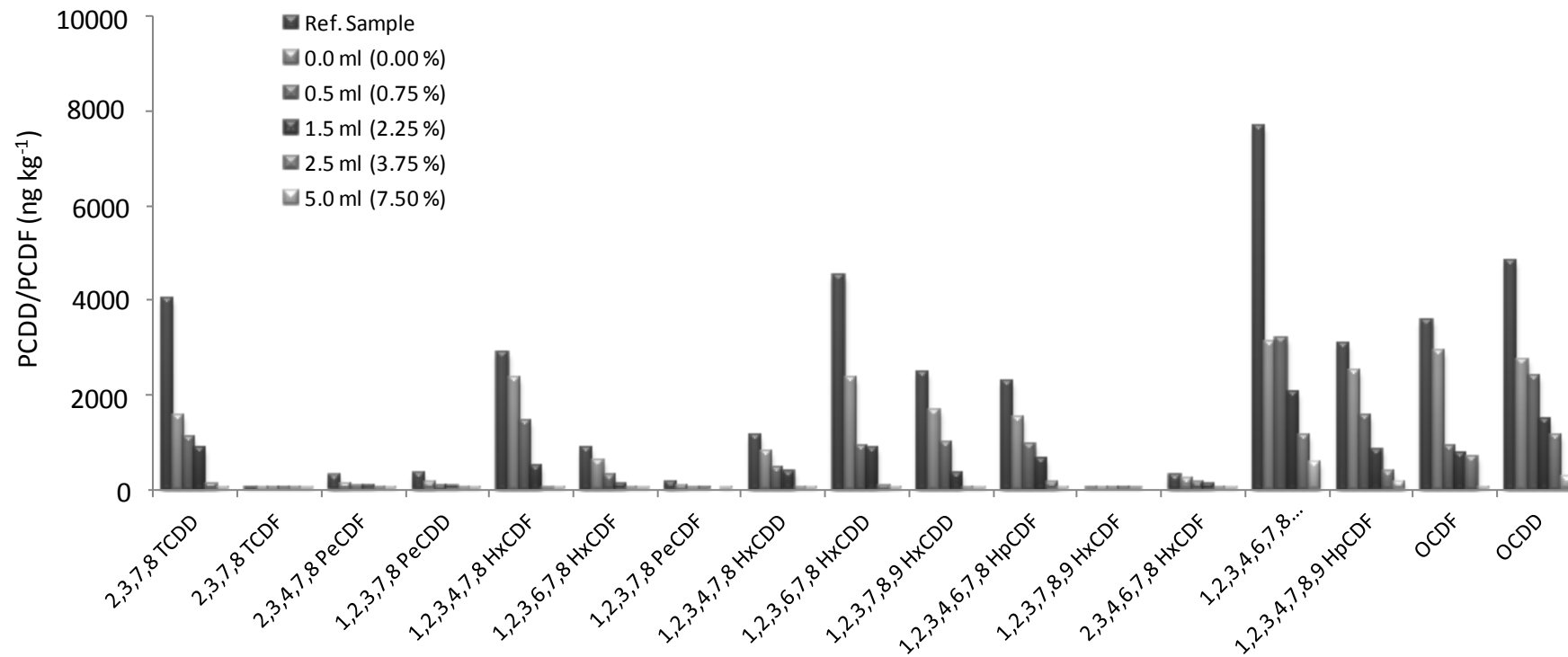


Figure 6. Total oxidation of individual isomers of PCDD/PCDF with and without the presence of various concentrations of H<sub>2</sub>O<sub>2</sub> at a temperature 450°C and pressure 33.5 ± 2 MPa for industrial soil

Figure 7. Reduction of 2,3,7,8-TCDD and 2,3,7,8-TCDF at different temperature, pressure and H<sub>2</sub>O<sub>2</sub> concentration for industrial soil

