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The influence of electrodialytic remediation on dioxin (PCDD/PCDF) levels in fly ash and air pollution control residues

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Abstract

Fly ash and Air Pollution Control (APC) residues collected from three municipal solid waste incinerators in Denmark and Greenland were treated by electrodialytic remediation at pilot scale for 8-10 h. This work presents for the first time the effect of electrodialytic treatment on polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), and how these levels impact on the valorization options for fly ash and APC residue.

PCDD/PCDF levels in the original residues ranged between 4.85–197 ng g^{-1}, being higher for the electrostatic precipitator fly ash. The toxic equivalent (TEQ) varied ten fold, ranging 0.18–2.0 ng g^{-1} I-TEQ, with penta and hexa-homologs being most significant for toxicity.

After the electrodialytic treatment PCDD/PCDF levels increased in the residues (between 1.4–2.0 times). This does not mean PCDD/PCDF were synthesized, but else that soluble materials dissolve, leaving behind the non-water soluble compounds, such as PCDD/PCDF. According to the Basel Convention, PCDD/PCDF levels in these materials is low (<15 μg WHO-TEQ kg^{-1}) and the fly ash and APC residue could eventually be valorized, for instance as construction material, provided end-of-waste criteria are set and that a risk assessment of individual options is carried out, including the end-of-life stage when the materials become waste again.

Keywords

Electrokinetic; PCDD; PCDF; dioxins; fly ash; APC residues.

1. Introduction

Dioxins are persistent organic pollutants which bioconcentrate in the food web, causing potentially serious health problems [1]. Dioxin is the common name for two groups of tricyclic, chlorinated organic compounds: polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). There are 75 PCDD and 135 PCDF, depending on the number and position of chlorine atoms on the benzene rings.

PCDD/PCDF are formed unintentionally during incineration of municipal solid waste and in other industrial processes and many countries have set regulatory limits for the emission of PCDD/PCDF into the air. In the European Union the limit was set at 0.1 ng I-TEQ Nm^{-3}. I-TEQ is the International Toxicity Equivalent, used as an indicator of the toxicity of a mixture of PCDD/PCDF, as detailed in section 2.5.

The implementation of abatement measures at incinerators resulted in an estimated overall decrease of 58% in PCDD/PCDF emissions to air in Europe between 1995 and 2000 [2]. As a result, declining PCDD/PCDF concentrations have recently been reported in a large European River system [3], suggesting that risks posed to aquatic life in this basin have been greatly reduced.

But while air emissions have been decreasing through improved PCDD/PCDF-capture from the flue gas, PCDD/PCDF get diverted into other waste fluxes, such as wastewater and solid residues from incineration facilities. Earlier national estimates indicate 3500 g I-TEQ are released per year *via* incineration residues and about 20 g I-TEQ per year *via* wastewater [4]. And while PCDD/PCDF emissions *via* wastewater are negligible, the release *via* incineration residues appears to be in the same order of magnitude as emissions to the atmosphere [4], and so these residues could become secondary reservoirs of PCDD/PCDF. Of concern are: **fly ash**, which is the solid residue collected from the flue gas prior to the addition of any sorbents; and **air pollution control (APC) residues**, which comprise the solid materials collected from the flue gas after the addition of sorbents or other chemicals used for gas cleaning. These residues amount to 4-10% in weight of all the waste incinerated, and large amounts of fly ash and APC residues are generated yearly worldwide. Fly ash and APC residues are generally fine powders, and APC residues are strongly alkaline, containing high concentrations of lime and other calcium compounds, as well as soluble metal chlorides [5–6].

Several potential uses for these residues have been envisaged in the last decades [7], in line with the circular economy and resource efficiency strategies in place in the European Union. Under this framework, several researchers have reported on the electrodialytic (ED) treatment of fly ash and APC residue at laboratory and pilot scale, targeting the successful removal of heavy metals and soluble salts and the valorization of these wastes [8-15]. Even though this technique has shown great potential, no studies so far have reported its effect on the PCDD/PCDF content in fly ash and APC residue, and this missing information is crucial to properly assess possible valorization options.

The objectives of this work were:

(i) To analyze PCDD/PCDF in the fly ash and APC residues from 3 municipal solid waste (MSW) incinerators in Denmark and Greenland with different flue gas cleaning processes and compare those with similar residues in other countries.

(ii) To study for the first time possible changes on PCDD/PCDF levels in fly ashes and APC residues due to electrodialytic remediation.

(iii) To discuss the implications of PCDD/PCDF levels for the valorization of fly ashes and APC residues.

2. Materials and methods

2.1 Fly ash and APC residue

Four different residues from MSW incineration were used in this work: **fly ash** from an electrostatic precipitator (**FA**) and **APC residues** from a wet **(WET**) and from a semi-dry (**SD, SD-carb**) flue gas treatment systems (table 1). The sample SD-carb was obtained by inducing carbonation. For this purpose, a sub-sample of SD was kept at room temperature under moist conditions for several weeks [16].

To avoid clogging of the electrodialytic apparatus, the fraction >1 mm of the residues was dry sieved out, and only the fraction <1 mm, representing 99% of the mass, was used in the experiments.

2.2 Electrodialytic pilot plant

The pilot plant consisted of an electrodialytic stack with continuously feeding of the APC/fly ash suspension (diluate), using pumps. Inside the stack, ions dissolved from the residues were transported by electromigration through ion-exchange membranes into the concentrate flow, which continuously recirculated between the storage tank and the electrodialytic stack (as described in [13, 16]).

The concentrate consisted of 30 L tap water with 400 mL 1:1 HNO3, and the electrode clean solution of 30 L distilled water with 400 mL 1:1 HNO3. The electrodialytic stack consisted of 5, 34 or 50 cell pairs (530 cm2 active surface area per cell) with Neosepta cation and anion exchange membranes. The spacers were 0.6 mm and 5 mm thick for the concentrate and diluate respectively. There were electrode compartments in each end of the electrodialytic stack with electrode clean solution circulating between them. The electrodes were titanium plates covered by a layer of metal oxides. The flow rates were adjusted in each experiment to maintain overpressure in the diluate compared to

the concentrate, with the diluate flow rate always kept at a maximum. The electrode tank was ventilated for exhaust gases. A more thorough description of the pilot plant can be found in [13, 16].

Table 1 – MSW incineration facilities and residues used in this work

Sample	FA	WET	SD and SD-carb
Location	Nuuk, Greenland	Glostrup, Denmark	Nykøbing Falster, Denmark
Facility	Nuuk	I/S Vestforbrænding	I/S REFA
Furnace	B&S	Vølund	Vølund
Capacity (t $year^{-1}$)	10 000 [17]	600 000	177 000
Incinerated waste (t $year^{-1}$)	9 371 [17]	522 258	111 039
Residues used in this work	Fly ash collected by ESP without addition of any substances for APC	Fly ash collected from bag filters and cyclone, (prior to the wet scrubber). Activated carbon is added to the bag filters to remove PCDD/PCDF and other harmful substances together with fly ash. NH_3 is injected into the furnace to reduce emissions of NOx (nitrous gases)	APC residues collected by ESP after a semidry treatment process with the injection of slaked lime and activated carbon. NOx removal by selective non-catalytic reduction
Quantities of residues	10 t $year^{-1}$ of fly ash	15 670 t $year^{-1}$ of FA and APC residues	3258 t $year^{-1}$ APC residues (in 2014)
Additional notes	Small incineration plant working at comparatively low temperatures.	Large-scale incinerator with state-of-the-art APC equipment	Large-scale incinerator with state-of-the-art APC equipment

2.3 Electrodialytic experiments

Six electrodialytic experiments were made, varying the material and operating conditions (table 2). Experiment 5 is a replicate of experiment 4. In the remaining cases one experiment was made for each set of experimental conditions. L/S was kept constant at 10 L/kg, with either 8.0 kg fly ash/APC residue and 80 L tap water (experiments 1 and 2), 5.3 kg fly ash/APC residue and 53 L tap water (experiments 3-5), and 1 kg of fly ash/APC residue and 10 L tap water (experiment 6), dependent on the

number of cell pair which results in different stack volume. At the end of the electrodialytic experiments the diluate was filtered through filter paper at normal pressure, and remaining fly ash/APC residue was dried in an oven at 40 °C prior to further analysis.

Table 2 – Experimental conditions for the electrodialytic experiments

Experiment number	1	2	3	4	5	6
Sample	FA	WET	SD	SD	SD	SD-carb
Cell pairs (number)	5	34	50	34	34	50
Time (h)	10	8	10	10	10	10
Residence time (h)	1.8	1.4	1.8	1.7	1.7	1.8
Current (mA/cm^2)	4.7	5.7	5.7	5.7	5.7	5.7

2.4 Analytical

Analysis of 17 dioxins (7 PCDD and 10 PCDF) were made on fly ash and APC residues before and after treatment by an external laboratory using the following procedure. Prior to the extraction, 13C labelled internal standards for quantification of PCDD/PCDF were added to the fly ash samples (1 g). Spiked samples were extracted with a toluene/acetic acid solution (5% v/v glacial acetic acid in toluene) [18] for 48 hours in a Soxhlet apparatus. Extracts were concentrated almost to dryness in a rotary vacuum evaporator and then re-dissolved in hexane. Hexane extracts (10 mL) were pre-cleaned by shaking with concentrated sulfuric acid (10 mL) at laboratory temperature and then cleaned via liquid chromatography using a multi-layer silicagel column [19]. Hexane/dichloromethane (5% dichloromethane in hexane) eluates (50 mL) were concentrated with the modified Kuderna-Danish concentrator to 0.5-1 mL. Florisil columns (1 g) and combination of hexane and dichloromethane for separation of PCDD/PCDF from other compounds were used. First hexane fraction containing PCBs, second dichloromethane fraction containing PCDD/PCDF and non-ortho PCBs were concentrated by Kuderna-Danish concentrator. The final extracts containing PCDD/PCDF were concentrated up to dryness under a stream of nitrogen and then the 13C labelled injection standards were added. Finally, 2 microliters of the final extracts were analyzed by HRGC-HRMS (GC: Trace GC Ultra equipped with auto sampler Thermo Electron Corp. Tri Plus, column STX-500 (60 m x 0.25 mm, film 0.15 µm) Restek; MS: Thermo Electron Corp. DFS operated in MID mode, reference gas PFTBA; Resolution R10≈10000). Certified reference material of fly ash BCR490 was used as internal quality control sample to routinely check analysis. Results are reported in dry basis (expressed as mass of PCDD/PCDF per mass of total solids)

2.5 Calculation of the Toxicity Equivalent

To characterize and compare different fly ash and APC residues the total Toxicity Equivalent (TEQ) was calculated based on the international system set up in 1989, referred as I-TEQ. In this method toxicity equivalent factors (TEFs) are defined for each congener, expressing its toxicity relative to 2,3,7,8-TCDD, which is the most toxic congener with TEF=1.

The total toxicity equivalent (TEQ) is calculated by weighting individual PCDD/PCDF masses using the TEF values: the mass of each congener is multiplied by its TEF value, and the values obtained are added up into a single toxicity equivalent value. Of the total congeners 7 PCDD and 10 PCDF have toxicity according to the international system (Table S1–Supplementary material).

To allow comparison with other works the Word Health Organization TEF values [20] are also used in this work, which include the same 17 dioxin congeners but also dioxin-like PCB. This TEQ value is referred as WHO-2005-PCDD/PCDF-PCB-TEQ, which in this work is abbreviated to WHO-TEQ. TEF values for WHO-TEQ and for I-TEQ are practically the same (please refer to table S1), the two exceptions being 1,2,3,7,8-PeCDD (for which WHO-TEF=1 while I-TEF=0.5) and OCDD/F (for which WHO-TEF=0.0003 while I-TEF=0.001). Since PCB concentrations were not measured in the present work, WHO-TEQ values herein were calculated considering PCB concentrations to be zero. For comparison of the results in the literature with those in the present work, when values for individual congeners were not available it was considered that the I-TEQ value is approximately 10% higher than the corresponding WHO-TEQ value.

2.6 Dissolution percentage

Measurement of the dissolution of fly ash and APC residues was carried out by placing 100 g of residue in 500 mL deionised water, mixing for 2 minutes, settling for 10 minutes and then filtrating (VWR qualitative filter paper, 413, 5-13 µm). The procedure was repeated two more times and the solid material remaining after drying was compared to the initial mass.

3. Results and discussion

3.1 PCDD/PCDF in fly ash and APC residues

Mass concentrations for the 17 congeners (TM-17) in the fly ash and APC residues used in this work ranged from 4.85 to 197 ng g-1 for PCDD/PCDF, while the toxicity ranged from 0.18 to 2.0 ng g-1 I-TEQ (table 3). When changing from I-TEQ to WHO-TEQ the results were similar, with only a slight decrease (5%) for FA sample. Fly ash (FA) from the Nuuk incinerator in Greenland had PCDD/PCDF levels 15 to 40 times higher, and TEQ values 5 to 10 times higher than the APC residues. The Nuuk incinerator is an older, small-scale incineration facility, where the technology and operating conditions are quite different from the ones in large-scale Danish incinerators. Lower temperatures and consequent unstable combustion might result in the formation of products of incomplete combustion, which might be precursors for PCDD/PCDF [21]. Electrostatic precipitators represent a low cost technology, but one which might lead to the formation of PCDD/PCDF [22], especially in old MSW incinerators without control of the flue gas treatment temperature. MSW incinerators are divided into four broad classes [23] and their description and emission factors are shown in Table S2 (Supplementary material). Class 2-incinerators, such as the one from Nuuk (FA sample), have emission factors approximately 30 times higher than Class 4-incinerators, such as the ones from Denmark, and the rations obtained in the current work are in the same order of magnitude.

Table 3 – Concentration of PCDD and PCDF (ng g^{-1} and I-TEQ) in fly ash and APC residues (SD values are represented as average ± standard deviation; n= 4)

	FA	WET	SD	SD carb
2,3,7,8-TCDD	0.03	0.03	0.02 ±0.01	0.02
1,2,3,7,8-PeCDD	0.22	0.09	0.08 ±0.01	0.06
1,2,3,4,7,8-HxCDD	0.31	0.07	0.06 ±0.01	0.04
1,2,3,6,7,8-HxCDD	2.30	0.26	0.19 ±0.04	0.11
1,2,3,7,8,9-HxCDD	0.81	0.14	0.10 ±0.02	0.08
1,2,3,4,6,7,8-HpCDD	27.0	1.90	0.98 ±0.09	0.96
OCDD	98.0	5.50	1.78 ±0.32	2.20
2,3,7,8-TCDF	0.08	0.12	0.10 ±0.03	0.08
1,2,3,7,8-PeCDF	0.12	0.13	0.13 ±0.02	0.11
2,3,4,7,8-PeCDF	0.56	0.15	0.14 ±0.02	0.09
1,2,3,4,7,8-HxCDF	0.90	0.20	0.21 ±0.06	0.10
1,2,3,6,7,8-HxCDF	1.00	0.23	0.20 ±0.03	0.09
1,2,3,7,8,9-HxCDF	0.30	0.06	0.03 ±0.01	0.02
2,3,4,6,7,8-HxCDF	4.10	0.41	0.20 ±0.03	0.14
1,2,3,4,6,7,8-HpCDF	15.00	1.30	0.58 ±0.07	0.47
1,2,3,4,7,8,9-HpCDF	4.30	0.27	0.08 ±0.01	0.06
OCDF	42.00	1.60	0.32 ±0.12	0.24
Total (ng g^{-1})	197	12.40	5.19 ±0.02	4.85
Total WHO-TEQ (ng g^{-1})	1.91	0.35	0.27±0.02	0.18
Total I-TEQ (ng g^{-1})	2.01	0.35	0.27±0.02	0.18

PCDD/PCDF in the samples before and after carbonation (SD vs SD-carb) showed a reduction of 7% in the mass concentration (ng TM-17 g-1) and of 33% in the toxicity value (ng I-TEQ g-1) (Table 3). During carbonation, CO2 from the atmosphere reacts with the alkaline material in the residue, leading to a pH decrease and to the precipitation of calcite (a process that can take from several days to several thousand years). The carbonation phenomenon increases the total mass of the residue, where bound CO2 may amount to 25-50% of the initial mass of the residue [24]. This dilution effect explains the decreased PCDD/PCDF concentration in the carbonated sample (SD-carb) when compared to the non-carbonated one (SD). A similar behavior was previously reported [24], where PCDD/PCDF concentrations in carbonated APC residues decreased 5-53% when compared to similar, non-carbonated material.

The concentrations of PCDD/PCDF in the residues in the present work are in the lower range of other reported values for similar materials in the last 30 years (Figure 1). The latest values reported for PCDD/PCDF concentrations in Europe date from 2002 in the UK [24]. Data from other European countries, such as Spain, Germany, Italy, UK and Denmark (included in figure 1) are from before 2002 (compiled from [4, 6, 22, 24-26]).

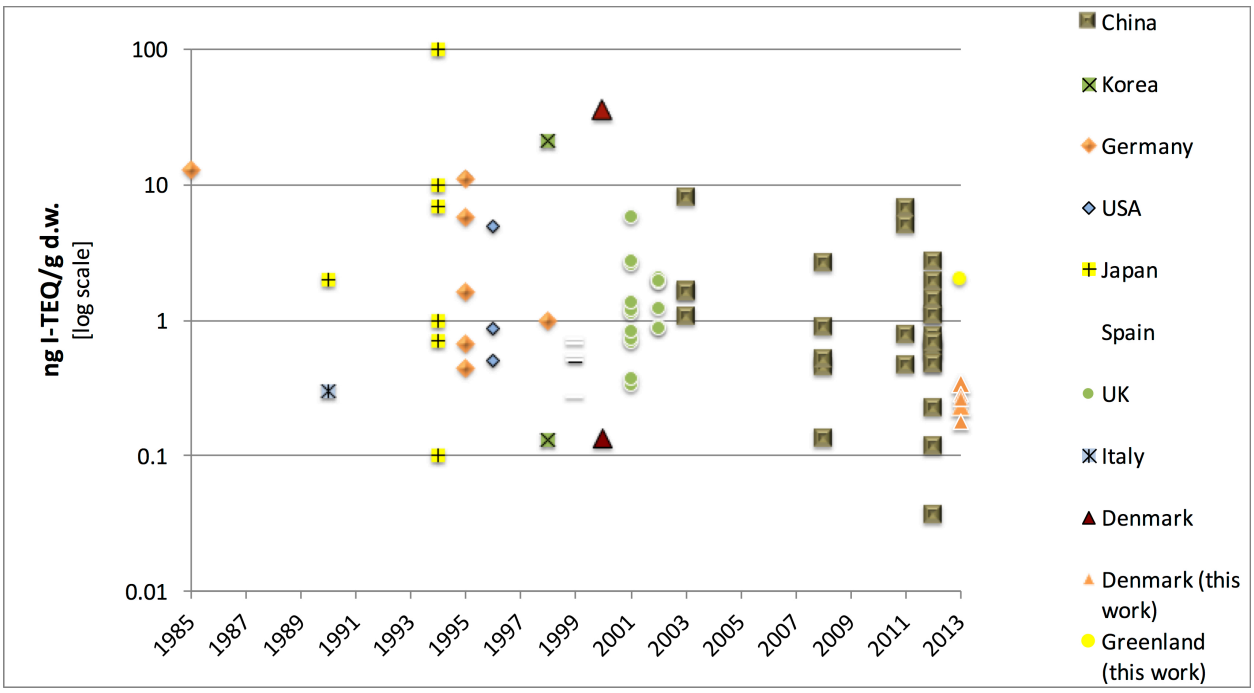

Figure 1 – Overview of PCDD/PCDF levels (ng I-TEQ g^{-1} of dry weight) in air pollution control residues from municipal solid waste incinerators

There is limited data on TEQ levels in APC and fly ash from U.S. facilities. In some cases, information exists for mixtures of fly ash/APC and bottom ash, as it is common

in the U.S. to manage these two fractions as a single material. Values for fly ash and APC residues (excluding bottom ash) date back to 1996 and range from 0.51–4.98 μg I-TEQ/kg [27].

Other countries such as Japan and Korea have also reported levels of PCDD/PCDF in fly ash and APC residues [27–28]. In 2002 the first large-scale MSW incinerator was installed in China [30] and since then most available studies on the topic refer to this country [29-31].

The evolution of PCDD/PCDF levels along time shows a reduction in the range between the highest and lowest values for the more recent data: while before the year 2000 values mostly ranged across 3 orders of magnitude, between 0.1–100 ng I-TEQ g-1, after the year 2000 the concentrations decreased 10-fold, mostly falling in the range 0.01–10 ng I-TEQ g-1. The values obtained in the current work are in the lower range of the chart: relatively low values and low variability were found in the APC residues (between 0.18–0.35 I-TEQ g-1 dry matter), while for fly ash the value was one order of magnitude higher.

3.2 Analysis of congener profiles

The relative dominance of each homologue in fly ash and APC residues is shown in figure 2. Concentrations of higher-chlorinated homologues (octo and hepta) were much higher than of lower chlorinated homologues (tetra, penta and hexa), which is in accordance with previously reported results [32]. Higher-chlorinated homologues have favorable adsorbing reactions on APC residues, and so lower chlorinated homologues escape from these residues more readily [33].

TEF values of octo-chlorinated homologues (OCDD and OCDF) are low (Table S1, supplementary material), explaining their reduced contribution for TEQ (<2%) even though their concentrations are highest in the residues. On the contrary, penta and hexa homologs are most significant for toxicity, representing between 68 and 80% of total TEQ.

Findings showed that 23478-PeCDF is the single most significant toxic congener in the three APC samples (SD; SD-carb; WET), contributing between 22% and 26% to I-TEQ.

In FA sample the 23478-PeCDF congener is 14% of TEQ, being second to 234678-HxCDF (20%). Different factors, such as operating conditions, metals present on the fly ash surface, gas composition and the type of APC devices affect the patterns of congener distribution [33].

Carbonation did not affect the congener profile, thus the profile was similar for SD and SD-carb. However, the concentration of each congener and the total I-TEQ are lower for the carbonated sample, as discussed above (section 3.1).

The ratio [PCDDs]:[PCDFs] for the residues in this work ranged from 1.6–2.5. The rate being higher than one suggests PCDD/PCDF are mainly formed through the precursor route, in detriment of the de novo synthesis [34].

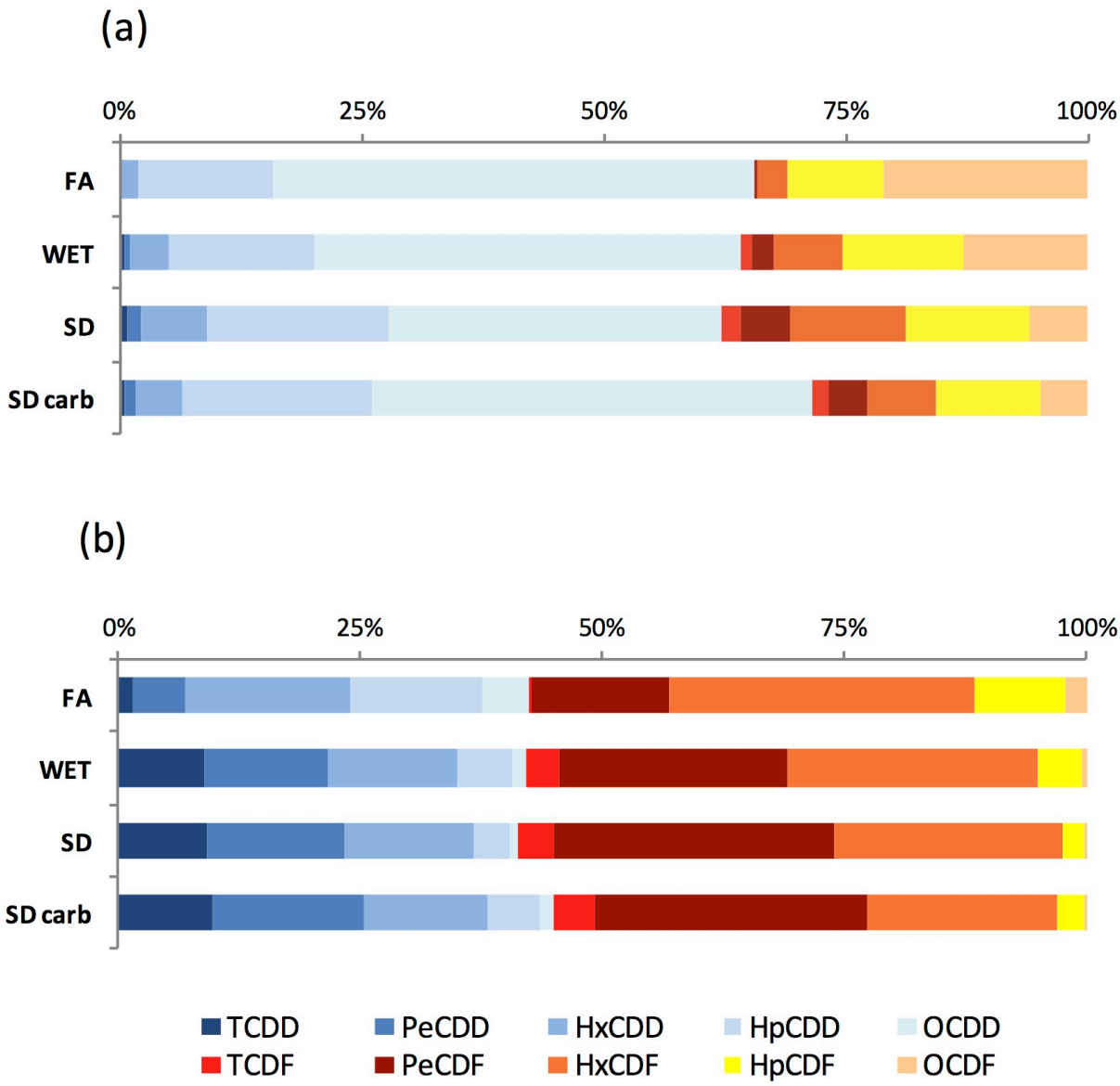

Figure 2 – Homologue's profiles (% I-TEQ) in fly ash (sample: FA) and air pollution control residues (samples: WET, SD, SD-carb): (a) % of total mass of PCDD/PCDF; (b) % of total I-TEQ

3.3 Effect of electrodialytic treatment of the levels of PCDD/PCDF in fly ash and APC residue

PCDD/PCDF levels in the residues increased 1.2 to 2.0 times after electrodialytic treatment (figure 3-a). PCDD/PCDF are synthesized in industrial-chemical processes (such as chloro-organic chemicals and the pulp and paper industries) and thermal processes [2]. High temperatures, alkaline media, UV-light, and presence of radicals favor the formation of PCDD/PCDF [2]. In thermal processes, PCDD/PCDF are formed above 250 ºC from chlorinated precursors (e.g. PCB, chlorinated phenols and chlorinated benzenes) or via de novo synthesis from the pyrolysis of unrelated compounds in the presence of chlorine and catalysts [2].

Given known synthesis mechanisms of PCDD/PCDF, and the fact that electrodialytic treatment is carried out at room temperature, we do not expect the formation of PCDD/PCDF during electrodialytic treatment, and the increase in PCDD/PCDF levels is attributed to another factor. During electrodialytic treatment the residues are suspended in an aqueous media, and soluble compounds dissolve from the waste material, being transported by the electric field away from the residues. The overall mass of the residue decreases in the process, while non-water soluble substances (such as PCDD/PCDF) did not dissolve, resulting in an enrichment (increased concentrations) in PCDD/PCDF in the waste material after treatment. Measurements of the dissolution of fly ash and APC residues in water were made for FA (34% dissolution), WET (between 12% and 19% dissolution), SD (dissolution between 7%–48%) and SD-carb (50% dissolution. Considering the dissolution results, the following enrichment factors were expected for PCDD/PCDF: 1.5x for FA; 1.2x for WET; 1.1-1.8x for SD; and 2.0x for SD-carb. Enrichment factors obtained were: 1.3x for FA; 1.4x for WET; between 1.3x and 1.7x for SD; and 2.0x for SD-carb. The percentages of material dissolving in water can explain the higher concentrations of PCDD/PCDF found after ED treatment, when compared to the original waste, and the water dissolution test can thus provide a rough indication of enrichment factors to be expected during electrodialytic treatment for PCDD/PCDF.

The variation in I-TEQ expectedly followed the increase in PCDD/PCDF concentrations (figure 3-b), from 1.3x in SD to 2.35x in SD-carb. The homolog profile before and after electrodialytic treatment did not change significantly (figure 3-c), and these findings are consistent with the increase in PCDD/PCDF levels in the treated material occurring as a result of the dissolution of soluble matter.

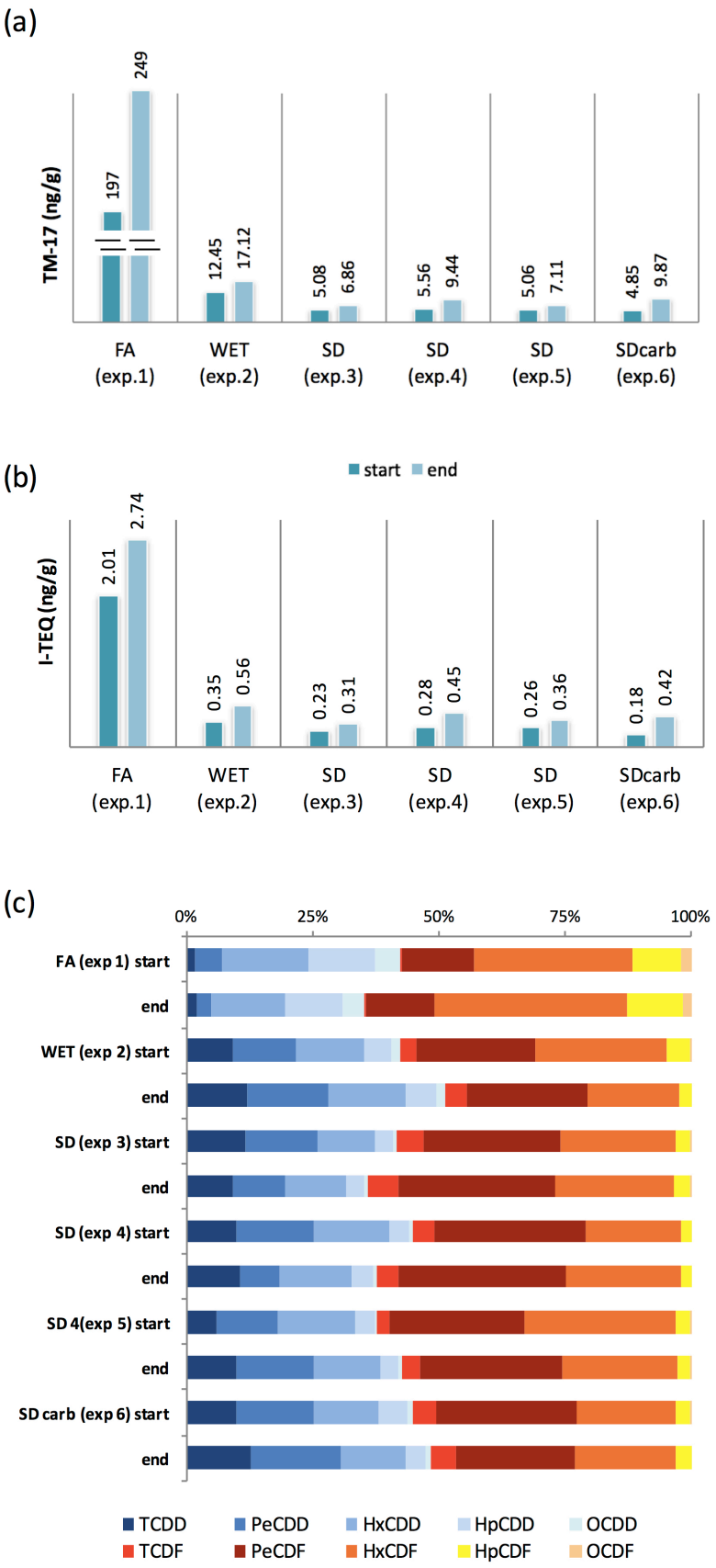

Figure 3 – Levels of PCDD/PCDF in fly ash and APC residues before and after electrodialytic treatment: (a) ng TM-17 g^{-1}; (b) ng I-TEQ g^{-1}; (c) Homologue profiles (% I-TEQ)

3.4 Impact of PCDD/PCDF concentration on the valorization of fly ash and APC residues

Several valorization options for fly ash and APC residue have been identified in the last two decades, namely cement and concrete production, road pavement, glass and glass ceramics, agriculture, stabilizing agent, adsorbent and zeolite production [7, 35]. When assessing these options, the levels of heavy metals and soluble salts have been considered, whereas PCDD/PCDF content has barely been discussed. This section discusses the impact of PCDD/PCDF concentration on the valorization options of fly ash and APC residue.

3.4.1 Legal framework on the valorization of fly ash and APC residue

Fly ash and APC residue represent a potential risk for human health due to the high levels of metals and PCDD/PCDF [6]. European Regulation (EC) 850/2004 on persistent organic pollutants (POP) addressing the environmental protection and the protection of human health states that waste containing PCDD/PCDF "shall be disposed of or recovered, without undue delay". In a recent amendment of this Regulation (Commission regulation (EU) No 1342/2014 of the 17 of December) the limit of 15 µg WHO-TEQ kg-1 is set for PCDD/PCDF in fly ash and APC residue (and other residues). The same limit also appears on the technical guidelines for management of waste containing POPs according to the Basel Convention, in which a "low in POP" waste is provisionally defined as having less than 15 µg WHO-TEQ kg-1.

Due to the current legislation, the widespread valorization of fly ash and APC residue as secondary raw material it will only be possible if end-of-waste (EoW) specifications are established. The criteria will most likely imply, among other specifications, limits on the PCDD/PCDF concentration, similarly to what already happens for EoW criteria for metal scrap (15 µg WHO-TEQ kg-1) and for compost and digestates (30 ng I-TEQ kg-1). In addition, England, Wales and Northern Ireland have defined their own criteria for poultry litter ash [36] in which PCDD/PCDF levels are set at a maximum of 20 ng WHO-TEQ kg-1.

3.4.2 Comparison of PCDD/PCDF concentration in fly ash and APC residue with regulatory values for wastes and other materials

Even if no indication exists of when (or if) European EoW for MSW incineration fly ash and APC residues will be established, it is possible for a country (or a group of countries) to develop and implement its own EoW specifications. In this respect it is of interest to know how the concentrations of fly ash and APC residues in this work

compare with some of the regulatory limits identified in the previous section for wastes and also with screening values existing for other materials. Figure 4 shows limit values for PCDD/PCDF in (i) compost/digestates in several nations, compiled from [37]; (ii) EoW criteria for compost (proposal), for metal scrap, and for poultry litter [36]; (iii) the limits in the POP directive (European Regulation (EC) 850/2004); and (iv) the values observed in this work for fly ash and APC residues before and after electrodialytic treatment.

The highest and lowest value for PCDD/PCDF concentrations differ around 3 orders of magnitude, being lower for all agriculture-related applications (10-100 ng I-TEQ kg-1 of dry weight) and higher for industrial applications such as EoW criteria for metal scrap or the value in the POP directive.

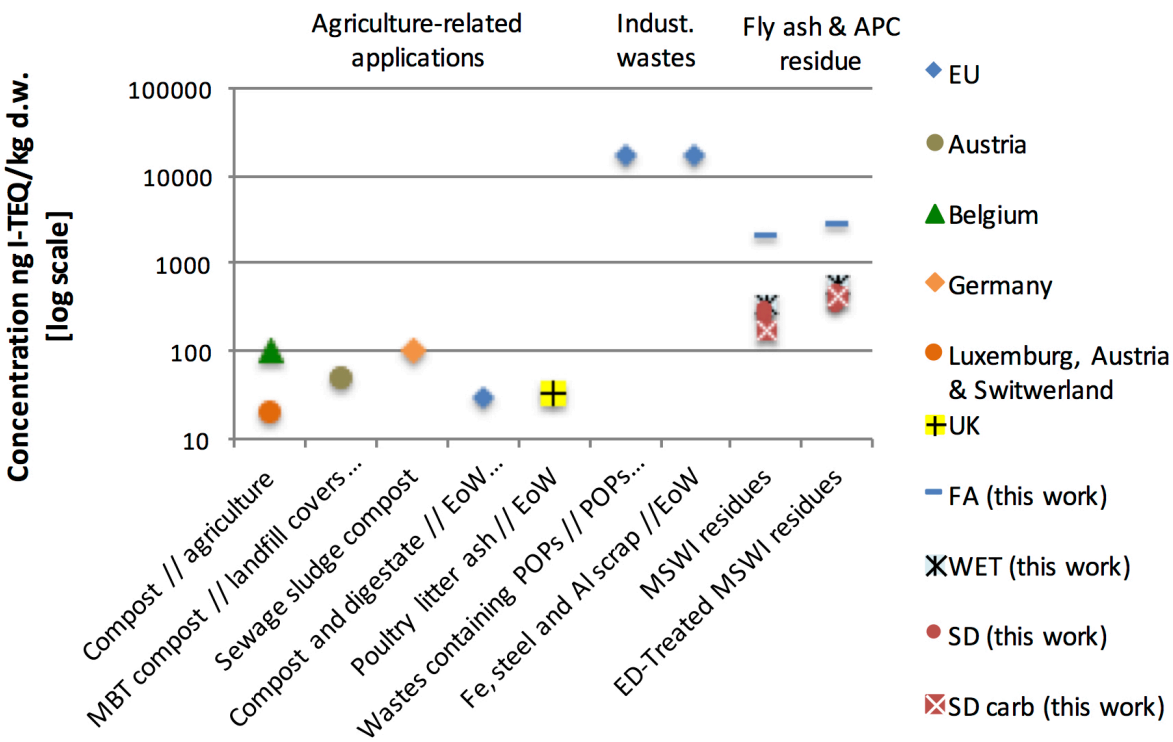

Figure 4 – Limit values for PCDD/PCDF in different materials

All 4 materials used in this work are located in the medium range, and even though electrodialytic treated materials have higher concentrations when compared to untreated, differences are not significant enough to change the relative position of fly ash and APC residues in the graph. PCDD/PCDF levels in both treated and untreated

residues are higher than those set for agriculture-related applications and lower than limits set in the POP directive or the EoW criteria for metal slag.

It is important to also take into account that when fly ash and APC residue are incorporated in other materials (e.g. construction materials) a dilution takes place and the levels of PCDD/PCDF will only be a fraction of the total in the original residues. Moreover, release of PCDD/PCDF into the environment from products incorporating residues might be considerably reduced, due to encapsulation in the new material, or else enhanced: a study by Wei et al [38] suggested that by incorporating wastes (metal slags and harbor sediments) containing PCDD/PCDF into construction materials (fired pellets) PCDD/PCDF might be destroyed if sintering occurs at 950 ºC or PCDD/PCDF might be synthesized when the sintering occurs at 1100 ºC. So it is recommended that a case by case assessment of each option is carried out by performing a risk assessment on the use of construction materials incorporating fly ash and APC residues. This assessment must necessarily include the after-life, when the construction material becomes waste again (construction and demolition waste).

4. Conclusion

It was found that fly ash from Greenland had higher PCDD/PCDF and toxicity levels than APC residues from Denmark, and this was attributed to the age and type of facility and to the flue gas cleaning process involved. All the residues had concentrations in the lower range of similar residues around the world.

After electrodialytic treatment PCDD/PCDF levels increased in the fly ash and APC residues. Synthesis of PCDD/PCDF is not expected at the conditions of ED treatment, so the increase is attributed to the dissolution from the fly ash/APC residue of the higher soluble materials, leaving behind the non-water soluble compounds, such as PCDD/PCDF. Dioxin levels before and after the electrodialytic treatment are nevertheless in the same order of magnitude. In practice, neither the original nor the treated residues can be used in a wide range of agriculture-related applications due to the high levels of PCDD/PCDF. However, according to the Basel Convention, PCDD/PCDF levels in these materials is low (<15 µg WHO-TEQ kg-1) and the fly ash and APC residue can eventually be valorized in construction materials, where the PCDD/PCDF content is further decreased due to dilution effects and where the PCDD/PCDF can become tightly encapsulated into the new construction material. However, a case by case risk assessment of each option is still required prior to setting EoW criteria for these wastes.

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