



Mass balance for POPs in a real scale fluidized bed combustor co-incinerating automotive shredder residue

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ABSTRACT

The European directive 2000/53/EC implies a “reuse and recovery” rate for end-of-life vehicles (ELVs) of 95% to be reached by the year 2015. One of the options to increase the actual average European “reuse and recovery” rate of approximately 78% (EU 15, 2008) is incineration of automotive shredder residue (ASR) with energy-recovery. The mass balance and the congener fingerprints for PCDD/Fs, dioxin-like PCBs, PCBs and PAHs in a real scale fluidized bed combustor (FBC) incinerating 25% ASR with 25% refuse derived fuel (RDF) and 50% waste water treatment sludge (WWT sludge) were investigated. The PCDD/F, dioxin-like PCB, PCB and PAH concentrations in this input waste mix were more than hundred times higher than in the usual waste feed of the incinerator (30% RDF and 70% WWT sludge). In the outputs of the FBC, however, the concentrations of these POP groups were comparable or only slightly higher than in the outputs generated during the incineration of the usual waste feed. The considered POPs in the waste were destroyed efficiently and the formation of new POPs during cooling of the flue gas appeared to a large extent independent of the POP concentrations in the incinerated waste.

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1. Introduction

In Europe (EU 15), approximately 14.4×10^6 new passenger cars are registered each year [1]. The total number of passenger cars in the EU 15 is estimated to increase from approximately 200×10^6 today to 250×10^6 in 2030 [2]. As a consequence, the yearly number of end-of-life vehicles (ELVs) is estimated to increase from approximately 11×10^6 today to 16×10^6 in 2030 [2]. In order to manage the growing amount of waste generated during the demolition of ELVs, the European parliament and council adopted in 2000 the directive 2000/53/EC. It aims at making vehicle dismantling and recycling more environmental friendly and implies minimum “reuse and recovery” and “reuse and recycling” rates of 95 and 85% respectively by the year 2015.

When in Belgium an end-of-life vehicle (ELV) is demolished by an approved center, first hazardous fluids (e.g. motor oil, gasoline and cooling liquids) and hazardous or reusable parts (e.g. batteries, catalysts and tires) are removed. The dismantled ELV is subsequently shredded and ferrous metals are magnetically removed for recycling. The remaining shredder residue is further separated

by a combination of flotation, eddy-current-separation and hand-sorting into different non-ferrous fractions, a plastic fraction and a residual mixed fraction, which is, together with the fluff collected by the air suction installation at the main shredder, referred to as automotive shredder residue (ASR) [3]. It is a heterogeneous mixture of inert and combustible materials (both representing about 50%) including plastics, glass, fabric, wood, rubber, etc. ASR accounts for approximately 10% of the initial ELV's mass and is actually sent to landfill [3]. In order to comply with the European directive on ELVs by 2015, further treatment of this ASR is necessary. A first category of ASR recovery techniques aims at increasing the recycling rate. This can be obtained by advanced mechanical separation of grinded ASR into streams with an economical interest e.g. separated plastic fibers, which can be used as dewatering agent for sludge prior to incineration. Another way to increase the recycling rate for ELVs could be the incorporation of ASR in the core of new plastic components produced by a dual-injection molding process. Also direct incorporation of ASR into concrete seems feasible for some applications such as road construction [4,5]. A second category of recovery techniques focuses on energy recovery from the combustible part of ASR. To this end pyrolysis can be applied, resulting in a combustible gas stream and a solid residue, which represents typically about 50% of the initial ASR mass [4]. Another way to recover the energy of the combustible part of ASR consists

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of co-incineration in a fluidized bed combustor (FBC) where steam and electricity are generated from the hot flue gas.

The aim of this work is to evaluate the mass balance for different persistent organic pollutant (POP) groups in such an ASR co-incineration process with energy recovery and to compare the POP masses in inputs and outputs to those obtained when the FBC is operated with usual waste feed. ASR is indeed known to contain high concentrations of PCDD/Fs, PCBs and also plasticizers such as di-2-ethylhexyl-phthalate (DEHP) [6–9].

During an 8 days trial, ASR was added to the usual waste feed of the SLECO FBC (Europe's largest FBC) for waste-to-energy conversion. The usual waste feed consists of a mix of refuse derived fuel (RDF) resulting from municipal solid waste that was biologically dried and mechanically separated, and of wastewater treatment (WWT) sludge. This study is the first of its kind where the PCDD/F, PCB, dioxin-like PCB and PAH concentrations were experimentally determined during a trial in all input and output streams. In many other papers dealing with POP mass balances, the input concentrations are taken from the literature [10–12]. Moreover, as the experiment took place in a real scale FBC, the incineration conditions and the analysed input and output streams are realistic and not e.g. artificially obtained in a laboratory scale incinerator. As all streams were sampled simultaneously under the same steady-state incineration conditions, fewer questions arise whether the input concentrations really correspond to the output concentrations. Moreover, all samples were analysed according to the same procedures and the results are expressed in the same way: all the PCDD/F and dioxin-like PCB concentrations are expressed as TEQ according to the recommendations of the WHO [13], the PCB concentration is reported as the sum of the mass of the seven Ballschmider marker PCBs and the PAH concentration is reported as the sum of the mass of the 16 EPA PAHs. The mass of PCDD/Fs, dioxin-like PCBs, PCBs and PAHs in the input (RDF, ASR and WWT sludge) is compared to the mass of these POP groups in the output (flue gas and solid residues). Additionally the PCDD/F, dioxin-like PCBs and PCB fingerprints in the ASR, RDF, WWT sludge and output streams are discussed and compared. Finally, in an attempt to estimate and compare the overall input and output of POPs – not just the different POP-groups separately – a POP-weighting methodology [12] is applied to the FBC.

The POP concentrations in the inputs and outputs are also compared to those in the inputs and outputs generated when the FBC is operated with the usual waste feed. This allows investigating the influence of the high POP concentrations in the ASR on the POP concentrations in the output.

2. Methods and materials

2.1. Experimental

2.1.1. Installation

In the FBC in which the experiment was carried out, high calorific RDF from mechanical biological treatment of municipal solid waste (MSW) affords the heat necessary for drying and incinerating low WWT sludge and for steam and electricity generation. The installation, constructed in 2005–2006 in Doel in the Flemish region of Belgium, has an annual capacity of 466×10^3 t of mixed waste, making it the largest and the most recent FBC built for this purpose in Europe. In 2008, 313×10^3 t of RDF and 134×10^3 t of WWT sludge (on average 25% dry matter) were incinerated. The FBC (see Fig. 1) is of the ROWITEC internal rotating fluid bed type in which a sand mass is fluidized by hot air. The RDF is reduced in size and iron parts are removed before it is introduced in the fluidized sand bed, together with the WWT sludge. In the freeboard, a gas temperature of at least 850°C , a residence time of at least 2 s and an oxygen

excess of at least 6% are maintained to ensure proper burn out. The energy from the flue gas is recovered in a vertical waste heat boiler. The produced superheated steam (40 bar, 400°C) is sent to a turbine (capacity of 34 MW) for electricity production. The flue gas is dedusted in an electrostatic precipitator and flows through a flue gas cleaning installation consisting of a semi-dry Circoclear reactor, a baghouse filter and a caustic soda scrubber. A mixture of clay and activated carbon particles (dioxorb) is injected in the semi-dry reactor to ensure efficient PCDD/F removal. At the bottom of the FBC, the sand and ashes are removed after which the sand is sieved and sent back into the incinerator. The bottom ashes are treated in a bottom ash recovery plant, where granulates are produced, which can be used as foundation material in road construction. The fly ash and boiler ash are used for the solidification of the flue gas cleaning residue, which is sent to a landfill, especially designed for storage of hazardous inorganic waste (class I landfill).

The average dry matter content of the RDF, ASR and WWT sludge was 90, 98 and 24%, respectively.

No significant changes had to be made to the flue gas cleaning installation during the experiment e.g. the reagent flows stayed the same.

2.1.2. Input waste streams

The RDF incinerated in the FBC is one of the remaining fractions of mechanical biological treatment of Flemish MSW. In Flanders, separate collection systems exist for organic kitchen and garden waste, glass, paper and cardboard, metal packaging (tins and cans), drink packaging and hazardous wastes (e.g. motor oil, batteries, paint, pesticides and solvents). The “residual household waste” consists mainly of non-sorted organic waste (approximately 30%), plastic packaging (approximately 15%) and paper and cardboard (approximately 10%) [14]. It is either incinerated directly, typically in a grate furnace, or first undergoes mechanical biological treatment (MBT). The MBT-process of interest here, consists of biological drying (the shredded waste is put in an insulated bunker during 1 week and is dried by the heat resulting from largely aerobic biological activity) during which the mass is reduced by 25–30%, followed by mechanical, magnetic, eddy-current and hand separation. The resulting output streams are inert materials (sand, china and glass) accounting for 10–15% of the initial waste mass, metals (5% of the initial waste mass) and RDF containing mainly plastics, paper and dried organic material (55% of the initial waste mass). The RDF “as received (AR)” has an average lower heating value (LHV) of 12 MJ/kg and can be used as fuel in different applications, such as in the FBC. A photograph of the incinerated RDF is given in Fig. 2.

The second waste stream incinerated in the FBC is WWT sludge. Approximately 270×10^3 t (dry matter) of sludge are produced in Flanders each year, approximately 37% is sewage water treatment sludge and approximately 47% is industrial WWT sludge. On average, 69% of the sludge is (co-) incinerated [15]. The sludge incinerated in the FBC mainly comes from industrial and municipal biological wastewater treatment plants. It is a mixture of dewatered and digested sludge with an average dry matter content of 24%. The average LHV (AR) of the sludge incinerated in the FBC is 2 MJ/kg.

In the framework of the European directive on ELVs (directive 2000/53/EC), the Belgian governments authorized 96 centers for depollution and demolition of ELVs. In 2008, approximately 142×10^3 ELVs were scrapped and a “reuse and recycling” rate of 90% was obtained, which puts Belgium together with Germany at the top of Europe since the average recycling rate for the EU 15 reached only 78% in 2008 [16]. On the other hand, this means that 10% of the ELV's mass is sent to landfill as ASR, representing 1.3×10^3 t in 2008 [3]. The co-incinerated ASR consists of the “heavy” ASR fraction, which is the remaining fraction after separation of ferrous, non-ferrous and plastic materials and does not

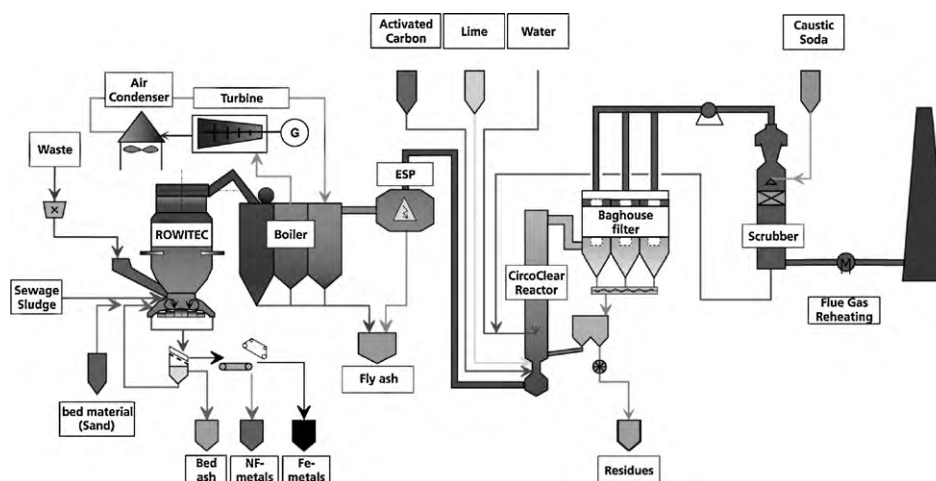


Fig. 1. Schematic representation of the FBC in which the ASR was co-incinerated.

include the fluff collected by the air suction installation at the main shredder. It contains a mixture of combustible (mainly PU-foam, plastic fibers and foil) and inert materials (sand, small stones, iron and rust particles). The ASR particle size was reduced to typically $5\text{ mm} \times 5\text{ mm}$ in order to make it suitable for injection in the FBC. The average ash content of the incinerated ASR is 53%, the average LHV (AR) is 19 MJ/kg . Fig. 3 gives a photograph of the ASR incinerated during the trial.



Fig. 2. Photograph of the incinerated RDF (the black square is $10 \times 10\text{ mm}$).



Fig. 3. Photograph of the incinerated ASR (the black square is $10 \times 10\text{ mm}$).

In order to maintain a stable temperature in the steam boiler, practice has shown that the input waste mix should have a LHV (AR) of approximately 8.5 MJ/kg . During the co-incineration experiment this was obtained by mixing 25% RDF, 25% ASR and 50% of WWT sludge (mass%). The usual waste mix of the FBC consists of 70% RDF and 30% WWT sludge (mass%).

2.1.3. Sampling and analysis

The POP-concentrations used to calculate the mass balances were determined on samples taken on site of the FBC plant during the experimental co-incineration of ASR, conducted from 17 to 24 November 2008.

The flue gas was monitored with equipment located on a measuring platform at the stack. The flue gases were sampled continuously during the 8 days of the trial using sampling equipment of the AMESA (Adsorption Method for Sampling) type, according to the EN 1948-1 standard as described in [12]. PCDD/Fs and dioxin-like PCBs were subsequently determined by a certified laboratory by GC–MS according to the EN 1948-2 standard. Clean-up for PCDD/Fs was performed using a multi-layer column of modified silica gel, followed by an aluminium oxide and activated carbon column. PCBs were cleaned-up over silica gel and analysed according to the CMA/3/I method [17]. PAHs were cleaned-up by means of a multi-layer alumina and silica gel column. The detection limits were 0.001 ng/Nm^3 for PCDD/F and dioxin-like PCBs, $0.005\text{ }\mu\text{g/Nm}^3$ for PCBs and $0.004\text{ }\mu\text{g/Nm}^3$ for PAHs. The certified laboratory had to participate regularly in government-organised inter-comparisons in order to demonstrate quality.

The different waste types incinerated in the FBC were already mixed and homogenized at the production location before they were transported to the plant. On both 18 and 20 November 2008, a representative 5-l sample was taken from each truck load of the waste streams. On each day, about 20, 25 and 50 truck loads of ASR, RDF and WWT sludge were delivered, respectively. At the end of the day, the samples of each waste stream were thoroughly mixed and shredded. Part of this shredded mixture was sent to the certified lab for analysis. In this way, the measured POP concentrations could be considered average concentrations for the wastes delivered that day. In the FBC the input wastes are thoroughly mixed and the solid residues of the combustion process are representative of this mixture. On both 18 and 20 November 2008, the residues were sampled at different times and the samples were mixed thoroughly before analysis. PCDD/Fs and dioxin-like PCBs were determined by GC–MS after soxhlet extraction according to the German AbfKlärV, Annex 1 [18]. The PCBs were analysed by GC–MS after extraction

Table 1

Overview of MRDs and potency factors used for the calculation of weighed POP masses.

	MRD ^a (mg/(kg body weight × day))	Comment
PCDD/Fs and dioxin-like PCBs	1 × 10 ⁻⁹ TEQ	TDI ^b for dioxin-like compounds with TEF-values [34]
PCBs	2 × 10 ⁻⁵	MRL ^c for chronic oral exposure to Aroclor 1254 [35]
PAHs	2 × 10 ⁻²	RfD ^d for naphthalene [36]
	3 × 10 ⁻¹	RfD ^d for anthracene [20]
Di-2-ethylhexyl-phthalate (DEHP)	6 × 10 ⁻²	MRL ^c for chronic oral exposure to DEHP [37]
	Potency factor ^e ((kg body weight × day)/mg)	Comment
PCDD/Fs and dioxin-like PCBs	1.56 × 10 ⁵ TEQ	Potency factor for exposure to dioxin-like compounds with TEF-values (EPA) [38]
PCBs	2.0	Potency factor for oral exposure to commercial PCB mixtures (EPA) [35]
PAHs	4.5–11.7	Lowest and highest reported potency factor for benzo(a)pyrene [39]
Di-2-ethylhexyl-phthalate (DEHP)	1.4 × 10 ⁻²	Potency factor for DEHP (EPA) [37]

^a MRD stands for minimal risk dose and is the estimate of the amount of a substance, expressed in mg/(kg body weight day), which can be ingested daily over a lifetime by humans without adverse non cancer health effects.

^b TDI stands for tolerable daily intake and is an MRD derived by the World Health Organisation.

^c MRL stands for minimal risk level and is an MRD derived by the American Agency for Toxic Substances and Disease Registry.

^d RfD stands for reference dose and is an MRD derived by the US Environmental Protection Agency (EPA).

^e The potency factor is the slope of the dose–response curve at low doses (linear part), expressed in (kg body weight × day)/mg.

as described in the CMA/3/I method [17]. The PAHs were analysed by HPLC–UV fluorescence after soxhlet extraction according to the CMA/3/B method [19]. DEHP was analysed by GC–MS after extraction with acetone and dichloromethane according to a method based on EPA method 606 and 8091A. The detection limits were 1 pg/g_{dw} for PCDD/F, 10 pg/g_{dw} for dioxin-like PCBs, 1 ng/g_{dw} for PCBs, 10 ng/g_{dw} for PAHs and 0.5 μg/g_{dw} for DEHP.

The POP concentrations in the solid residues generated during operation with the usual feed were determined on samples taken in August 2008. The flue gas was sampled in April 2008 for determination of the dioxin-like PCB, PCB and PAH concentration. The PCDD/F concentrations in the flue gas of the FBC are constantly monitored and reported as 15-day average concentrations. The PCDD/F concentration range used for the calculation of the weighed output in the flue gas corresponds to the minimum and maximum 15-day average concentration for 2008.

For the determination of the total PCDD/F, dioxin-like PCB, PCB and PAH concentrations, the measured concentrations of the individual congeners were added. In the calculation of the relative contribution of the individual congeners to the total concentration (fingerprint), concentrations below the detection limit were assumed zero. PCDD/F- and dioxin-like PCB-concentrations are transformed to toxicity equivalents (TEQ) using the WHO TEF values [13].

2.2. Weighing methodology

In order to compare the total amount of POPs – not just the different POP-groups separately – in the input and output of the FBC, the weighing method proposed by Van Caneghem et al. [12] was used.

To obtain the weighed POP mass in a given input (RDF, ASR or WWT sludge) or output stream (flue gas, fly and boiler ash, bottom ash or flue gas cleaning residue) “*j*”, the mass of the individual POPs “*i*”, obtained by multiplying the mass of the stream “*j*” (mass_{*j*}) with the concentration of the POP “*i*” in this stream (POP_{*i*} concentration_{*j*}), is multiplied with a POP weighing factor (POP_{*i*} weighing factor). The weighed masses of the individual POPs are then aggregated to give a POP mass for input or output stream “*j*” (POP mass_{*W,j*}) as shown in Eq. (1):

$$\text{POP mass}_{W,j} = \text{mass}_j \times \sum_i (\text{POP}_i \text{ concentration}_j \times \text{POP}_i \text{ weighing factor}) \quad (1)$$

A total weighed POP mass for input and output is obtained by adding the weighed POP masses of the different waste and output streams, respectively:

$$\text{Total POP mass}_W = \sum_j \text{POP mass}_{W,j} \quad (2)$$

The ratio of the total weighed POP mass for the input (Total POP mass_{*W,input*}) over the total weighed POP mass for the output (Total POP mass_{*W,output*}) indicates whether a waste incinerator acts as a weighed POP sink or source (see Eq. (3)):

$$\text{Ratio} = \frac{\text{Total POP mass}_{W,\text{input}}}{\text{Total POP mass}_{W,\text{output}}} \quad (3)$$

The “minimal risk dose¹” (MRD) for chronic oral exposure is used to weigh the input and output masses for a given POP; only non-carcinogenic effects are taken into account (the weighing factor in Eq. (1) is set equal to 1/MRD). This parameter was preferred because POPs resist well to biological and chemical degradation and are thus stable over time in normal environmental conditions, so chronic rather than acute exposure is the main issue in the situation considered here. Furthermore, toxicological information from the World Health Organisation and the American Agency for Toxic Substances and Disease Registry indicates that food is the primary source of human exposure for the POPs considered.

As many of the considered POPs are (suspect) carcinogenic, the “potency factor²” for oral exposure is used to weigh the POP masses, taking into account carcinogenic effects.

Table 1 gives an overview of the MRDs (expressed in mg/kg body weight day) and potency factors (expressed in (mg/kg body weight day)⁻¹) selected from the literature and applied in this study. The PCBs (expressed as the sum of 7 Ballschmutter marker PCBs) are weighed using the MRD and potency factors for exposure to the commercial PCB mixture Aroclor 1254. The 7 Ballschmutter marker PCBs represent only approximately 30% of the total PCB content of Aroclor 1254, so the PCBs are relatively underestimated in the total weighed POP input and output. MRDs are not available for all of the 16 EPA PAHs. Therefore, the PAHs are weighed using the lowest and highest MRD for individual components reported

¹ MRD stands for “minimal risk dose” and is the estimate of the amount of a substance, expressed in mg/(kg body weight × day), which can be ingested daily over a lifetime by humans without adverse non-cancer health effects.

² For oral exposure to low doses, there seems to be a linear relationship between cancer risk and dose. The potency factor is the slope of the dose–response curve at low doses, expressed in (mg/(kg body weight × day))⁻¹.

in the literature, resulting in a weighed PAH range. The lowest weighed PAH amount represents the best case, in which all the PAHs would consist of the least toxic EPA PAH for which an MRD was found in the literature (anthracene). The highest value represents the worst case in which all the PAHs would consist of the most toxic EPA PAH for which an MRD was found in the literature (naphthalene). Benzo(a)pyrene is the only PAH for which a potency factor was derived, although also e.g. benzo(a)anthracene is classified as a probable human carcinogen [20]. In order to take into account the carcinogenic effects of the PAHs, the amount in the input and output was weighed by means of the highest and lowest potency factors for benzo(a)pyrene reported in the literature. Although assuming that all the PAHs are present as benzo(a)pyrene leads to an overestimation of the share of the PAHs in the total weighed input and output, it was found important to include the carcinogenicity of PAHs.

3. Results and discussion

3.1. POP mass balance during the ASR co-incineration experiment

3.1.1. POP concentrations in the input wastes

During the 8 days trial, a mixture of 25% ASR, 25% RDF and 50% WWT sludge was incinerated in the FBC. Table 2 gives the POP concentrations in the two mixed samples of each input waste stream (see Section 2.1.3), the lowest value first.

The PCDD/F and PCB concentrations (242–329 pg TEQ/g and 13,000–15,000 ng/g respectively) in the ASR correspond well to the concentrations reported in 1998 by Sakai et al. [7] (250 pg TEQ/g for PCDD/Fs and 1800–24,000 ng/g for PCBs) although the same author reported a lower PCB-concentration range (44–270 ng/g) in 2007 [21]. Also Aae Redin et al. [9] and Börjeson et al. [8] reported the lower concentration values for PCBs in ASR.

Approximately 90% of the total PCDD/F content is accounted for by hepta- and octa-CDD; the furans represent only about 7%, with hepta- and octa-CDF being the most abundant. PCB 28 (approximately 55%), PCB 52 (approximately 15%) and PCB 101 (approximately 10%) are the main PCBs present in this waste stream.

ASR has the highest PAH concentrations of the three input waste streams, but no literature data were found for comparison. The most abundant PAHs in the analysed ASR are fluoranthene (20%), fenanthrene and pyrene (both approximately 15%), but also chrysene, benzo(a)anthracene and benzo(b)fluoranthene (each approximately 10%) are present in considerable amounts.

The dioxin-like PCB concentration in the analysed ASR is approximately 10 times higher than reported by Sakai et al. [21], but PAH concentrations reported in that work are comparable to the ones in the considered ASR. The dioxin-like PCB fingerprint is dominated by low chlorinated PCBs, PCB 105 (approximately 40%), PCB 77 (approximately 30%) and PCB 118 (approximately 20%) being most important. The DEHP concentration of 2900–8300 µg/g in the ASR appear somewhat lower than the 11,000 µg/g reported by Sakai et al. [7].

The PCDD/F concentrations in the RDF (0.954–3.92 pg TEQ/g_{dw}) are low but in line with the average concentration of 4.0 and 4.43 pg TEQ/g_{dw} reported by Hedman et al. [22] and Abad et al. [23], respectively.

The dioxin-like PCB concentration in the RDF (1.57–6.11 pg TEQ/g_{dw}) is comparable to the concentration of 2.9 pg TEQ/g reported for Japanese RDF by Ishikawa et al. [24]. The same authors [24] reported a PCB-concentration of 52.4 ng/g, which is 3–12 times lower than in the RDF considered here.

The PCDD/F and PCB concentrations in the RDF are roughly a factor 100 lower than in the ASR, the PAH concentrations are a

Table 2
POP concentrations and yearly mass flows of the wastes incinerated in the FBC.

	PCDD/Fs (pg TEQ/g _{dw})	Dioxin-like PCBs ^a (pg TEQ/g _{dw})	PCBs ^b (ng/g _{dw})	PAHs ^c (ng/g _{dw})	DEHP (µg/g _{dw})	Mass flow usual feed (t _{dw} /year)	Mass flow trial (t _{dw} /year)
RDF	0.954–3.92	1.57–6.11	170–620	5300–8400		313,185	223,704
Sludge	0.591–3.92	2.36–2.37	130–380	340–740		134,222	111,852
ASR	242–329	481–631	13,000–15,000	37,000–140,000	2900–8300		111,852
Total input co-incineration (25% ASR, 25% RDF and 50% sludge) (kg/year)	$(2.73–3.80) \times 10^{-2d}$	$(5.45–7.18) \times 10^{-2d}$	$(1.51–1.86) \times 10^3$	$(4.81–16.8) \times 10^3$	$(3.24–9.28) \times 10^5$		
Total input usual waste feed (70% RDF and 30% sludge) (kg/year)	$(3.78–13.8) \times 10^{-4d}$	$(8.08–22.3) \times 10^{-4d}$	$(6.4–20.2) \times 10^1$	$(1.71–2.73) \times 10^3$			

^a Sum of PCB 77, PCB 81, PCB 105, PCB 114, PCB 118, PCB 123, PCB 126, PCB 156, PCB 157, PCB 167, PCB 169 and PCB 189.

^b Sum of PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, and PCB 180.

^c Sum of 16 EPA.

^d Expressed in kg TEQ/year.

factor 10 lower. The PCDD/F, dioxin-like PCB and PCB fingerprints are however very similar to the ones of ASR.

The PAH concentrations in the RDF (5.3–8.4 µg/g) appear somewhat higher than reported by Moeller and Reeh [25] for composted Danish MSW (1.2 µg/g) and by Brändli et al. [26] for Swiss digested green and kitchen waste (1.45 µg/g). As in ASR, fenanthrene (approximately 30%), fluoranthene (approximately 20%) and pyrene (approximately 15%) are the most important PAHs.

The PCDD/F concentrations in the WWT sludge (0.591–3.92 pg TEQ/g) are somewhat lower than the ranges reported in the literature; e.g. 6.04–263.84 pg TEQ/g for Spanish WWT sludge of mixed urban and industrial sources [27], 9–14 pg TEQ/g for German municipal WWT sludge [28], 17.7–183 pg TEQ/g for anaerobically digested WWT sludge in the UK [29]. In contrast to the ASR and RDF, the PCDD/F fingerprint of sludge is dominated by furans (representing approximately 70% of the total PCDD/F content), with hepta- and octa-CDF being the most important congeners, indicating that WWT sludge is contaminated by other PCDD/F sources than ASR and RDF.

The dioxin-like PCB concentrations in the incinerated sludge (2.36–2.37 pg TEQ/g) are in line with reported concentrations ranging from 1.9 to 6.6 pg TEQ/g for Spanish sludge of rural, urban and industrial sources [30], 4–23 pg TEQ/g in German municipal WWT sludge [28] and 6.08–20.7 pg TEQ/g for anaerobically digested WWT sludge in the UK [29]. The difference in fingerprints with ASR and RDF is less pronounced for the dioxin-like PCBs than for the PCDD/F, also in the considered WWT sludge PCB 105 and 118 are the most abundant.

The PCB concentrations in the analysed sludge samples (130–380 ng/g) are comparable to previously reported values e.g. 3–596 ng/g for Spanish WWT sludge of mixed urban and industrial sources [27], 635 ng/g in sludge from WWT plants in the Paris region [31] and 83–277 ng/g in German municipal WWT sludge [28]. In contrast to the RDF and ASR, the PCB fingerprint of the WWT sludge is dominated by high chlorinated congeners, PCB 138 (approximately 25%), PCB 153 (approximately 25%) and PCB 180 (approximately 20%) being most abundant. As for PCDD/F this indicates a different contamination source for WWT sludge than for ASR and RDF.

The PAH concentrations in the WWT sludge (0.34–0.74 µg/g) appear somewhat lower than reported by Pérez et al. [32] (1.13–5.52 µg/g) and Abad et al. [27] (median 1.5 µg/g). Naphthalene is the only PAH present in the WWT sludge above the detection limit. The PAH fingerprint is completely different from the fingerprints for ASR and RDF, again confirming that WWT sludge is contaminated by other POP sources.

3.1.2. POP concentrations in the output streams

Table 3 gives the yearly mass flows and the POP concentrations in the two mixed samples taken from the different output streams. They are rather similar to the concentrations previously reported for a grate furnace incinerating MSW [12] except for the PCDD/F and dioxin-like PCB concentrations in the bottom ash, which are much lower for the FBC. The highest POP concentrations are found in the flue gas cleaning residue. The PCDD/F fingerprints of the flue gas, fly and boiler ash and flue gas cleaning residue are dominated by furans (mainly hepta- and octa-CDF), in contrast to the PCDD/F fingerprint of the RDF and ASR, which are dominated by dioxins. The dioxin-like PCB fingerprint of the outputs is also significantly different from the fingerprints for WWT sludge, RDF and ASR: higher chlorinated dioxin-like PCBs are more abundant. The difference in PCDD/F and dioxin-like PCB fingerprint between input and output confirms that waste incinerators destroy these POPs present in waste and that new POPs are formed during the cooling of the raw flue gases. The PCDD/F and dioxin-like PCB fingerprints of the output streams correspond well to the ones reported by Joung et al.

[33] for slag obtained by heating of char resulting from pyrolysed ASR.

From all the output streams of the FBC, only the flue gas comes directly in the environment. As mentioned above, the POPs in the other residues are landfilled in landfills specially designed to minimize environmental impact. Table 4 gives the ratio of the PCDD/Fs, dioxin-like PCBs, PCBs and PAHs mass' in the incinerated waste (25% ASR, 25% RDF and 50% WWT sludge) and the mass of these POP groups in the flue gas. The FBC co-incinerating ASR clearly is a sink of PCDD/Fs, dioxin-like PCBs, PCBs and PAHs since the input over output (only flue gas) ratios range from approximately 2000 to almost 50,000. Table 4 also gives the input over output ratios when the POP masses in all the output streams are considered. In this case, the mass of the PCDD/Fs in the input is comparable to the mass in the output. For the other POP groups the FBC is clearly a sink: the mass of dioxin-like PCBs is approximately 150–400 times higher in the output compared to the input; for the PCBs and the PAHs the input over output ratios range from approximately 5000 to 7000 and from approximately 1000 to 8000, respectively.

3.1.3. Comparison of total amount of POPs in input and output

In an attempt to compare the total amount of POPs in the input to the total amount of POPs in the output, the masses of the different POP groups are weighed according to the methodology described in Section 2.2. The range of the total weighed input POP mass is calculated according to Eqs. (1) and (2) using the toxicity data (range) given in Table 1 and the concentration ranges in Table 2. In the case of weighing with MRDs, the PCBs contribute for approximately 45% to the total weighed POP input, followed by the dioxin-like PCBs with approximately 35% and the PCDD/Fs with approximately 20%. If the potency factors are used as weighing factor in Eq. (1), the PAHs are the main contributors to the total weighed input (>50%), followed by the dioxin-like PCBs and the PCDD/Fs. The contribution of DEHP is maximum 10%. The range of the total weighed output POP mass is calculated according to Eqs. (1) and (2) using the data (ranges) given in Tables 1 and 3. For both weighing with MRDs or potency factors, the PCDD/Fs contribute for approximately 98% to the total weighed output, followed by the dioxin-like PCBs with approximately 2%. The contribution of PCBs and PAH is negligible. If in the output only the POPs in the flue gases are taken into account, the input over output ratio ranges from 9700 to 13,000 in case of weighing with MRDs and from 1800 to 21,500 when potency factors are used as weighing factors (Table 5). The FBC co-incinerating ASR clearly destroys more POPs than it emits into the atmosphere. If the POPs in all the output streams (flue gas, fly and boiler ash, bottom ash and flue gas cleaning residue) are considered, the weighed POP-input is 6–19 times higher than the weighed POP-output (see Table 5) in case of weighing with MRDs or 9–127 times higher in case of weighing with potency factors. Also in this case, the FBC co-incinerating ASR appears a weighed POP sink.

3.2. Comparison of POP concentrations in inputs and outputs during co-incineration of ASR and during incineration of usual waste feed

In Table 3, the total POP masses in the usual waste feed consisting of a mixture of 70% RDF and 30% WWT sludge are calculated. Hereby it is assumed that the concentrations determined on the RDF and sludge samples taken during the co-incineration trial are representative of the RDF and sludge usually incinerated. This is confirmed by the correspondence with the POP-concentrations reported in the literature (see Section 3.1). The PCDD/F mass in the usual waste feed is approximately 20–100 times lower than in the mix of 25% ASR, 25% RDF and 50% WWT sludge. Furthermore, the usual waste feed contains approximately 25–100 times less dioxin-like PCBs, approximately 7–30 times less PCBs and approximately

Table 3

POP concentrations and yearly mass flows of the FCB's output fractions.

	PCDD/Fs (pg TEQ/g _{dw})	Dioxin-like PCBs ^a (pg TEQ/g _{dw})	PCBs ^b (ng/g _{dw})	PAHs ^c (ng/g _{dw})	Mass flow (t _{dw} /year)
Incineration of 25% ASR, 25% RDF and 50% sludge					
Flue gas	6.7 ^d	0.649 ^d	n.d.	786 ^e	2,278,031 ^f
Fly and boiler ash	23.0–205	0.004–0.567	4.2–4.8	n.d.	52,546
Bottom ash	n.d.–0.00078	0.0101–0.0169	n.d.	10–110	38,502
Flue gas cleaning residue	797–1420	14.8–25.2	3.8–4.3	n.d.–12	12,704
Total output (kg/year)	$(1.13\text{--}2.88) \times 10^{-2g}$	$(1.90\text{--}3.56) \times 10^{-4g}$	$(2.69\text{--}3.07) \times 10^{-1}$	2.05–4.79	
Incineration of usual waste feed (70% RDF and 30% sludge)					
Flue gas	4–12 ^d	3.0 ^d	23 ^e	7350 ^e	2,278,031 ^f
Fly and boiler ash	30.5	n.d.	n.d.	n.d.	52,546
Bottom ash	0.0412	0.0216	n.d.	270	25,909
Flue gas cleaning residue	980	11.9	n.d.	36	12,704
Total output (kg/year)	1.41×10^{-2g}	1.59×10^{-4g}	5.24×10^{-2}	2.42×10^1	

n.d.: concentration below the detection limit: 1 pg/N m³ for PCDD/F; 10 pg/g_{dw} for co-planar PCBs; 1 ng/g_{dw} for PCBs; and 10 ng/g_{dw} for PAHs.^a Sum of PCB 77, PCB 81, PCB 105, PCB 114, PCB 118, PCB 123, PCB 126, PCB 156, PCB 157, PCB 167, PCB 169, and PCB 189.^b Sum of PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180.^c Sum of 16 EPA.^d Expressed in pg TEQ/N m³.^e Expressed in ng/N m³.^f Expressed in kN m³/year.^g Expressed in kg TEQ/year.**Table 4**

Mass input over output ratios for the considered POP groups.

	PCDD/Fs	Dioxin-like PCBs	PCBs	PAHs
Incineration of 25% ASR, 25% RDF and 50% sludge				
Total input/output (flue gas)	1780–2490	36,900–48,600	n.d.	2680–9360
Total input/total output	0.95–3.35	150–380	4900–6900	1000–8200
Incineration of usual waste feed (70% RDF and 30% sludge)				
Total input/output (flue gas)	14–150	120–330	1200–3900	100–160
Total input/total output	0.03–0.1	5–14	1200–3900	70–110

2–10 times less PAHs. As discussed in Section 3.1, this difference is due to the high concentration of these POPs in the ASR.

The POPs in the output were also determined during operation of the FBC with the usual waste feed. The comparison of the POP-concentrations in the outputs during usual waste feed and during co-incineration of ASR in Table 3 indicates that the higher amount of POPs in the input waste does not seem to increase the POP concentrations in the flue gas. During the co-incineration of ASR, they were in the same order of magnitude for the PCDD/Fs and even a factor 4–10 lower for dioxin-like PCBs and PAHs. In the fly and boiler ash, the concentrations of PCDD/F, dioxin-like PCBs and PCBs are higher in case of co-incineration of ASR, but the increase can be considered relatively limited given the high POP concentrations in the ASR. Also in the flue gas cleaning residue the PCDD/F and dioxin-like PCB concentrations are at most a factor 2 higher in case of ASR co-incineration. In the bottom ash generated during the experiment with ASR, the dioxin-like PCB and PAH concentrations are approximately a factor 2 lower than in “usual” bottom ash. The PCDD/F concentrations are unexpectedly low in the “ASR” bottom ash; the PCB concentrations were under the detection limit in both incineration scenarios. The PCDD/F and dioxin-like PCB fingerprints of the

output streams were very similar to the ones of the output streams in case of usual RDF and WWT sludge incineration.

For PCDD/Fs and dioxin-like PCBs it can be concluded that, although the total input mass is significantly higher during co-incineration of ASR, the mass in the output is comparable to the mass in the output generated during the incineration of the usual waste feed. During the co-incineration experiment, the mass of PCBs is at least 500 times higher in the input but only approximately 10 times higher in the output compared to usual waste feed incineration. Although the mass of the PAHs is significantly lower in the RDF-sludge mix, the mass of this POP group is higher in the output compared to the output generated during co-incineration of ASR.

Also for the FBC incinerating the usual waste feed, the POP masses were weighed and aggregated in an attempt to compare the total amount of POPs in the input to the total amount of POPs in the output for both incineration scenarios. During the co-incineration of ASR, the total weighed POP output was on average a factor of 1.3–1.4 times higher (for weighing with MRD and potency factor, respectively) than during usual working conditions, where the weighed POP input was on average 6–27 times higher. These fig-

Table 5

Weighed POP input over output ratios.

	Weighing with (1/MRD)	Weighing with potency factor
Incineration of 25% ASR, 25% RDF and 50% sludge		
Total input/output (flue gas)	9700–13,000	1800–21,500
Total input/total output	5.6–19	9.1–127
Incineration of usual waste feed (70% RDF and 30% sludge)		
Total input/output (flue gas)	120–740	40–420
Total input/total output	0.31–0.97	3.2–14

ures confirm that, for the considered waste mixtures, POPs in the waste were destroyed during incineration and that the formation of new POPs during the cooling of the flue gas was to a large extent independent of the POP concentrations in the incinerated waste.

3.3. POP mass balance during the incineration of usual waste feed

The mass of the PCDD/Fs in the usual waste mix is approximately 14–150 times higher than in the flue gas generated at its incineration (see Table 4). For the dioxin-like PCBs, the PCBs and the PAHs, the input over output (flue gas) ratios are even higher, indicating that the FBC emits significantly less POPs in to the atmosphere than there are present in the RDF-sludge waste mix. The total PCDD/Fs mass in all the output streams appears up to approximately 10 times higher than the PCDD/Fs mass in the waste mix (70% RDF and 30% WWT sludge). But for the other POP groups considered, the total mass in the output streams is significantly lower than the mass in the waste mix: the input over output ratios range from approximately 100 to 4000. As already mentioned in Section 3.2, the masses of the four considered POP groups were multiplied with a weighing factor and aggregated in both inputs and outputs. If, during operation with usual waste feed, in the output only the POPs in the flue gases are taken into account, the weighed POP input over output ratio equals 120–740 for MRD-weighing and 40–420 for weighing with potency factor (see Table 5). If the POPs in all the output streams are taken into account, the MRD-weighted POP-input appears about equal to the output; if the POPs are weighed with potency factors, the input can be considered equal to or in the best case approximately 10 times higher than the output. If potency factors are used as weighing factors (considering only cancer effects), it seems justified to consider the FBC a weighed POP sink.

4. Conclusions

The concentration range of PCDD/Fs, dioxin-like PCBs, PCBs and PAHs was determined in multiple samples of the input and output streams (flue gas, fly and boiler ash, bottom ash and flue gas cleaning residue) of Europe's largest FBC during co-incineration of 25% ASR with 25% RDF and 50% WWT sludge. It appeared that for the four POP groups considered, the mass in the input waste mix was several thousand times higher than the mass emitted into the atmosphere. If the PCDD/Fs in all the output streams were considered, this mass is comparable to the PCDD/F mass in the input waste mix. For the dioxin-like PCBs, PCBs and PAHs, the total mass in all the output streams is still significantly lower than in the input. In order to compare the total amount of POPs in the input and output, the masses of the individual POP groups were weighed with a factor based on MRDs or cancer potency factors and aggregated. The total amount of weighed POPs in the input appeared 6–130 times higher than in the output.

Due to the high POP concentration in the ASR, the mix of 25% ASR, 25% RDF and 50% WWT sludge contained significantly higher concentrations than the usual waste feed consisting of 30% RDF and 70% WWT sludge. When the POP masses in the output of the FBC generated during the two incineration scenarios were compared, only the PCB mass was higher during ASR co-incineration. The increase was however limited and lower than the increase in the waste mix due to the presence of ASR. When the masses of the POPs were weighed and aggregated, the total POP input appeared on average a factor 6–27 higher in case of ASR co-incineration for weighing with MRDs and potency factors, respectively. On the other hand, the weighed POP output was only slightly higher in case of ASR co-incineration (on average a factor 1.4–1.3 for weighing with

MRDs and potency factors, respectively). In general, it could be concluded that POPs in the waste were destroyed during incineration and the formation of new POPs during the cooling of the flue gas seemed to a great extent independent from the POP concentrations in the incinerated waste.

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