The presence, emission and partitioning behavior of polychlorinated biphenyls in waste, leachate and aerosols from Norwegian waste-handling facilities

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HIGHLIGHTS

- Despite the 1980s phase out, PCBs are still found in plastic waste in the mg/kg range.
- Waste recycling in Norway leads to environmental emissions of PCBs.
- Particles in leachate exhibit PCB partitioning similar to waste on site.
- Air emissions of PCB are mostly in the gas-phase, BFRs in the particle-phase.
- Air PCB concentrations in Norwegian and Chinese WEEE facilities are comparable.

GRAPHICAL ABSTRACT

ABSTRACT

Even though production and open use of polychlorinated biphenyls (PCBs) have been phased out in Western industrialised countries since the 1980s, PCBs were still present in waste collected from different waste handling facilities in Norway in 2013. Sums of seven indicator-PCBs (I-PCB$_7$: PCB-28, -52, -101, -118, -138, -153 and -180) were highest in plastic waste (3700 $\pm$ 1800 µg/kg, n=15), waste electrical and electronic equipment (WEEE) (1300 $\pm$ 400 µg/kg, n=12) and fine vehicle fluff (1800 $\pm$ 1400 µg/kg, n=4) and lowest in glass waste, combustibles, bottom ash and fly ash (0.3 to 65 µg/kg). Concentrations in leachate water varied from 1.7 to 2900 ng/L, with higher concentrations found at vehicle and WEEE handling facilities. Particles in leachate water exhibited similar PCB sorption properties as solid waste collected on site, with waste-water partitioning coefficients ranging from 10^5 to 10^7. I-PCB$_7$ in air samples collected at the sites were mostly in the gas phase (100–24000 pg/m^3), compared to those associated with particles (9–1900 pg/m^3). In contrast, brominated flame retardants (BFRs) in the same samples were predominantly found associated with particles (e.g. sum of 10 brominated diethyl ethers,

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ΣBDE_{10}, associated with particles 77–194,000 pg/m^3) compared to the gas phase (ΣBDE_{10} 6–473 pg/m^3). Measured gas-phase I-PCB$_7$ concentrations are less than predicted, assuming waste-air partitioning in equilibrium with predominant waste on site. However, the gas-particle partitioning behavior of PCBs and BFRs could be predicted using an established partitioning model for ambient aerosols. PCB emissions from Norwegian waste handling facilities occurred primarily in the form of atmospheric vapor or leachate particles.

1. Introduction

Polychlorinated biphenyls (PCBs) are among the initial "dirty dozen" substances regulated under the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2001) because they are persistent, bioaccumulative, toxic, prone to long-range transport and pose a potential risk to environmental and human health. PCBs were extensively produced in major industrialized countries as technical mixtures from ~1930 until 1994. During this time >1.3 million tonnes were produced, with peak production occurring around 1970 (Breivik et al., 2007). The cumulative historical consumption in Norway has been estimated at 1307 t (Miljødirektoratet, 2010). PCBs proved to be versatile chemicals and therefore found use in a large variety of applications. However, concerns about the potential environmental hazards emerging first in the late 1960s eventually terminated the usage of PCBs within applications where there was no or limited possibility for recollection. For example, open usage such as in plastics as plasticisers and flame retardants, within carbonless copy paper and several other such applications ended within the member countries of the Organisation for Economic Co-operation and Development (OECD) by 1973 (de Voogt and Brinkman, 1989). Usage of PCBs within closed electrical systems, such as capacitors and transformers, however, was discontinued later than open usages (Breivik et al., 2002). A characteristic feature of the historical use pattern of PCBs is its application in many long-lived products, including building materials like paints (Jartun et al., 2009), sealants (Kohler et al., 2005), as well as electrical equipment. Storage of obsolete equipment may further delay recycling and disposal (Saphores et al., 2009). For example, small capacitors containing PCBs, which were used in cars and various electrical household appliances (Harrad et al., 1994), have an estimated average use-life expectancy of about 10 to 15 years, with larger electrical equipment (larger capacitors and transformers) of up to 30 years (NTIS, 1972). For PCBs used in closed electrical systems, significant releases may not occur as long as the electrical equipment is kept intact during use or storage, but rather occur if those systems are improperly managed at the waste and recycling stage, as is evident from elevated emissions at informal e-waste recycling areas within developing regions (Han et al., 2010; Breivik et al., 2011). In the case of PCBs in building materials, the potential for continued releases call for even longer time perspectives (Bergsdal et al., 2014). These persistent PCB emission sources have the potential for continued and/or intermittent releases up to decades after the production peaked (Diamond et al., 2010).

Tracking release from historic use is complicated by the fact that there are additional primary PCB sources which may not reflect past production, but rather unintentional formation (de novo synthesis) (Zhang et al., 2015). This is also reflected in the Stockholm Convention, which lists PCBs in Annex C as among the chemicals which may be formed and released unintentionally from anthropogenic sources. PCBs are known to be released from various thermal processes, which in some cases can be influenced by the fuel involved itself being contaminated by PCBs (Kocan et al., 1991; Liu et al., 2013). In such cases, both unintentional formation and decomposition during thermal processes may occur simultaneously (Ishikawa et al., 2007). More recently, a number of studies also report that some PCBs are unintentional by-products from manufacturing of pigment (Grossman, 2013; Hu and Hornbuckle, 2010) as well as polymer resins (Herkert et al., 2018), which in turn may have implications for relevant waste streams.

Hence, how various materials and wastes that contain PCBs are being recycled and/or disposed of is likely to remain an issue for contemporary waste management strategies now and well into the future (Bergsdal et al., 2014). Even though new uses of PCBs were banned in Norway in 1980, there are still approximately 100 t of PCB estimated to be present in products and building structures (Miljøstatus, 2018). The PCB problem may not be solved without a better understanding of the occurrence and fate of PCBs during recycling and disposal.

In this work, the fate of PCBs was studied at 12 different sites throughout Norway and compared with that of the brominated flame retardants (BFRs) at the same facilities reported previously (Morin et al., 2017). Whereas atmospheric concentrations of BFRs were higher at WEEE/vehicle collecting facilities (e.g. total air concentration of the sum of 10 brominated diethyl ethers, Σ BDE$_{10}$, of 9000–195,000 pg/m^3) compared to incineration and landfilling facilities (80–90 pg/m^3), leachate concentrations were not significantly different between these facilities (ranging from 1 to 3500 ng/L). Samples were collected over a period of one year using both active and passive sampling techniques. Concentrations in solid waste handled at the facilities were measured along with air and leachate concentrations. These data were in turn used to quantify the partitioning behaviour of PCBs between waste, leachate and aerosol particles present at these sites. This study tested the following hypotheses: (a) waste handling facilities are inherently contaminated by PCBs, thereby contaminating waste sorted for recycling and the environment around the waste-handling facility, (b) the fate and transport of PCBs released to air and leachate water is affected by particulate matter generated from the waste, (c) the fate and transport behavior from waste handling facilities of PCBs deviates from that of BFRs.

2. Materials and methods

2.1. PCBs investigated

The analysis was limited to seven indicator congeners I-PCB$_7$, that were 2,4,4′-trichlorobiphenyl (PCB-28), 2,2′,5,5′-tetrachlorobiphenyl (PCB-52), 2,2′,4,5,5′-pentachlorobiphenyl (PCB-101), 2,3′,4,4′,5-pentachlorobiphenyl (PCB-118), 2,2′,3,4,4′,5′-hexachlorobiphenyl (PCB-138), 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB-153), and 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (PCB-180). Their physical-chemical properties are given in the supplementary information (Table S1a). Historically, I-PCB$_7$ are associated with past production of technical PCB mixtures that were sold under different trade names (e.g. Aroclor and Clophen) and are therefore considered suitable in the context of this study. These I-PCB$_7$ are also those selected by the International Council for the Exploration of the Sea (ICES) for monitoring purposes in the marine environment, due to their historical use and also their range of molecular weights and potential for direct identification and quantification in gas chromatograms (Webster et al., 2013).

2.2. Field work and waste sample collection

A large range of waste types and waste handling processes were investigated. In total, twelve waste-handling facilities, located in South-Eastern Norway, were sampled over a year (June 2013–June 2014) during two or three sampling campaigns at each site (June–October 2013, October–December 2013 and March–June 2014). Two facilities were

combustible incinerators (referred to as Incineration/Sorting facility A-B), three were landfills (referred to as Landfill A-C) and seven were WEEE and/or vehicle sorting facilities (referred to as WEEE/Vehicle A-E; only five unique locations are considered here as two WEEE/Vehicle sorting facilities are in close proximity, share water drainage and spread air emissions to each other). All landfills contained municipal and industrial waste but varied with respect to the processing of special types of wastes (bottom ash, fly ash and WWTP sludge digestate). At each site, solid waste fractions, as well as leachate water and air samples were collected. Prior to sampling, each solid waste fraction had already been crushed and/or filtered to a specific size fraction and placed in bins or piles by the waste-handling facility. Between 4 and 12 kg of each solid waste fraction was collected randomly from different bins or piles so that they were visually homogeneous and representative of a particular waste fraction. This sample was then further blended and homogenized in the lab, before 20–400 g of the homogenized sample was ground using various methods until they could pass through a 2 mm or 4 mm sieve. Details regarding the field work and sample preparation have been presented previously (Morin et al., 2015; Okkenhaug et al., 2015; Morin et al., 2017), and further descriptions are provided in Table S1b.

2.3. Derivation of waste-water partition coefficients

To address the mobility of the contaminants contained in the waste, a batch leaching test was performed to determine waste-water partition coefficients K_{waste}:

$$K_{waste} \ (L/kg) = C_{waste}/C_{water} \qquad (1)$$

where C_{waste} and C_{water} are the waste concentration (μg/kg) and the freely-dissolved water concentration (μg/L) at equilibrium. Note that "freely-dissolved" refers to molecules solvated by water and not associated with suspended solids, colloids or dissolved organic carbon (DOC). K_{waste} was determined using a standard method for metals in waste materials (EN 12457), changing the shake time duration from 1 day to 28 days to ensure equilibrium and using polydimethylsiloxane (PDMS) tubes (AM Systems Inc., Carlsborg, USA, wall thickness 65 μm) to quantify C_{water}. 28 days of equilibration was deemed to be sufficient time for 2- to 6-ring PAHs by Hawthorne et al. (2011a) when using a polymer with slower uptake kinetics than PDMS (Nam et al., 2016). To perform this experiment, 0.5–2 g of ground solid sample (≤ 4 mm) and 0.1 g of pre-cleaned PDMS tubes, were shaken for 28 days at room temperature with pre-extracted distilled water at a liquid-to-solid weight ratio, L/S, of 10, in a varying number of replicates (SI Table S2a). Afterwards PDMS tubes were removed and cleaned. The C_{PDMS} was quantified following the procedure described in Section 2.8 and previously for BFRs (Morin et al., 2017), and the C_{water} was then determined using K_{PDMS} values from the literature available in Table S1a. In addition, the amount of PCB leached from the waste fraction by dissolution, $C_{leachable}$ (μg/kg dw), was calculated (Eq. 2).

$$C_{leachable} = C_{water} \cdot L/S \qquad (2)$$

2.4. Leachate water samples

Leachate water was sampled on-site using both grab and active sampling. Grab samples were obtained by immersing a pre-sterilized 1 L green-tinted glass bottle in leachate water, either in an open stream or inside a manhole. The bottles were wrapped in aluminium foil and transported at 4 °C to the laboratory. After adding approximately 2 g of sodium azide (Sigma Aldrich, St. Louis, USA) to prevent microbial degradation, samples were stored at 4 °C until analysis (between 6 and 12 months after collection). Passive samples were obtained by deploying pre-cleaned PDMS tubes mounted within a permeable stainless-steel housing in the same leachate water as the grab samples

but left undisturbed to equilibrate for 2 to 3 months. Upon retrieval, they were rinsed with a few mL of milli-Q water to remove surface particles, wrapped in aluminium foil, transported at 4 °C to the laboratory, and stored at −20 °C until analysis. Further details regarding the leachate samples, as well as further description of kinetic uptake rates of PCBs into the PDMS passive samplers are provided in the SI.

2.5. Air samples

Samples of both ambient and indoor air were collected at the waste handling facilities using active and passive sampling techniques. Active sampling of both particle- and gas-phase compounds was performed in selected facilities using a high-volume (HighVol) air sampler (Digitel, Switzerland) over periods of 1 to 7 days. Sampling was typically done at an anticipated local hotspot such as close to a shredder, waste sorter, loading dock or in a central location. The HighVol was equipped with a PM_{10} cut-off, a 150 mm diameter glass fibre filter (GFF filter, Sigma Aldrich, USA) for collecting compounds associated with aerosol particles, and a polyurethane foam plug (PUF filter, Sunde Søm & Skumplast A/S, Norway) downstream of the GFF for collecting vapours. GFF filters were pre-cleaned with cyclopentane, followed by baking at 350 °C. The PUF was pre-cleaned by Soxhlet extraction with toluene (Halse et al., 2011), then double wrapped in aluminium foil and stored in low-density polyethylene bags until use. The HighVol air sampler had a flow rate of approximately 500 L/min. and was operated for 1 to 7 days. Any decreases in the flowrate over time due to filter loading were recorded automatically by the instrument, along with the total volume of air sampled corrected to standard temperature and pressure, V_{air}. The PM_{10} (μg$_{particles}$/m$^3_{air}$) was determined using this volume and the difference in the dry weight of the GFF filter before (M_{filter}) and after sampling (M_{sample}):

$$PM_{10} = (M_{sample} - M_{filter})/V_{air} \qquad (3)$$

The average dry weight of particles was ca. of 18% the filter weight (i.e. 0.33 g on a 1.85 g filter).

Atmospheric passive sampling of gas-phase compounds was conducted by deploying XAD-2-resin containing passive air samplers (Wania et al., 2003). Pre-cleaned XAD-2 beads (Supelco, Bellefonte, USA) were placed in a stainless-steel wire mesh tube (10 cm height, 2 cm diameter), enclosed in a protective stainless-steel housing designed to minimize particle deposition to the XAD resin (Wania et al., 2003). Passive samplers were exposed for 2 to 3 months at several locations in each facility (covering both ambient and indoor air, either near or further away from assumed point sources). The uptake rates in XAD-2 passive samplers are somewhat dependent on wind speed and compound diffusivity, which varies with molecular size and temperature. Based on an earlier calibration of the sampler for PCBs in ambient air (Armitage et al., 2013), a sampling rate of 0.5 m^3/day was applied for all congeners at both ambient and indoor locations. Although sampling rates indoors may be lower due to lower wind speeds, all indoor locations in this study were heavily ventilated. In some cases, the passive samplers were positioned nearby the HighVol samplers. One additional location was chosen to represent an urbanised area: the rooftop of the Norwegian Geotechnical Institute (NGI) in Oslo. Given the building was constructed in the 1960's the use of PCBs in construction materials cannot be excluded, it is therefore considered a "positive urban blank" rather than a "reference field blank". Upon retrieval, both active and passive air samples were wrapped in aluminium foil and transported at 4 °C to the laboratory where they were stored at −20 °C until analysis.

2.6. Chemicals

Acetone (HPLC grade), methanol (HPLC grade) and dichloromethane (analytical reagent grade) were purchased from Fisher Chemical

(Hampton, USA). Toluene ("for analysis of dioxins, dibenzofurans and PCB" grade) and n-hexane (Chromasolv for HPLC) were obtained from Sigma-Aldrich (St. Louis, USA).

2.7. Analytical standards

Analytical standards of each I-PCB$_7$ were purchased from Wellington Laboratories (Guelph, Canada) and used for calibrating the GC–MS method. The internal standards, purchased from Cambridge Isotope Laboratories (CIL, Tewksbury, USA) and the recovery standard (hepta-PCB 188) were ^{13}C labeled and identical with the native compounds.

2.8. Sample preparation

For analysis of dissolved organic carbon (DOC), subsamples were filtered through a 0.45 mm polyethersulfone membrane fitted to high density polypropylene syringes (VWR, Norway), and analyzed with a Shimadzu TOC-5000 analyzer (Okkenhaug et al., 2015). Grab water samples were filtered through 90 mm diameter glass microfiber filters (GF/B, Whatman, Little Chalfont, UK) followed by 0.45 μm nylon membrane filters (Sartorius, Goettingen, Germany) to collect the particles. The filtrate was passed through SPE disks (ENVI-18 Disk, Supelco, Bellefonte, USA) to collect the dissolved compounds of interest for PCB analysis.

All samples, including the loaded filters and SPE disks from the grab water samples, underwent pressurized liquid extraction (PLE) with a Dionex ASE 350 (Sunnyvale, USA). Toluene was heated to 130 °C under a pressure of 1700 psi. The heat up time was 7 min, static time was 3 min, the flush was set at 100% and the N$_2$ purge was 1 min. Each extraction included 3 cycles.

All PLE extracts underwent the same procedure. Between 0.1 and 100% of extract (due to a broad range of concentrations) was sampled and spiked with 40 μL of the internal standard solution as well as 100 μL of tetradecane as keeper (Fluka). 7 g of activated copper (Sigma-Aldrich) was added to the extract of the sludge digestate samples only for the reduction of sulfur. Extracts, reduced to approximately 1 mL using a rotary evaporator followed by N$_2$ purge, were eluted through a multi-layer column (3 g of KOH-silica, 1.4 g of activated silica, 4 g of 40% (w/w) H$_2$SO$_4$ silica and 3 g of Na$_2$SO$_4$, packed with glass wool at the bottom) with 2 washings with 50 mL of n-hexane. The eluate was rotary-evaporated followed by spiking with 40 μL of the recovery standard solution and finally evaporated under a gentle stream of N$_2$ so that the keeper was the only solvent left.

2.9. GC–MS analysis, quality assurance and control

PCBs were identified and quantified using isotopic dilution on a gas chromatograph 6890N (Agilent, Santa Clara, USA) coupled to an Autospec-Ultima mass spectrometer (Waters Corporation, USA). The chromatographic column used was a J&W fused silica capillary column DB-5 ms (Agilent) (60 m × 0.25 mm × 0.25 μm). All PCB analyses were conducted in an accredited lab for PCB analysis in abiotic, biotic and incineration samples (Umeå University). Glassware was rinsed in a laboratory dishwasher, washed with acetone and heated at 550 °C. The samples were spiked before clean-up with internal standards (IS) and all the results were recovery corrected. Both field blanks and/or laboratory blanks for the air and water samples were used to check for potential contamination. Fontainebleu sand (VWR, Sweden) was used as method blank for solid waste analysis. During a GC–MS sequence, potential signal drift was taken into account and solvent blanks were systematically analyzed in order to check for analytical contamination. Further details of the GC–MS method, including quality assurance and control protocols (e.g., IS recoveries and blank values for each type of samples), can be found in the SI-Section 3.

2.10. Data handling and statistical analysis

Handling and visual inspection of the data were performed using Microsoft Excel 2013. Statistical analysis including principle component analysis (PCA) of the PCB congener patterns was carried out using R Studio version 1.1.463.

3. Results and discussion

3.1. Solid and water leachable waste concentrations

Fig. 1 shows the total concentration in different categories of solid wastes and their leachable amounts of I-PCB$_7$ (panel A). The leachable waste concentrations were determined by equilibrium passive sampling using PDMS tubes thereby representing the freely-dissolved fraction (i.e. the fraction not associated with particles or DOC). The respective congener distribution in the different waste fractions is shown in panel B. The exact values measured in each sample as well as the annual mass of each waste produced in Norway can be found in Table S2a in the SI, with additional congener specific information in Table S2b–c.

PCBs were present in all waste streams, with the highest levels associated with plastics. The highest I-PCB$_7$ concentrations were found in plastic waste (3716 ± 1776 μg/kg, n = 15), WEEE (1283 ± 391 μg/kg, n = 12) and vehicle fluff waste ($C_{TotalFineVehicle,I-PCB7}$ = 1764 ± 1410 μg/kg, n = 4; $C_{TotalCoarseVehicle,I-PCB7}$ = 558 ± 296 μg/kg, n = 5). The sources of this pollution may be mixing with older waste, cross contamination at the facility (e.g. small PCB-containing capacitors/transformers might not have been sorted out well) or via recycling of PCB contaminated plastic from e.g. cables. Elevated concentrations of PCBs in WEEE/Vehicle waste indicates a long life-time expectancy of the original products handled at these facilities (Breivik et al., 2016). Despite PCBs being phased out in new applications since the late 1970s, electrical components, like capacitors might be a "stored" source of pure PCB fluids that can take a long time to dissipate or be completely disposed of by a society. Lower concentrations of PCBs were measured in combustibles ($C_{TotalCombustibles, I-PCB7}$ = 65 ± 4 μg/kg, n = 2), bottom ash ($C_{TotalBottomAsh, I-PCB7}$ = 28 ± 34 μg/kg, n = 2), digestate ($C_{TotalDigestate, I-PCB7}$ = 21 ± 2 μg/kg, n = 2), glass ($C_{TotalGlass, I-PCB7}$ = 0.7 ± 0.2 μg/kg, n = 4) and the lowest in fly ash ($C_{TotalFlyAsh, I-PCB7}$ = 0.3 ± 0.8 μg/kg, n = 6; though if one outlier is removed 0.004 ± 0.002 μg/kg, n=5). The PCB concentrations are similar in the combustible and bottom ash fractions suggesting that during incineration PCBs are destroyed to an extent that is similar to the reduction in solid mass.

Reports on PCB concentrations in solid waste are scarce compared to the number of studies dealing with PCB levels in environmental compartments (air, soil, water/leachate). Sakai et al. (1998) found 1200 μg/kg sum of all PCBs in Japanese electrical waste, comparable to this study of Norwegian waste sampled in 2013. However, for Japanese cars shredded in the 1990s, Sakai et al. (1998) quantified concentrations that were generally higher: 1200–24,000 μg/kg than what we report here. Japanese automotive shredder residues from 2007 contained concentrations between 44 and 270 μg/kg sum of all PCBs (Sakai et al., 2007) which is at the low end of the concentrations found in Norwegian coarse vehicle fluff here, sampled in 2013. Collectively this indicates that the concentrations of PCBs in Japanese car waste have decreased dramatically from the 1990s to 2000s. At the time of the present sampling campaign, the average age of cars sent to scrapping in Norway was 18.1 years (SSB, 2013), meaning they were constructed in 1995. However, some older cars or other discarded equipment containing PCB, such as capacitors, will intermittently be blended in, appearing in both the WEEE and Vehicle waste shredder residues. Though the exact sources of these PCBs are difficult to ascertain, we hypothesize that their presence in these blended plastic waste, WEEE and vehicle fluff is due to the mixing of old and new waste, both in the facilities and in our sampling campaign.
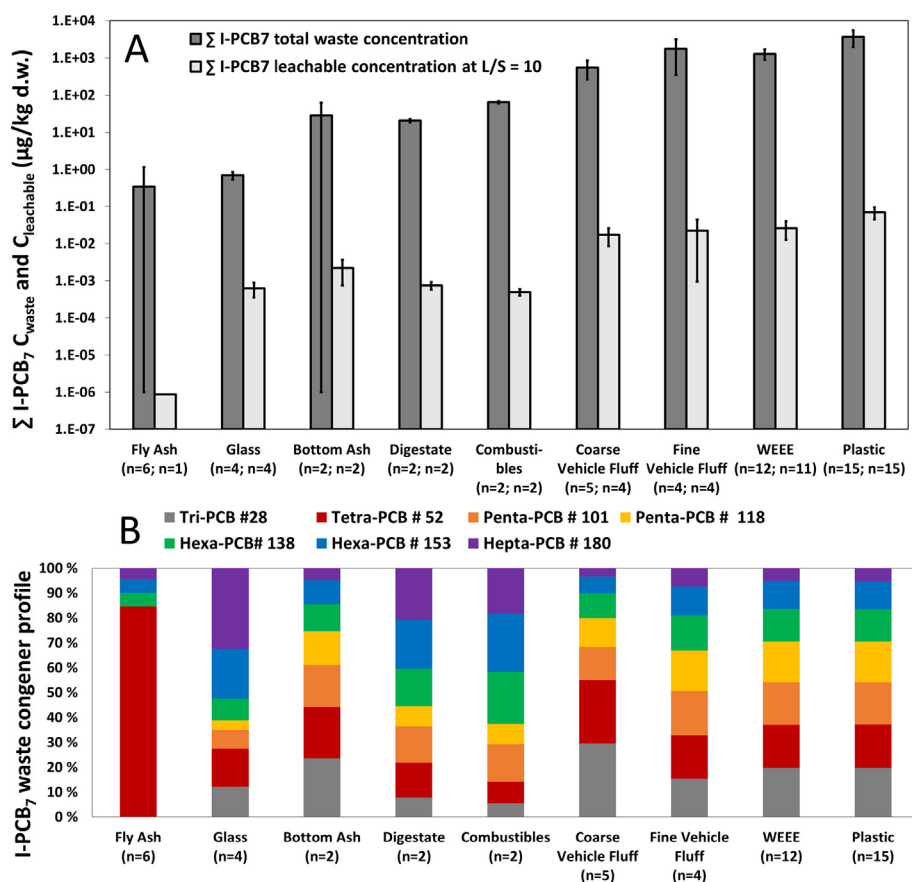
Fig. 1. (A) Total and water leachable fractions of the I-PCB$_7$ in different waste materials. (B) Congeneric composition of the I-PCB$_7$ in the different waste materials. The results presented for each category are weighted-averages based on the annual mass produced in Norway (SI Table S2a).

Sakai et al. (2007) quantified relatively high concentrations of sum PCBs in fly ash compared to this study: 22 μg/kg vs 0.3 μg/kg, respectively. Even though they quantified the sum of all PCBs compared to 7 PCB congeners in this study, this difference is surprisingly high. Especially if one outlying point is removed from the fly ash data as the average concentration is then 0.004 ± 0.002 μg/kg. This outlier may suggest that there are substantial variations in fly ash samples, possibly due the type of incineration plant and the sampling location within the incinerator chimney.

The PCB congener composition was similar for the plastic, WEEE, vehicle waste fractions and even bottom ash (Fig. 1, panel B). However, the congener pattern of fly ash is dominated by PCB-52, perhaps because de novo formation during incineration cannot be excluded (Jiang et al., 2015). Sakai et al. (2007) indicated that numerous PCB congeners can be formed during incineration. Combustible and digestate waste have a similar congener composition with a bias toward heavier congeners compared with the plastic dominated fractions. The congener pattern in glass is different than in any other waste fraction. The PCBs are most likely not coming from the glass itself but from bottle labels and potentially the ink used in these labels (Grossman, 2013). However, the presence of highly chlorinated PCBs (e.g. PCB-180), which are not typically found in pigments, also indicates cross-contamination from other waste streams.

The visual comparison of congener patterns presented above were confirmed by a principal component analysis (PCA), in which individual samples were plotted according to their PCB profile and waste category (Fig. S1). Most of the samples grouped according to their waste category indicating that I-PCB$_7$ profiles are waste type specific. Principal component 1 (PC1, X-axis) explained 44% of the variance in the dataset and is dominated by PCB 28 with positive loadings and PCB 153 with negative

loadings. PC2 (Y-axis) explained 35% of the variance. The most important compounds in PC2 are PCB 101 and 118 with positive loadings and PCB 52 and 180 with negative loadings. Compared to the other samples, PCB profiles of plastic, bottom ash, vehicle fluff and cable samples group closely together. The PCB profile in these samples cannot be directly explained with a specific PCB production mixture but shows a close resemblance with the congener distribution in the estimated historic global production of the I-PCB$_7$ congeners; PCB-28: ~24%, PCB-52: ~16%, PCB-101: ~13%, PCB-118: ~18%, PCB-138: ~11%, PCB-153: ~12%, PCB-180: 6%, relative to the sum I-PCB$_7$ (Breivik et al., 2007).

3.2. Waste-water partitioning

The fraction of the total I-PCB$_7$ solid content that is leachable is very similar between the PCB rich-waste fractions (plastic, WEEE, vehicle fractions) and the digestate (0.001 to 0.004%). The leachable fraction in the bottom ash is at least twice as high (0.008%) while the opposite is true for combustibles (0.0008%). Glass has the highest leachable fraction (0.09%) supporting the idea that PCBs in glass waste is primarily a results of surface contamination. No conclusion could be made for fly ash as only one sample had both solid and leachable concentrations above the LOQ.

Waste-water partitioning coefficients K_{waste} obtained from the leaching experiments (Table 1) indicate that the more chlorinated the PCB, the higher the K_{waste}, which infers reduced leachability. The values of log K_{waste} (L/kg) for the glass fractions (3.1–5.8) were lower than those for combustibles (4.4–7.3), digestate (4.7–7.1), plastic, WEEE (excluding the sub-fraction "Remains/Metal") and vehicle fluff (5.1–7.1). Log K_{waste} for bottom ash (4.0–6.7) and the WEEE sub-fraction "Remains/Metal" (4.2–6.4) were in an intermediate range. There was

Table 1
Waste-water partitioning coefficients (log K_{waste}) for the I-PCB$_7$ and different waste fractions analyzed in this study. ND indicates that PCB concentrations in the leachate were below the LOQ (where no error is indicated only single samples were analyzed).

		Tri-PCB #28	Tetra-PCB #52	Penta-PCB #101	Penta-PCB #118	Hexa-PCB #138	Hexa-PCB #153	Hepta-PCB #180
		Log K_{waste}	Log K_{waste}	Log K_{waste}	Log K_{waste}	Log K_{waste}	Log K_{waste}	Log K_{waste}
		(L/kg)	(L/kg)	(L/kg)	(L/kg)	(L/kg)	(L/kg)	(L/kg)
Glass	**All glass**	**3.3 ± 0.2**	**3.7 ± 0.2**	**4.3 ± 0.1**	**4.2 ± 0.1**	**5.0 ± 0.3**	**5.4 ± 0.1**	**5.7 ± 0.0**
Vehicle	Coarse fluff	5.1 ± 0.3	5.7 ± 0.2	6.4 ± 0.1	6.3 ± 0.1	7.0 ± 0.2	6.9 ± 0.2	7.1
	Fine fluff	5.1 ± 0.3	5.7 ± 0.3	6.5 ± 0.3	6.3 ± 0.2	7.1 ± 0.3	7.2 ± 0.2	7.1 ± 1.2
	All vehicle fluff	**5.1 ± 0.5**	**5.7 ± 0.3**	**6.4 ± 0.3**	**6.3 ± 0.3**	**7.0 ± 0.4**	**7.1 ± 0.2**	**7.1 ± 1.2**
WEEE	Remaining plastic	5.1 ± 0.2	5.6 ± 0.2	6.3 ± 0.1	6.2 ± 0.4	6.9 ± 0.5	7.0 ± 0.2	7.1 ± 0.0
	BFR plastic	5.2 ± 0.2	5.6 ± 0.4	6.5 ± 0.3	6.6	ND	7.0	6.9 ± 0.8
	Cable plastic	5.5	5.8	6.4	6.1	6.8	6.8	6.4
	Remains/metal	4.2 ± 0.2	4.6 ± 0.2	5.3 ± 0.3	5.3 ± 0.2	6.0 ± 0.2	6.0 ± 0.2	6.4 ± 0.1
	All WEEE	**5.0 ± 0.3**	**5.4 ± 0.5**	**6.1 ± 0.5**	**6.1 ± 0.4**	**6.7 ± 0.3**	**6.6 ± 0.5**	**6.7 ± 0.7**
Plastic	Packaging plastic	5.1 ± 0.2	5.6 ± 0.2	6.3 ± 0.1	6.2 ± 0.4	6.9 ± 0.5	7.0 ± 0.2	7.1
	Composite, non WEEE and vehicle	5.1 ± 0.2	5.6 ± 0.2	6.3 ± 0.1	6.2 ± 0.4	6.9 ± 0.5	7.0 ± 0.2	7.1
	Composite, WEEE and vehicle	5.1 ± 0.3	5.7 ± 0.2	6.4 ± 0.1	6.2 ± 0.3	6.9 ± 0.2	6.9 ± 0.2	7.0
	All plastic	**5.1 ± 0.4**	**5.6 ± 0.4**	**6.4 ± 0.2**	**6.2 ± 0.6**	**6.9 ± 0.9**	**6.9 ± 0.4**	**7.1 ± 0.1**
Combustibles	Coarse in Norway	5.0 ± 0.1	5.6 ± 0.1	6.5 ± 0.0	6.2 ± 0.1	7.1 ± 0.2	7.2 ± 0.1	7.3 ± 0.3
	Fines in Norway	4.4	5.0	5.8	5.6	6.5	6.5	6.9
	All combustibles in Norway	**4.7 ± 0.5**	**5.3 ± 0.4**	**6.1 ± 0.5**	**5.9 ± 0.4**	**6.8 ± 0.4**	**6.9 ± 0.5**	**7.1 ± 0.3**
Bottom ash	Coarse	4.0 ± 0.2	4.4 ± 0.1	5.2 ± 0.1	5.3 ± 0.2	5.8 ± 0.1	5.9 ± 0.1	6.0 ± 0.1
	Fine	4.8 ± 0.1	5.1 ± 0.2	5.8 ± 0.1	5.8 ± 0.2	6.4 ± 0.2	6.5 ± 0.2	6.7 ± 0.2
	All bottom ash	**4.4 ± 0.3**	**4.8 ± 0.2**	**5.5 ± 0.1**	**5.5 ± 0.3**	**6.1 ± 0.2**	**6.2 ± 0.2**	**6.3 ± 0.2**
Fly ash		ND	ND	ND	ND	ND	ND	ND
Landfill	**Digestate**	**4.6 ± 0.3**	**5.1 ± 0.2**	**5.9 ± 0.2**	**5.7 ± 0.3**	**6.6 ± 0.3**	**6.7 ± 0.2**	**7.1 ± 0.2**

insufficient data to report a K_{waste} for fly ash. In summary, plastic rich waste fractions have higher K_{waste} and glass waste fractions the lower K_{waste} values, likely due to absorption into the matrix occurring in the former and only adsorption to the outer surface (including labels) occurring in the latter. However, the reason why combustibles and digestate have log K_{waste} as high as plastic waste is less clear; but these fractions could both contain strong sorbents, such as soot, plastics and refractory organic carbon (Cornelissen et al., 2005).

3.3. Waste facility leachate concentrations

The concentrations of I-PCB$_7$ were measured in leachate water collected at various landfills and WEEE/Vehicle sorting facilities (Fig. 2). Panel A presents the total water sample concentrations and the filtered leachate concentrations for the I-PCB$_7$. Panel B presents the relative contributions of each congener in the total leachate samples. Raw data of the exact concentrations of each congener are reported in Table S3a–h.
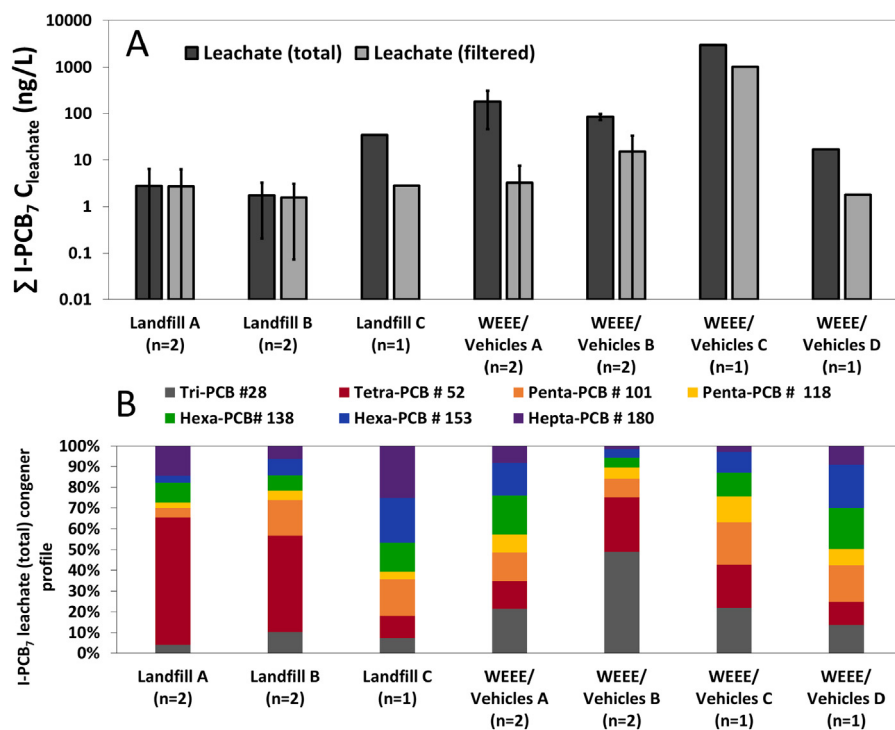

Fig. 2. PCB concentrations (total and filtered) in leachate water sampled at various landfills and WEEE/Vehicle sorting facilities. Panel A) I-PCB$_7$, Panel B) Congeneric composition of the I-PCB$_7$ in the total water sample.

The I-PCB$_7$ total leachate concentrations varied from 1.7 ng/L to 2942 ng/L. The lowest and highest concentrations were measured at Landfill B and WEEE/Vehicle C, respectively (Fig. 2 panel A). These concentrations overlap with the ones found in the batch leaching test with solid waste samples from these facilities. Landfill B processes municipal waste and fly ash, while WEEE/Vehicle C also contains a high content of plastic-rich waste. The landfill concentrations (1.7–34.8 ng/L) overlap with the low end of the range of WEEE/Vehicle concentrations (17–2942 ng/L). A concentration of 68 ng/L for the sum of all PCB congeners in water from a leaching test with automobile shredder residue (i.e. fluff) is in the same range as these values for WEEE/Vehicle waste (Sakai et al., 1998). Also comparable with these values are concentrations of I-PCB$_7$ between 40 and 75 ng/L in water from two wells at Norwegian municipal landfills (Cornelissen et al., 2009). On the other hand, very high I-PCB$_7$ values have been reported in the leachate from Portuguese landfills of 713–2098 ng/L (Herbert et al., 2006), overlapping with the high end of our study. Even higher values of 770,000 ng/L have been reported in a Malaysian landfill (Yusoff et al., 2013), which is much higher than observed here.

For all leachate samples in this study, except landfills A and B, the filtered dissolved concentrations were substantially lower than the total concentrations indicating that PCBs are mainly sorbed to suspended solids in the leachate water. Cornelissen et al. (2009) indicated that PCBs in landfill wells were mainly sorbed to dissolved organic matter and particulate matter (80–99.9%). Moreover, the dissolved fraction is dominated by congeners with a lower degree of chlorination (landfill A, landfill B, WEE/Vehicle B, SI Table S3a–h). The PCB congener composition in the total water sample at the WEEE/Vehicle facilities (Fig. 2B) resembles that observed in plastic rich solid waste fractions (Fig. 1B), except for the WEEE/Vehicle B where PCB-28 and -52 dominate. This indicates that little fractionation of PCBs according to their solubility has occurred suggesting that the leachate water composition is dominated by suspended solids with a similar PCB pattern as the original waste. Landfills A and B have a large contribution of PCB-28 and -52 (57–65% of I-PCB$_7$) while leachate from Landfill C is dominated by the heavier PCBs (PCB-138, -153 and -180 comprise 61% of I-PCB$_7$).

The number of leachate samples at individual waste handling facilities was limited, typically to just 1 to 2 samples (Table S1c), as the sampling campaign was more focused on comparing concentrations at different facilities and studying the partitioning behavior in these facilities than studying contaminant dynamics in a particular facility. Therefore, the influence of fluctuations in leachate concentrations through the year, as well as the reproducibility of the obtained measurements is not represented. These initial results should therefore be interpreted with these considerations in mind.

3.4. Particle-dissolved phase partitioning in leachate water

Filtered water samples and passive water samplers are compared in Fig. S2 in the SI. While the former includes PCBs associated with colloidal and DOC fraction smaller than 0.45 μm, the latter represents just the freely-dissolved fraction not associated with any colloids or DOC. For the most water-soluble PCB-28, the concentrations are similar, except at the WEEE/Vehicle C facility. When all I-PCB$_7$ are included, concentrations measured with passive samplers are lower than in the filtered grab samples. This is expected based on previous studies of PCB contaminated sites, showing substantial fractions of PCBs are associated with colloids and dissolved organic matter (Hawthorne et al., 2011b).

It is possible to calculate the particle-water partitioning coefficient in leachate K$_D$ (L/kg) from the collected data (SI Table S3a–h). In order to derive the concentration in the filtered suspended solids (C$_{leachate\_SS}$ in μg/kg$_{ss,dw}$), this can be done by subtracting the concentration in the filtered (>0.45 μm) leachate (C$_{leachate,filtered}$) from that in unfiltered leachate (C$_{leachate,total}$), and divide by the mass of suspended solids in the

leachate (SS$_{leachate}$ kg$_{dw}$/L)) according to Eq. (3a):

$$C_{leachate,SS} = (C_{leachate,total} - C_{leachate,filtered})/(SS_{leachate}) \quad (3a)$$

Alternatively, we can combine the PDMS-derived freely-dissolved leachate concentration (C$_{leachate,PDMS}$), with measurements of SS$_{leachate}$ and DOC concentrations (kg/L), according to Eq. (3b):

$$C_{leachate,SS+DOC} = (C_{leachate,total} - C_{leachate,PDMS})/(SS_{leachate} + DOC) \quad (3b)$$

For clarity, PCBs associated with DOC are included in C$_{leachate,filtered}$ but not in C$_{leachate,PDMS}$. K$_D$ can then be derived via either Eqs. (4a) or
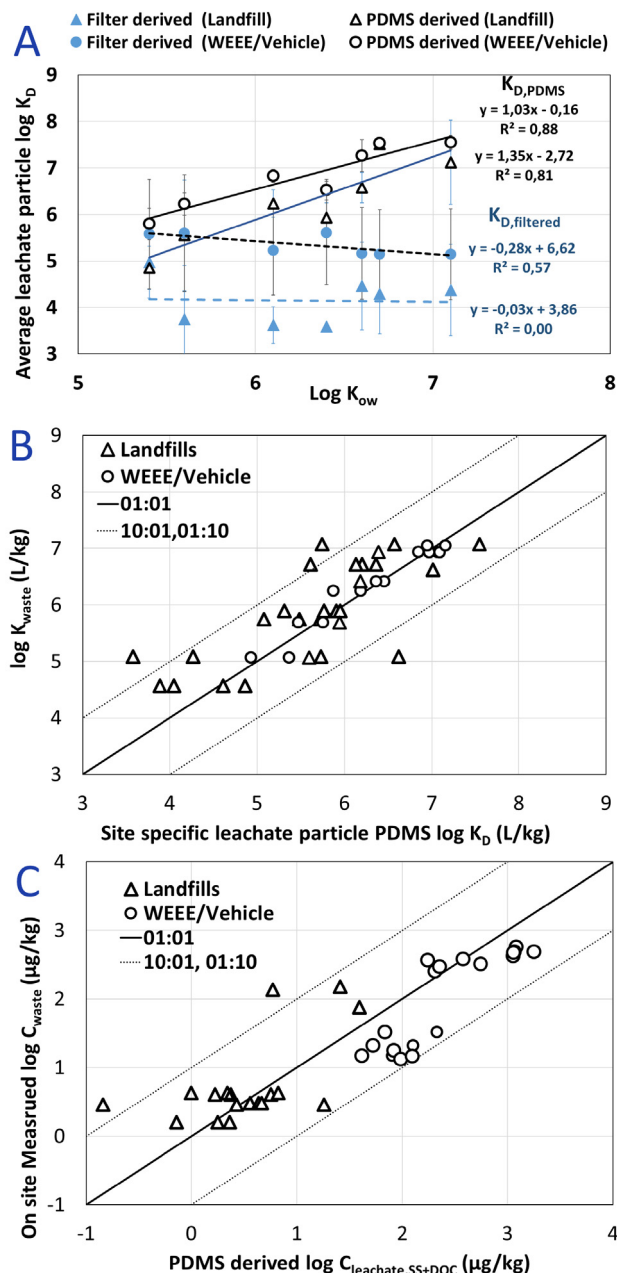

Fig. 3. A) Comparison of log K$_D$ (average of K$_{D,filtered}$ and K$_{D,PDMS}$) vs log K$_{ow}$ for different types of sites; B) Comparison of partitioning into the dominating waste type K$_{waste}$ found at a specific waste facility (from Table 1) with K$_{D,PDMS}$; C) Comparison of measured C$_{waste}$ found at a given waste handling facility vs predicted values based of C$_{leachate\_SS+DOC}$ using PDMS data (Eq. (3b)).

(4b).

Filtered water : $K_{D,filtered} = C_{leachate,SS}/C_{water,filtered}$

Passive sampler : $K_{D,PDMS} = C_{leachate,SS+DOC}/C_{water,PDMS}$ (4b)

The average log $K_{D,filtered}$ and $K_{D,PDMS}$ for each PCB congener is plotted against its log K_{ow} in Fig. 3A, with raw data presented in Table S4a–b. The data have been divided into samples taken at landfills and WEEE/Vehicle facilities, respectively. $K_{D,PDMS}$ values increase with K_{ow} while the opposite is true for $K_{D,filtered}$ values. This is accountable by considering that PCBs associated with small colloids and DOC are measured in $C_{leachate,filtered}$ but are not taken up by the passive samplers ($C_{leachate,PDMS}$). Hence it appears that $K_{D,PDMS}$ is a more reliable indicator of partitioning in leachate, but some caution is needed as the heaviest PCBs may not be at equilibrium with the PDMS passive sampling material within the timeframe of the sampling (as elaborated in the SI-Section S2).

$K_{D,PDMS}$ values from field sites are compared in Fig. 3B with the average K_{waste} value from Table 1 that best represents the waste at that site used. For example, for a landfill with bottom ash as the dominant waste type, the K_{waste} for bottom ash is plotted against the $K_{D,PDMS}$; or for a WEEE/Vehicle site, the K_{waste} for plastics at WEEE/vehicle locations are plotted against $K_{D,PDMS}$ for leachate. As is evident in Fig. 3b, $K_{D,PDMS}$ and K_{waste} for the dominant waste type agree with each other within a

factor of 10, suggesting that the partitioning behavior of leachate particles is similar to that of the dominant waste fraction at a facility.

The good correlation between K_{waste} and $K_{D,PDMS}$ (Fig. 3B) supports the hypothesis that the fate and transport of PCBs released to leachate water is dominated by particulate matter generated from the waste. In order to further demonstrate this, C_{waste} values for the most dominant waste fractions at a specific site were compared to $C_{leachate,SS+DOC}$ at the same site in Fig. 3C, for all of the PCBs. C_{waste} and $C_{leachate,SS+DOC}$ are generally within a factor 10 of each other. Hence, it can be concluded from the available data that the concentrations and partitioning behaviour of PCBs to particles in leachate from waste-handling facilities is similar to the concentrations and partitioning to waste being handled at the facility, supporting the earlier notion that the PCB-contaminated particulates that dominate leachate may be generated from the waste itself. We caution that this conclusion is based on a limited number of data points and specific locations. Also, results for higher molecular weight PCBs are uncertain due to slower (de)sorption kinetics, both for waste and the PDMS samplers (see the SI Section 2).

3.5. Waste facility air concentrations

Ambient and indoor air concentrations of I-PCB$_7$ measured in single samples at the various landfills and WEEE/Vehicle sorting facilities are shown in Fig. 4; raw data are presented in Table S5a–d. The following types of concentration are reported: concentrations of PCBs in the gas phase, $C_{air,gas}$ (pg/m^3), which is measured by both active sampling (PUF samples) and passive sampling (XAD-2 samples); concentrations
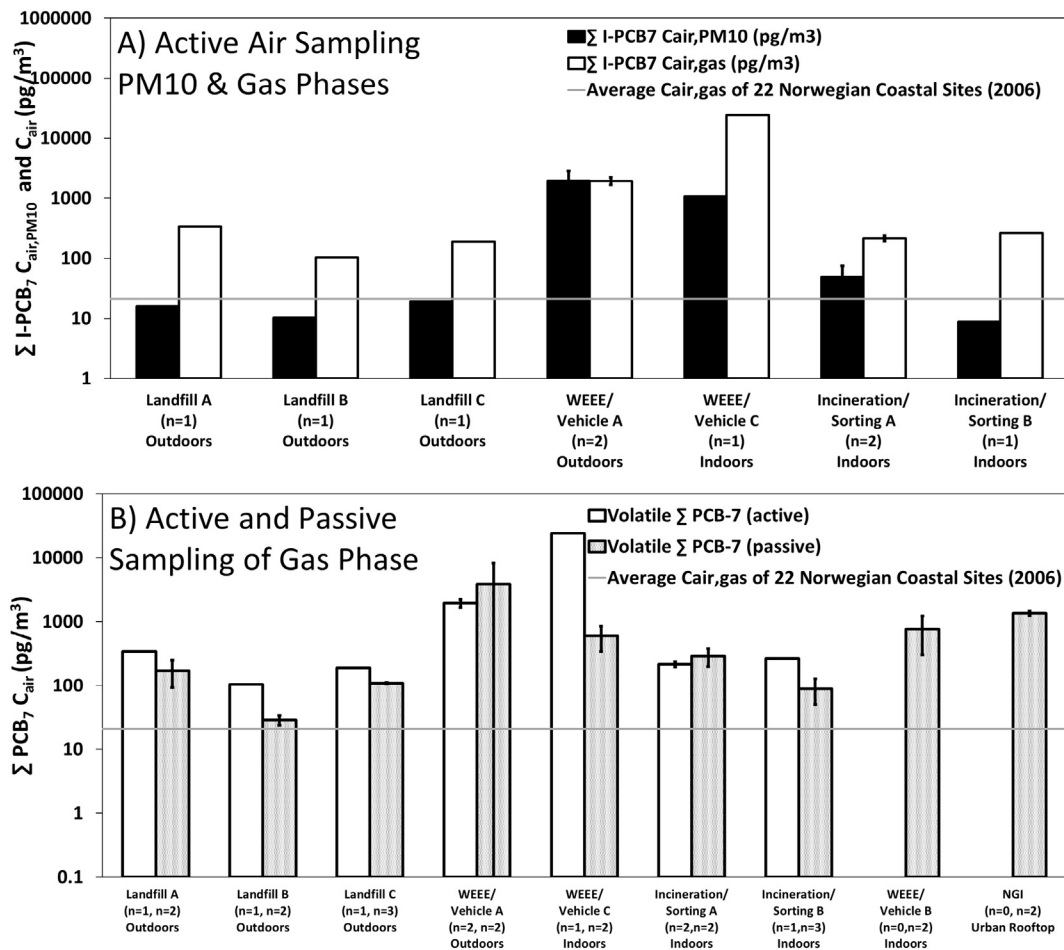

Fig. 4. Concentrations of Σ I-PCB$_7$ in air samples in waste handling facilities compared with outdoor concentration of 21 ± 17 pg/m^3 observed as an average of 22 coastal Norwegian sites, including cities sampled in 2006 (Halse et al., 2012). Panel A) PCB concentration in air associated with PM$_{10}$ particulate matter and in gas phase from active sampling, Panel B) comparison of gas phase concentrations from active and passive sampling.
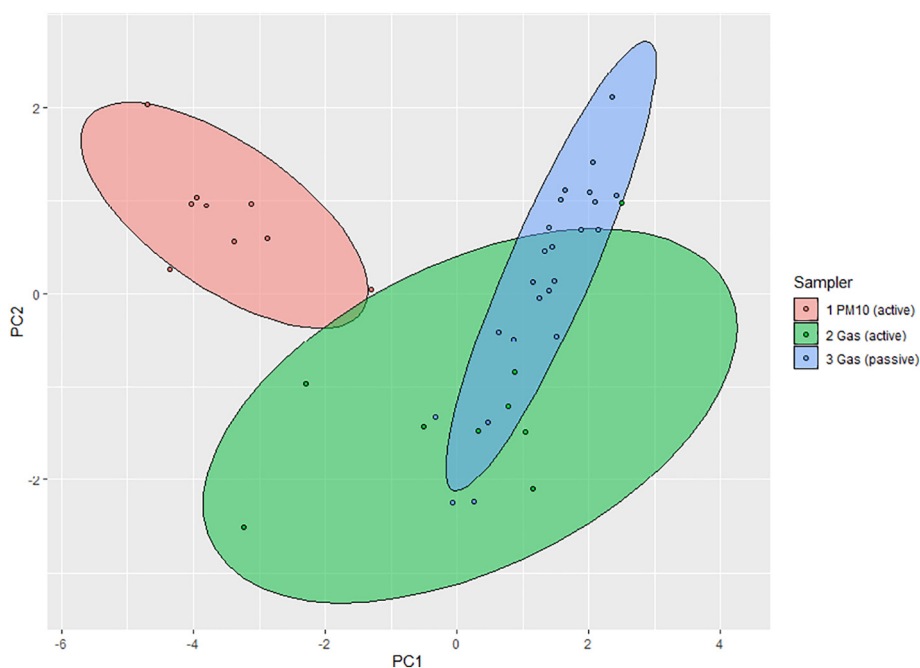
Fig. 5. Principal Components Analysis (PCA) of congener distribution (I-PCB$_7$) in the different air samples grouped according to sampling method. Ellipses show 95% confidence intervals for the respective groups (for specific I-PCB$_7$ congener distribution patterns see Fig. S3 in SI).

of PCBs sorbed to PM$_{10}$ aerosol particles, C$_{air,PM10}$ (pg/m^3), which is measured by active sampling (GFF samples); and the concentration of PCBs on the PM$_{10}$ particles themselves, C$_{PM10}$ (pg/g), which is derived by dividing C$_{air,PM10}$ by the particle concentrations on the GFF samples (g/m^3).

The active sampling (Fig. 4A) resulted in a higher C$_{air,gas}$ compared to the C$_{air,PM10}$, indicating PCBs are primarily found in the gas-phase. Fig. 4B compares C$_{air,gas}$ obtained with active and passive samplers. The latter are lower except at WEEE/Vehicle A (high standard deviation) and Incineration/Sorting A. There is no consistent difference in concentrations measured outdoors or indoors at the facilities. The most evident trend is that concentrations at WEEE/Vehicle sites tend to be the highest regardless of the sampling method, along with the passive sample (Fig. 4B) obtained at the urban reference location (NGI rooftop, an older building where the use of PCB containing construction materials cannot be excluded). This result is consistent with the waste handled at WEEE/vehicle sites having the highest PCB concentration (Fig. 1).

The composition of PCB congeners (presented in Fig. S3) showed a higher contribution of the lighter PCBs in PUF samples confirming the expected partitioning behavior that sorption to aerosols increases with increasing chlorination (Arp and Goss, 2009). A principal component analysis (PCA), in which individual samples are plotted according to their PCB profile and sampling method show a clear difference between the sampling methods (Fig. 5). Principal component 1 (PC1, X-axis) explained 71% of the variance in the dataset and is dominated by PCB 28 with positive loadings and PCB 138 and 153 with negative loadings. PC2 (Y-axis) explained 21% of the variance. The most important compounds in PC2 are PCB 52 and 101 with negative loadings and PCB 28 and 180 with positive loadings. It is noted that the active sampling method could be biased if the PUF suffers from breakthrough of volatile compounds (e.g. PCB-28 and PCB-52) (Bidleman and Tysklind, 2018; Arp and Goss, 2011) or if the GFF does not capture all particle-bound PCBs effectively due to blow-off artifacts from the GFF particles to the PUF (Galarneau and Bidleman, 2006). Further, a general consideration in interpreting the data is the limited number of data points (ranging from n = 1 to n = 2), therefore temporal fluctuations or sampling reproducibility at specific locations are not fully captured.

The range of I-PCB$_7$ concentrations in particle (C$_{air,PM10}$: 9–1900 pg/m^3) and gas phase (C$_{air,gas}$: 100–24,000 pg/m^3) in this study are comparable to what has been reported for China if open burning is excluded. Xing et al. (2009) reported mean values for gas phase concentrations ranging from 1100 pg/m^3 for a reference site to 4700 pg/m^3 in a residential area and 415,000 pg/m^3 for an open waste burning site (sum of 37 PCBs). Levels in the particulate phase ranged from 14,800 to 57,300 pg/m^3; which is higher than in the present study. Levels in the range of 216 to 1077 pg/m^3 have been reported for the sum of 28 congeners in Indian urban areas (Zhang et al., 2008). This is in the same order of magnitude as we observed at the NGI office building in Oslo, 1200–1400 pg/m^3. However, these results might be biased high by the age of the NGI office (built in the 1960s). If NGI roof-top data are omitted and data compiled in Breivik et al. (2011) are used as the basis for comparison (concentrations of 7-PCBs in ambient air in major cities to be ~> 100 pg/m^3, informal e-waste sites in China ~ 1000–10,000 pg/m^3 and the highest concentrations for open burning areas 100,000 pg/m^3), the air concentrations at formal waste handling facilities in Norway are similar to those found near informal waste handling in China.

3.6. Gas-particle partitioning

Some of the PCBs were predominantly found in the gas phase and some were predominantly bound to PM$_{10}$ (Table S5b and S5c). This has an impact on the fate of these compounds originating from the waste-handling facilities. Substances in the gas phase can be degraded faster by reaction with photooxidants or sunlight directly. Assuming equilibrium in the atmosphere has been achieved during the time of sampling, the phase distribution can be quantified with a gas-particle partition coefficient, K$_P$ (m^3/g) according to Eq. (5).

$$K_P = C_{PM10}/C_{air,gas} \qquad (5)$$

Fig. 6 compares the K$_P$ values for PCBs measured at the landfills with those predicted using a poly-parameter LFER model for ambient aerosols representative of urban and rural locations (calibrated by aerosols sampled in Duebendorf during Fall and Berlin during Winter at 15 °C,
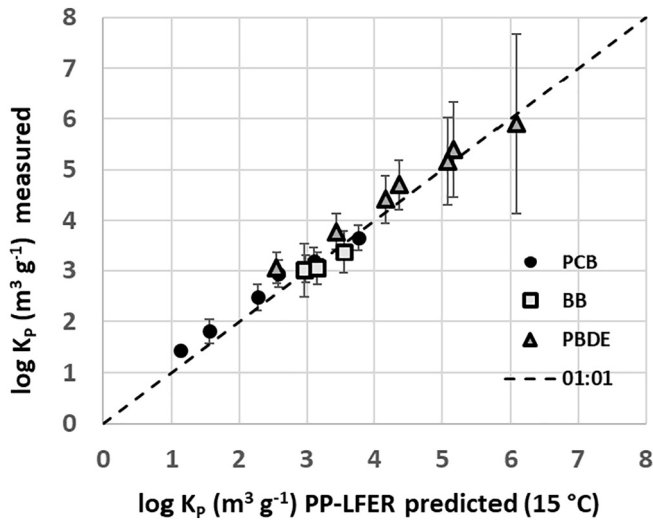
Fig. 6. Comparison of average log K_P values measured at the waste-handling facilities for ambient aerosols for polychlorinated biphenyls (PCB), brominated benzenes (BB) and polybrominated diphenyl ethers (PBDE) from this study and Morin et al. (2017) with a polyparameter-linear free energy relationship model for ambient aerosols (Arp et al., 2008a, 2008b). The error bars indicated the variability across the entire sampling campaign.

see Arp et al. (2008a, 2008b)). In an earlier study, Morin et al. (2017), measured brominated flame retardants (BFRs), including brominated benzenes (BBs) and polybrominated diphenyl ethers (PBDEs) in the same samples as the PCBs in this study. The K_P values for BFRs are also included in Fig. 6.

Measurements and predicted values are in close agreement (Fig. 6), indicating that the gas-particle partitioning behavior at waste handling facilities is not different from that at other ambient locations. K_P values for PCBs are generally smaller than for PBDEs, though PCB-118 to PCB-180 overlap with BDE-28 and BDE-47 having predicted log K_P at 15 °C of 2.6–3.8. The brominated benzenes (BBs) are somewhere in the middle, with a predicted log K_P (15 °C) of 2.9 to 3.6. Essentially, there is a transition from the predominantly gaseous PCBs with a low degree of chlorination (i.e. small K_P value) to the predominately particle-sorbed, higher brominated PBDEs (i.e. a large K_P value). Another observation from Fig. 6 is that variability in measurements increased with K_P, which could be a result of: higher brominated PBDEs in the gas phase being closer to limits of detection resulting in higher uncertainty in the concentrations used in the K_P calculation; larger PBDEs potentially not being in equilibrium because of "blow on" artifacts (Galarneau and Bidleman, 2006), increased dependence of K_P values on temperature

(Arp et al., 2008b); along with the general long-times to reach equilibrium with low-volatility substances; and finally, the possible scavenging of larger PBDEs by the filters used during sampling (this would bias the K_P values to be too high) (Arp and Goss, 2009). To better illustrate the variability in log K_P values, they are plotted for the individual sampling locations in Fig. S4.

The gas-particle partitioning behavior of PCBs, PBDEs and alternative flame retardants at waste facilities resembles that of partitioning to aerosol particles collected elsewhere; and therefore, no unique sorption behavior in these atmospheres appears to be present.

3.7. Waste-air partitioning

Equilibrium waste-air partition coefficients $K_{waste,air}$ (L_{air}/kg_{waste}) were derived using Eq. (6), which assumes partitioning from the bulk phases of waste and not the surface of waste:

$$K_{waste,air} = C_{waste}/C_{air,gas} = K_{waste}/K_{aw} \qquad (6)$$

where K_{aw} (L_{water}/L_{air}) is the air-water partition coefficient ($K_{aw} = C_{water}/C_{air,gas}$). log K_{aw} values for the I-PCB$_7$ studied here range from −1.9 to −2.5 (Table S1a). Correspondingly, the derived $K_{waste,air}$, (Table S5f) are all two orders of magnitude greater than the corresponding waste-water partition coefficients K_{waste} (Table 1).

To assess if volatilization from solid waste can account for the gas phase I-PCB$_7$ concentrations measured at the sampling sites, $C_{air,gas}$ values for the waste-handling facilities were estimated using a rearrangement of Eq. (6), i.e. by assuming equilibrium partitioning between the bulk waste phase and gas phase. We used C_{waste} for only the predominant type of waste found at a particular site and the $K_{waste,air}$ for that waste. As air and waste was sampled at the same time, a comparison with $C_{air,gas}$ data measured by active sampling is presented in Table S5g and S5h for all I-PCB$_7$, and shown in Fig. 7.

The estimated equilibrium $C_{air,gas}$ values are consistently larger than actively measured values (Fig. 7). This was expected, as wind and ventilation at the sampling sites would prevent equilibrium from being established between waste and gas phase. The closest match was for an indoor location (WEEE/Vehicle C), for which the equilibrium assumption would be more appropriate. The concentrations for I-PCB$_7$ obtained by passive sampling would deviate even more from equilibrium ($C_{air,gas}$), because they were generally lower than those from the active sampling campaign (Fig. 5). Looking at the data for individual PCBs in Table S5h, we observe that it is mainly the smaller PCBs (28 and 52) that have the largest deviation from equilibrium. Estimated equilibrium $C_{air,gas}$ values for heavier PCBs (e.g. 180) actually are smaller than measured gas phase concentrations. This is likely due to the measurement biases described previously. We note that the K_P for particles at the
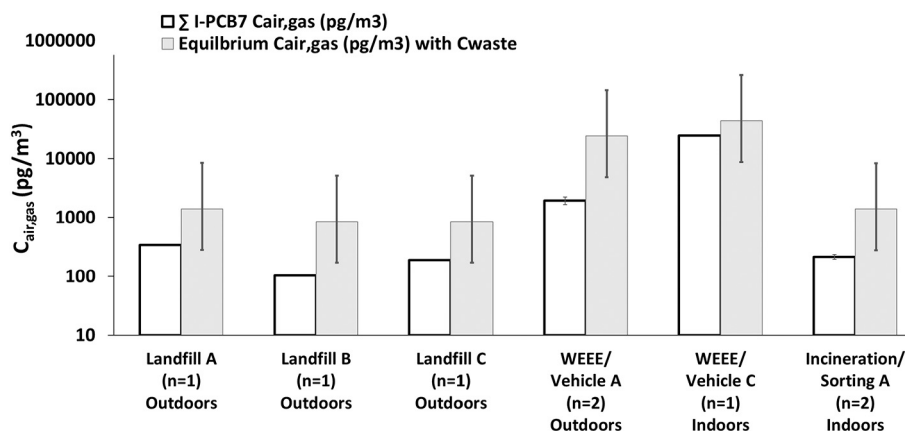

Fig. 7. Concentrations of ∑ I-PCB$_7$ in the gas phase of active air samples compared to the gas phase concentrations at equilibrium with the predominant waste fraction based on the derived $K_{waste,air}$ values. Assumed error of predicted concentrations is a factor 5.

WEEE/vehicle facilities were similar to the predominant $K_{waste,air}$ values, with overlapping standard deviations (Table S6a), whereas for the Landfill and Incineration/Sorting sites the onsite log K_P values were generally 1 to 2 orders of magnitude greater than the predominant $K_{waste,air}$ values. Based on the previous section, one interpretation of this is that WEEE/vehicle $K_{waste,air}$ values resemble the K_P values of ambient aerosols the closest; therefore, making the gas-particle partitioning of PCBs for these two materials hard to distinguish.

4. Conclusions

The results obtained support the first hypothesis of this study, that the investigated waste handling facilities are inherently contaminated by PCBs, as a result of the waste sorted for recycling, and contaminate the surrounding environment. Regarding the second hypothesis, that the fate and transport of PCBs released to air and leachate water is affected by particulate matter generated from the waste, this was only supported for leachate, and in particular at WEEE/vehicle facilities. Leachate I-PCB$_7$ were predominantly sorbed to suspended solids and DOC, and not in the freely-dissolved phase. In the case of WEEE/vehicle facilities PCBs on the suspended solids had matching PCB congener profiles with the waste present. In addition, the leachate-particle water partitioning behaviour as measured with PDMS, $K_{D,PDMS}$, resembled waste-water partition coefficients, K_{waste}, for the predominant waste-fractions at a facility. In the air phase, I-PCB$_7$ were predominantly present as a gas. Derived waste-air partition coefficients were found to be not appropriate for estimating air-phase concentrations or partitioning behaviour. Based on a good correlation of K_P values for I-PCB$_7$ at these facilities with a model developed for ambient aerosols, it appears there is no clear indication that the air particles sorb differently from ambient aerosols. In other words, though waste may be a source of PCBs to the atmosphere, it does not appear to alter gas-particle partitioning behaviour locally.

The third hypothesis of this study was that PCBs fate and transport behaviour from waste-handling facilities deviates from earlier observations for BFRs (Morin et al., 2017). This was not supported for leachate, where the total unfiltered concentration of I-PCB$_7$ (2–2900 ng/L) was similar to that of 10 polybrominated diphenyl ethers ($\sum BDE_{10}$ 1–3500 ng/L), which were the most dominate type of BFR measured. $K_{D,PDMS}$ for BFRs were not determined as it could not be concluded that equilibrium had been reached (Morin et al., 2017). However, it is anticipated based on the low water solubility of these substances, that BFRs are associated mainly with particles and DOC in the leachate, as is the case in this study with PCBs. Therefore, the transport of behaviour of PCBs and BDEs in leachate is expected to be quite similar. In the air phase, the total (gas and PM$_{10}$) concentration of I-PCB$_7$ was most abundant at WEEE/vehicle facilities (3900–25,400 pg/m^3) (Table S5d) which overlapped with the low end of total air concentrations of ΣBDE_{10} concentrations (9000–195,000 pg/m^3) (Morin et al., 2017). Further, for both I-PCB$_7$ and ΣBDE_{10}, total air concentrations were much lower at landfills, being 114–354 pg/m^3 (Table S5d) and 80–900 pg/m^3, respectively. However, the major difference was that ΣBDE_{10} are mainly associated with particles and I-PCB$_7$ dominate in the vapor phase, supporting the third hypothesis.

Despite production and open use of PCBs being phased out since the 1980s, they still enter the waste stream in Norway and therefore also enter recycling streams and have the potential to spread to the environment around waste-handling facilities. Ambient air levels at these, well regulated, formal recycling facilities are in the same order of magnitude as those observed at informal facilities in China. The highest concentrations of PCBs were found in plastic-rich WEEE/vehicle waste fractions. The question remains where these PCBs are entering the waste stream. A different sampling strategy than used in this study would be needed to resolve this question, such as one that investigates products that are disposed of before shredding.

5. Environmental implications

Both legacy and emerging contaminants in products will inherently contaminate waste streams. It is an important waste management issue to develop strategies of better sorting to minimize the emissions of such contaminants to the areas around waste handling facilities, to the workers within the facilities and potentially to the recycled raw materials being produced at such facilities (Arp et al., 2017). The present focus on the circular economy emphasizes the urgency to recycle raw materials for achieving sustainability. But there is a dilemma here in relation to how much legacy and emerging contaminants can be allowed to recirculate and potentially accumulate in circular material flows. The results from this study indicate that incineration or other forms of thermal treatment might be needed to eliminate PCB and similar contamination of the waste stream, to favour recycling of purer materials. This does not imply that all waste should be incinerated, but rather that better sorting is needed based on hazardous substance content to allocate waste for recycling or incineration. In this way, chemical risks in a circular economy could be better managed. An integrated approach of material recycling and thermal treatment, as well as measures to monitor and control concentrations of PCBs and other contaminants, will be needed going forward.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.136824.

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