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The Presence and Leachability of Antimony in different Wastes and Waste Handling Facilities in Norway

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The environmental behaviour of Antimony (Sb) is gathering attention due to its increasingly extensive use in various products, particularly in plastics. Because of this it may be expected that plastic waste is an emission source for Sb in the environment. This study presents a comprehensive field investigation of Sb concentrations in diverse types of waste from waste handling facilities in Norway. The wastes included waste electrical and electronic equipment (WEEE), glass, vehicle fluff, combustibles, bottom ash, fly ash and digested sludge. The highest solid Sb concentrations were found in WEEE and vehicle plastic (from 1238 to 1715 mg kg^{-1}) and vehicle fluff (from 34 to 4565 mg kg^{-1}). The type of acid used to digest the diverse solid waste materials was also tested. It was found that HNO_3:HCl extraction gave substantially lower, non-quantitative yields compared to HNO_3:HF. The highest water-leachable concentration for wastes when mixed with water at a 1:10 ratio were observed for plastic (from 0.6 to 2.0 mg kg^{-1}) and bottom ash (from 0.4 to 0.8 mg kg^{-1}). For all of the considered waste fractions, Sb(V) was the dominant species in the leachates, even though Sb(III) as Sb_2O_3 is mainly used in plastics and other products, indicating rapid oxidation in water. This study also presents for the first time a comparison of Sb concentrations in leachate at waste handling facilities using both active grab samples and DGT passive samples. Grab samples target the total suspended Sb, whereas DGT targets the sum of free- and other chemically labile species. The grab sample concentrations (from 0.5 to 50 µg L^{-1}) were lower than the predicted no-effect concentration (PNEC) of 113 µg L^{-1}. The DGT concentrations were substantially lower (from 0.05 to 9.93 µg L^{-1}) than the grab samples, indicating much of the Sb is present in a non-available colloidal form. In addition, air samples were taken from the chimney and areas within combustible waste incinerators, as well as from the vent of WEEE sorting facility. The WEEE vent had the highest Sb concentration from <100 to 2200 ng m^{-3}), which were orders of magnitude higher than the air surrounding the combustible shredder (from 25 to 217 ng m^{-3}), and the incinerator chimney (from <30 to 100 ng m^{-3}). From these results, it seems evident that Sb from waste is not an environmental concern in Norway, and that Sb is mostly readily recovered from plastic and bottom ash.

1. Introduction

The environmental presence and behavior of Antimony (Sb) is gathering attention due to its increasingly extensive use in various products. Historically the most common use was in munitions, but currently it is more commonly used in plastics (either as a flame-retardant or catalyst), alloys, glass and semiconductors.[1] Prior to the 1990s, the annual amount of Sb mined fluctuated between 10 and 80 thousand tons, largely based on the need for munitions; though outside of World War years a general increase was evident based on its use in an increasing number of products. During the 1990s, the production of Sb in China increased, current levels since 2010 have stabilized at approximately 160,000 ton per year.[2, 3] Increased use has resulted in an increased and often uncontrolled release of Sb compounds into the environment. Substantial emissions are related to mining and smelting activities[4] and spent ammunition at shooting ranges.[5, 6] The primary application of Sb is currently in flame retardants, in the form of antimony trioxide, Sb_2O_3,[2] which is commonly used as a synergist with brominated flame retardants (BFR).[7] In the EU the supply of antimony is considered to be critical, due to its economic importance and its relatively high supply risk related to flame retardation and micro capacitors.[1]

When consumer products containing antimony are disposed of, they can either be landfilled, combusted or recycled. However, currently little information is available regarding how much antimony ends up in these types of waste handling scenarios, and further, very little knowledge is available regarding the environmental emissions of Sb in waste, and whether this can pose a potential risk to the local environment.

Antimony is a non-essential element, and listed as a priority pollutant by the US Environment Protection Agency due to its toxicity,[8] with Sb_2O_3 considered as a probable carcinogen to humans by the International Agency for Research on Cancer (IARC).[6, 7] The guideline for the concentration of Sb allowable in drinking water in Norway is 5 µg L^{-1}, [9] which is lower compared to the guideline set by WHO of 20 µg L^{-1}.[10] Regarding the landfilling of waste, limits of how much of Sb can be leached following a standard batch test (NS-EN 12457) have been put in place, with leachate levels above 0.7 mg kg^{-1} requiring disposal in an ordinary waste landfill, and levels above 5 mg kg^{-1} being the upper allowable limit for hazardous waste.[11]

Antimony occurs in various oxidation states (-III, 0, III, V). The most common inorganic species in the environment are trivalent $Sb(OH)_3$ and the pentavalent $Sb(OH)_6^-$. These species behave differently, thus the redox state is important for the fate of Sb in the environment. In general, inorganic Sb compounds are considered more toxic than organic ones, with Sb(III) more toxic than Sb(V).[12] Under oxic conditions Sb is mainly present as $Sb(OH)_6^-$ in soil solution and water bodies.[13, 14] Until this study, redox speciation analysis of Sb in extracts of waste fractions has been relatively scarce in literature.

Based on the knowledge that Sb is mainly used as a flame retardant, primarily in plastics, the hypothesis we pursue in this study is that leachate from waste plastic and facilities treating waste plastic emit more Sb than other types of waste and facilities that do not treat waste plastic. In addition to pure plastic waste, we also consider "plastic rich" waste, such as separated plastic waste of electrical and electronic equipment (WEEE). WEEE is produced at approximately 20 – 50 million tons per year globally, being the fastest growing waste stream, increasing 3-5% annually.[7] Another important waste fractions is waste from automobile shredder residues (ASR), and end-of-life vehicles which is converted to "vehicle fluff" (a mixture of plastics, textiles, soil/sand, sponge and rubber).[15]

The available information in the literature we can use to test our hypothesis is scattered, but generally in agreement with it. It is well documented that polyethylene terephthalate (PET) bottles are prone to water leaching of Sb.[16-18] Elevated Sb concentrations in dust (indoor, 6.1 – 232 mg kg^{-1}) have been observed in WEEE recycling villages in China, up to 148 times compared to non WEEE sites, indicating that WEEE recycling is an important source of Sb pollution.[19] However, comprehensive studies on Sb leaching from diverse waste and waste treating facilities are lacking in the literature (existing literature on specific types of waste and waste-facilities is presented throughout the Results and Discussion). Thus, in the present study, we conducted a comprehensive field investigation of diverse types of waste and waste handling facilities in Norway. In addition to testing our centrally hypothesis, we also aimed to better understand the mobility, bioavailability and speciation of Sb from waste fractions and Norwegian waste handling facilities, in order to gain a deeper understanding of how waste can emit Sb into the environment.

2. Experimental

2.1. Field Campaign

In order to have a broad range of waste handling methods and types of solid waste fractions, twelve different facilities located in South-Western Norway were sampled. These facilities were chosen to provide a broad range of waste handling methods and types of solid waste fractions, particularly in relation to the waste fractions glass, vehicles, WEEE, plastics and combustibles. Three sampling campaigns were conducted from mid-2013 to mid-2014 (June-October 2013, October-December 2013 or March-June 2014), with all of the facilities being visited during two of the sampling campaigns, and some during all three. Among those facilities, three were landfills containing municipal and industrial waste although varying in the processing of special types of wastes (bottom ash, fly ash and sludge digestate), seven were dedicated to shredding and sorting WEEE and/or vehicle waste and two were for sorting combustible waste (from municipal or industrial source). As these facilities handle waste in accordance with Norwegian laws and regulations, they are considered representative of waste facilities elsewhere in Norway. The types of solid waste samples collected are presented in Table 1.

In order to give site anonymity, the locations are referred to as Landfill A–C, WEEE/Vehicle sorting facility A-E and Incineration/Sorting facility A-B. Note that some of the WEEE/Vehicle locations consisted of different plants sharing the same water drainage, thus they were merged as one "combined" facility. Solid waste fractions, leachate water and air samples were collected from these facilities, as presented below, based on the diversity of unique solid waste fractions and logistics. A more detailed description of this fieldwork is presented in the Electronic Supporting information (ESI).

2.2. Solid Waste Samples

Between 4 and 12 kg of individual solid waste samples were collected randomly by hand (whilst wearing nitrile gloves) into 4 L polyurethane bags, which were visually representative of a particular waste fraction. Samples were transported back to the laboratory and stored at 4 ºC until further processing.

In the laboratory, the obtained waste samples were homogenized in the polyurethane bags by shaking or manual mixing (wearing a nitrile glove), then between 20 –400 g of each solid waste samples were randomly sampled from various parts of the bag and then further homogenized by grinding them down and sieving them to 2 mm or 4 mm. Various tools were used for grinding depending on the material, including a BB Retsch jaw crusher, a kitchen hand blender (Braun or Phillips), a handpowered malt mill, a mortar and pestle, or just a sieve in the case of fine materials. Hard plastics and metal materials which could not be crushed (> 4 mm) were removed. This may introduce a slight bias compared to the original sample.

Table 1. Types of Waste Fractions Sampled

Group	Waste Fraction	Definition
Glass	Recycled	Glass specifically sorted for recycling
	Composite	Mixture of clear and colored glass samples
Vehicle	Coarse Fluff	Non-metallic residue after car shredding larger than 8 mm
	Fine Fluff	Non-metallic residue after car shredding between 2 – 8 mm
WEEE	Remaining plastic	All WEEE plastic that is not cable plastic or BFR plastic
	BFR Plastic	Plastic containing BFRs that is separated at sorting facilities.
	Cable Plastic	Plastic stripped from cables
	Remains / Metal)	Other materials from WEEE sorting (glass, metals and other residue)
Plastic	Packaging plastic	Plastic sorted for recycling, or potentially recyclable
	Composite, other	Plastic that is not sorted for recycling, nor originating from WEEE and vehicles
	Composite, WEEE&Vehicle	Plastic from WEEE (mentioned above), as well as the plastic component of car fluff
Comb.	Fine	Combustibles between 2 – 16 mm
	Coarse	Combustibles > 16 mm
Ash	Bottom ash	Remaining ash residue in the incineration chamber from waste incineration
	Fly ash	Ash residue collected from chimney filters from waste incineration
Sludge	Digestate	Sewage sludge that is digested for methane production, typically landfilled.

Comb. = Municipal and Industrial waste combustibles.

2.3 Digestion of Solid Waste Samples

Total Sb extraction of the different waste materials and filter samples was carried out using two different microwave digestion methods that were tested out in parallel: 1) using ultra-pure concentrated HNO_3 and HF (4:1) and 2) using ultra-pure concentrated HNO_3 and HCl (10:1). Both extraction methods are often used for determination of total Sb content in solid environmental samples. However it has been shown that the Sb values derived from various acid extractions often deviate strongly.[20] Documentation of Sb yield in extraction of solid waste samples is scarce in literature. Thus, testing out both extraction methods in our study was of interest to find a suitable extraction method, particularly considering the variation in sample matrices (digested organic matter, glass, plastic, metals, etc.). For both extractions methods 0.5-2.5 g dry material was stepwise heated up to up to 260° C, using a Milestone Ultraclave, for 1 h and 15 min. Solid waste samples with high heterogeneity (WEEE, Vehicle fluff) were analysed in quadruplicates.

2.4. Leach Test

A one-step batch test was conducted on the solid waste media material according to a modified version of EN (European Norm) 12457 "Characterization of waste – Leaching - Compliance test for leaching of granular waste materials and sludges." Approximately 4 g of the sample material (size ≤ 4 mm) was shaken for 7 days with milli-Q water at a liquid-to-solid ratio (L/S) of 10 (10 litre liquid per kilogram of solid) on an end-over-end shaker. The pH at the end of this exposure was then recorded. The test was carried out at room temperature (20 ± 2 ºC). Each sample was filtered (through 0.45 µm polyethersulfone membrane). The filtrate of each sample was divided into different fractions: 1) one containing dihydrogen citrate 1M (50% in volume),2) one with concentrated HCl (3% in volume) and 3) one with concentrated HNO3 (3%) for quantifying Sb(III), Sb(V) and total Sb, respectively. The eluate was stored cold (4 °C) prior to analysis.

The concentration of Sb in the water (C_{water}, mg L^{-1}) was measured in the eluate (see below). The amount of Sb leached per dry weight, $C_{leachable}$ (mg kg^{-1}) of material was then derived using the formula

$$C_{leachable} = (C_{water} \times V_{water}) / (M_{waste}) \qquad (1)$$

Where V_{water} (L) was the amount of water added to the batch system plus the amount of water in the waste sample, M_{waste} (kg) is the dry weight of solid waste added. The water contained in the waste was determined by measuring the weight loss of a subsample before and after drying at 110 °C for 19 hours.

2.5. Leachate water grab sampling

Leachate water grab samples were obtained by submerging 200 mL HDPE (high density polyethylene) plastic bottles in the leachate water streams at selected facilities (either an open stream, or inside a culvert or manhole, see ESI Table S1.1 for more information). The bottles were transported cool (4 °C) to the laboratory and frozen until analysis. The water samples were later thawed and ultra-pure HNO_3 and HCl was added to the whole sample equal to 10% and 2%, respectively, of final volume. The bottles were vigorously shaken and 10 mL sample were transferred to clean Teflon tubes for Ultraclave digestion. All leachate water grab samples were spiked with 100 µl internal standard containing Sc, Ge, Rh, In and Bi in 2 % ultra pure HNO_3 before digestion.

The concentration of dissolved organic carbon (DOC), F^-, Cl^-, NO_{3^-} and SO_4^{2-} were determined in subsamples withdrawn after thawing, but before acidification. These subsamples were filtered through 0.45 µm Polyethersulfone membrane filters fitted to unused high density poly propylene (HDPP) syringes (VWR, Norway). The concentrations of F^-, Cl^-, NO_3^- and SO_4^{2-} were quantified using a Lachat IC 5000 ion chromatograph, and DOC was quantified by use of a Shimadzu TOC-5000 analyser.

2.6 Leachate water DGT sampling

DGT (Diffusive Gradients in Thin Films) disks are passive samplers where free and labile ions have to diffuse from environmental water samples through a protective membrane filter and an inert hydrated gel before reaching a resin.[21] There are different resins available, but in this investigation the DGT disks were loaded with a Chelex resin for metal cation binding and a Fe-oxide gel for Sb binding. The hydrated gel acts as a filter by preventing larger molecules and colloids from diffusing through. Though concerns have been raised about how accurately DGT can mimic uptake through a cell membrane in certain environments and in the presence of labile organic complexes,[22] DGT can be used as a better indicator of the bioavailability or exposure of a metal or metalloid in environmental samples compared to more traditional methods like filtration or equilibrium solution extractions.

For leachate water sampling, three DGT Fe-oxide disks and three DGT-Chelex resin disks were submerged in in the leachate waters at the same time as the grab samples were obtained. StowAway TidbiT (Onset Computer Corporation, MA, USA) temperature loggers (recording every 5th min.) were also installed. Each exposure periods lasted for 1 week. After exposure, the DGT disks were collected and thoroughly rinsed with distilled water, put in unused clean plastic bags and stored at 4 ºC pending analysis.

The Fe-oxide and Chelex resins were removed from the DGT units, transferred to clean unused test tubes (poly propylene, PP, quality) and eluted with 1.6 M ultra pure HNO_3 for 24 hours. Blanks were also prepared using non-deployed DGT units. All samples were spiked with 100 µl internal standard before analysis. (The water in some of the runoff streams had dried out during some of the exposure campaigns and hence only 1 to 2 of the DGT replicates were analysed for those sites).

2.7 Air Sampling

The outflowing air from an air vent of WEEE/Vehicle facility B and from the chimney of Incineration/Sorting facility A was sampled for Sb by subcontracting the company Eurofins.The amount of air leaving the vent/chimney was sampled and corrected for standard temperature and pressure conditions following ISO 10780:1994.[23] The total suspended particulate (TSP) fraction of dust from the chimney was collected by using isokinetic suction through a filter. The filter was then dissolved in nitric acid and hydrogen peroxide, and then quantified for Sb using EN 14385:2004[24] and the Danish Standard MEL 8A.[25]

Additionally, inside the loading dock of Incineration/Sorting Facility A and near a shredder by Incineration/Sorting facility B, ambient particulate matter was sampled using a high-volume (HighVol) air sampler (Digitel, Switzerland), equipped with a 10 µm cutoff and 150 mm Ø glass fiber filter (GF filter, Sigma Aldrich, USA) to collect the PM10 particles (i.e. particles with a 10 µm aerodynamic diameter or smaller). The initial air sampling speed was set to approximately 500 L/min. The GFF filters were stored cold (4 °C, prior to analysis). A more detailed description of sample treatment and calculations of Sb particle concentration, C_{dust} (mg kg^{-1}_{dust}) and Sb in air, C_{air} (pg m^{-3}), is given in the ESI.

2.8 Sb quantification

Concentrations of Sb in the digested solid waste material (C_{waste}), grab samples of water leachate from the waste-handling facilities ($C_{leachate}$), the DGT-elutes ($C_{leachate,DGT}$) and dust (C_{dust}) were quantified with the assistance of an Agilent Technologies 8800 Triple Quad Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The calculated DGT-labile time averaged Sb concentration (Sb_{DGT}) was calculated from the total mass of Sb accumulated in the resin during exposure, following Fick`s first law of diffusion through the hydrogel. The Sb-specific diffusion coefficients, which were obtained from Luo et al.[26], were corrected based on the average temperature as logged during the DGT exposure using the Stoke-Einstein relationship as reported in Garmo et al.[27] More details about these DGT calculations are presented in the ESI.

For speciation analysis of the water-leachable concentration of the solid waste material ($C_{leachable}$), the concentrations of Sb(III) and total Sb (Sb_{tot}) were measured using hydride generation inductively coupled plasma optical emission spectrometry (HG-ICP-OES; Optima 5300 DV, Perkin Elmer inc., USA). In this method concentrations of Sb(III) and total Sb (Sb_{tot}) are determined, and Sb(V) is calculated from the difference between Sb_{tot} and Sb(III) concentrations. Sb(III) is reduced and converted to SbH_3 by mixing with $NaBH_4$. Total Sb is analyzed by reducing Sb(V) to Sb(III) with KI-ascorbic acid solution (5% KI, 5% ascorbic acid, 10% HCl) in 10% HCl prior to analysis. Sb(III) is selectively reduced at near-natural pH, where no reduction of Sb(V) takes place. Standards for ICP analysis were matrix-matched to achieve similar conditions as in the samples.

2.9 Data treatment

Statistical analysis was carried out to test the statistical significance of geochemical variables on the observations of Sb reported (*t*-tests, correlations and multiple regression analysis), using JMP statistical software.[28] The level of statistical significance is reported in the text.

3. Results and discussion

3.1. Solid Waste Digestion

The type of acid used to digest the solid waste materials had a substantial influence on the resulting C_{waste} values for Sb, with the HNO_3:HCl extraction giving consistently and often substantially lower yields than HNO_3:HF (Figure 1).

The relative recovery of Sb with HNO_3:HCl (in %) compared to HNO_3:HF (set to 100%) in the different waste fractions were for combustibles (<1-11%), glass (<1-7%), fly ash (<10%, except one sample with 72 %), bottom ash (~1%), vehicle fluff (<1-3%, except one sample with 69%), and diverse WEEE plastics (<1-19%).

Antimony extraction acid mixtures that include HF are known to give a higher yield in soil and rock solid samples, due to the extraction of Sb strongly bound to silicates [20, 29]. However, substantial amounts of silicate bound Sb in our solid waste samples are not expected, as predominantly Sb is added in products as Sb_2O_3. In fly ash and bottom ash, Sb is expected to occur in solid solution with ettringite and possible Ca antimonite.[30, 31] For the solid samples Sb was expected to be more loosely bound, as in the sludge digestate, the HNO_3-HCl digestion gave only 24-37% recovery. Our results show that extraction of solid samples for Sb analysis should include HF to achieve satisfactory recovery (as has been concluded by other authors[29]). All solid waste Sb results given in the following sections are based on extraction with HNO_3:HF.

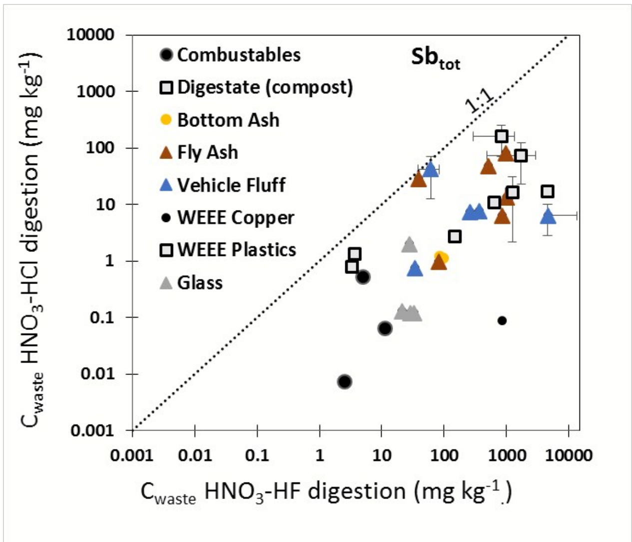

Figure 1. Antimony concentrations in solid waste samples analyzed by ICP-MS though extracted by microwave digestion using concentrated HNO_3-HCl (10:1) (y-axis) and HNO_3-HF (4:1) (x-axis). The dotted line indicates a 1:1 relationship. Error bars indicate quadruplicate analysis for some WEEE plastic and vehicle fluff samples.

3.2 Solid and leachable Sb concentration

Averages of C_{waste} and $C_{leachable}$ of the different waste fractions are presented in Figure 2 and Table 2, with additional data presented in the ESI Table S1.2. Note that there are two types of waste fractions presented in these tables: unique waste fractions (i.e. those that could be sampled, e.g. cable plastic, vehicle fluff), and composite waste fractions (e.g. consisting of multiple unique waste fractions). For unique waste fractions, average concentrations, average of log-transformed concentrations, minimum, maximum and median values are provided. For composite waste fractions, weighted averages are provided based on the amount of mass produced per year, $\dot{m}_{waste}$, of the different unique waste fractions (see Table 2). As an example, $\dot{m}_{waste}$ for coarse and fine combustibles respectively are 734 ± 183 and 183 ± 46 Mtonnes y^{-1}, and the respective $C_{waste,Sb}$ are 11 and 3 mg kg^{-1}. Therefore, the weighted average for both coarse and fine combustibles is 9 mg kg^{-1} (= [11*734+3*183]/[734+183]). Standard deviations were derived using standard propagation of uncertainty protocols.

3.2.1. WEEE, Vehicle Fluff, Plastics.

High and variable Sb waste concentrations, C_{waste}, were found in Vehicle fluff (from 34 to 4565 mg kg^{-1}) and WEEE (from 150 to 4600 mg kg^{-1}), of which the plastic subfraction dominated the Sb content (from 1238 to 4600 mg kg^{-1}). These measurements are all below the proposed Norwegian guideline level for hazardous waste for hazardous waste (10 000 mg kg^{-1}).[32] The dominant form of Sb in these plastic dominated waste fractions is likely Sb_2O_3 (as a flame retardant or catalysis in plastic production), though with some contributions from Sb alloys in metal residues. In a Norwegian vehicle fluff study from 2013 the average Sb concentration of fluff was reported to be ca. 100 mg kg^{-1}, with a maximum measurement of 500 mg kg^{-1}.[33] These value were within range of our values, though on the low side (Table 2). Ranges of estimated antimony in different pure plastics, including polyethylene (10 mg kg^{-1}), polypropylene (8.5 mg kg^{-1}), polyvinylchloride (45.3 – 70 mg kg^{-1}) and PET-bottles (159.2 – 397 mg kg^{-1})[17, 34, 35] are in general less that what we measured for mixed WEEE and Vehicle fluff plastics, perhaps due to additional requirements for fireproofing these materials.

The highest leachable Sb concentration, $C_{leachable}$, was also found in the plastic waste fraction (1.34 ±0.79 mg kg^{-1}), exceeding the leaching limit for ordinary waste landfills in the Norwegian and European landfill legislation (0.7 mg kg^{-1}).[11] Lower Sb leaching was observed in the mixed WEEE fractions (0.58 ±0.30 mg kg^{-1}), which is below the leaching limit for ordinary waste landfill. Substantial lower Sb leaching was measured in vehicle fluff (0.15 ±0.04 mg kg^{-1}). Lower Sb mobility in this waste fraction could be due to high iron content (up to 6%, based on simultaneously obtained ICP-MS data) partly occurring as iron (hydr)oxides. Antimony has a high affinity to iron (hydr)oxides,[36] and sorption to such solid particles could explain the lower mobility in these samples.

3.2.2. Glass

Low total Sb concentrations were measured in the recycled glass fraction (30 ±9 mg kg^{-1}), and low Sb concentrations were measured in the water extracts (0.02 ±0.01 mg kg^{-1}), well below the leaching limit for inert waste landfill (0.06 mg kg^{-1}) given in the Norwegian and European landfill regulation. In optical glass (e.g. cathode ray tubes, camera lenses) Sb is used as decolorizer and fining agent at concentrations up to 1000 – 6000 mg kg^{-1}.[35] Glass bottles have lower concentrations of Sb (e.g. 7.6 - 10.1 mg kg^{-1})[17], which are more similar to our measurements. It is therefore plausible that our estimate for composite glass may be on the low side, due to lack of representative inclusion of optical glass residues.

3.2.2. Combustibles and ash residues

Similar to glass, comparatively low total (9 ± 6 mg kg^{-1}) and leachable (0.04 ±0.02 mg kg^{-1}) Sb concentrations were found in the combustible waste fraction. This material, which has been sorted for combustion, consists of miscellaneous household and industrial waste fractions not separated for recycling, such as food packaging, paper waste, disposable diapers, wood pieces, discarded building supplies, all of which are shredded prior to waste incineration. Our measured total Sb concentration in this fraction was in the lower range compared to average concentrations in municipal solid waste reported in the literature of 10 to 60 mg kg^{-1}.[37, 38] One reason for this may be due to relatively good separation of plastic waste for recycling in our study area.

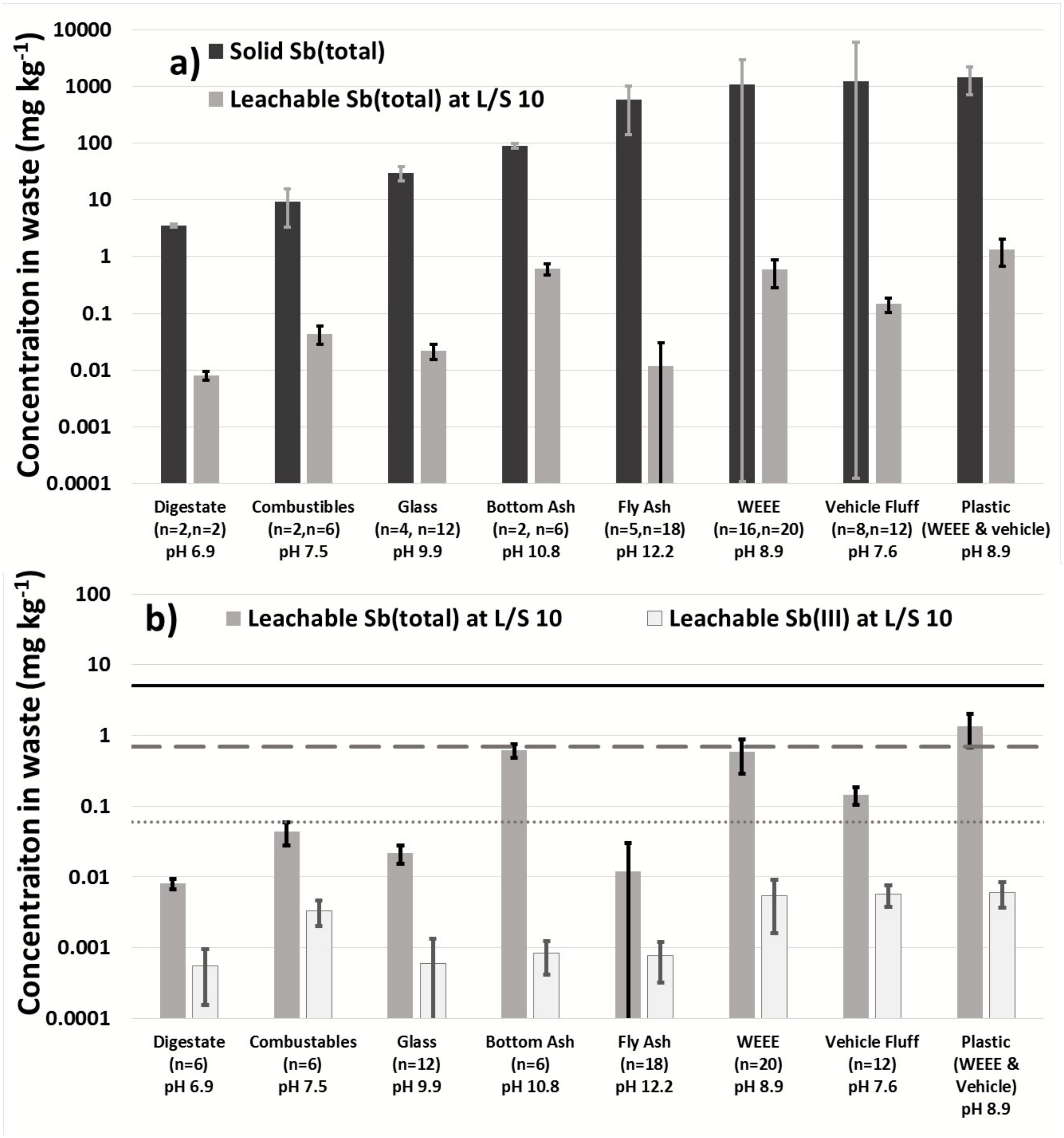

Figure 2. a) Averages of Sb (total) concentrations in solid waste, C_{waste} (left n-value), and their leachable Sb (total) concentrations, $C_{leachable}$ (right n-value), at a liquid water to solid waste ratio (L/S) of 10. The waste types are organized from the least to greatest concentrations. The plastic waste fraction was composed of WEEE and vehicle plastic sub-fractions. b) $C_{leachable}$ of Sb(total) and Sb(III) of the solid waste fractions. Also presented in b) are the Norwegian limits of $C_{leachable}$ Sb(total) for disposal in an inert landfill (0.06 mg kg^{-1}, dotted line), an ordinary landfill (0.7 mg kg^{-1}, dashed line) and a hazardous waste landfill (5 mg kg^{-1}, solid line).

Table 2. Solid and leachable concentrations of Sb in various unique waste fractions, the pH measured from the leach test, along with weighted averages for composite waste fractions based on the mass flow of the various unique waste fractions in Norway.

Group	Type	$\dot{m}_{waste}$ [a] (Mt y^{-1})	N[b]	$C_{waste,Sb}$ mg kg^{-1}	min-max mg kg^{-1}	log $C_{waste,Sb}$ mg kg^{-1}	n_s / n_l [c]	$C_{leachable,Sb(Tot)}$ µg kg^{-1}	$C_{leachable,Sb(III)}$ µg kg^{-1}	Leached %	pH
Glass	Recycled glass	100 ± 25	1 (u)	33		1.5	1 / 3	20 ± 1	0.6 ± 0.6	0.06	10.2
	Composite glass	114 ± 29	3 (u)	28 ± 6	21 - 33	1.4 ± 0.1	3 / 9	23 ± 5	0.6 ± 0.8	0.08	9.8
	All glass [d]	**214 ± 54**	**4 (c)**	30 ± 9		2.7 ± 1.3	**4 / 12**	22 ± 6	0.6 ± 0.7	0.07	**9.9**
Vehicle	Coarse Fluff	23.5 ± 5.9	3 (u)	1662 ± 2518	61 - 4565	2.7 ± 1.3	6 / 6	160 ± 20	7.6 ± 1.7	0.01	7.6
	Fine Fluff	8.9 ± 2.2	2 (u)	145 ± 157	34 - 256	2.0 ± 0.6	2 / 6	108 ± 18	0.7 ± 0.3	0.07	7.6
	All fluff [d]	**32.3 ± 8.0**	**5 (c)**	1245 ± 1896		2.5 ± 1.4	**8 / 12**	146 ± 41	5.7 ± 1.9	0.01	**7.6**
WEEE	BFR plastic	2.0 ± 0.5	1 (u)	4600		3.7	1 / 2	404 ± 33	10.9 ± 4.3	0.01	8.3
	Cable Plastic	15.0 ± 3.7	3 (u)	538 ± 348	150 - 823	2.6 ± 0.4	6 / 9	489 ± 262	22.7 ± 22.5	0.09	8.2
	Remaining plastic	48.0 ± 12.0	2 (u)	1476 ± 338	1238-1715	3.2 ± 0.1	8 / 6	1417 ± 599	6.0 ± 1.9	0.10	9.5
	Remains / Metal	80.0 ± 20.0	1 (u)	860		2.9	1 / 3	106 ± 60	1.6 ± 0.9	0.01	9.5
	All WEEE [d]	**145 ± 36**	**7 (c)**	1082 ± 339		3.0 ± 0.4	**16 / 20**	584 ± 298	5.4 ± 3.8	0.05	**8.9**
Plastic	Packaging[e]	194 ± 48.5	2 (u)	1476 ± 338	1238-1715	3.2 ± 0.1	*8 / 6*	1417 ± 599	6.0 ± 1.9	0.10	9.5
	Composite, Other[e]	207 ± 52	2 (c)	1476 ± 338		3.2 ± 0.1	*8 / 6*	1417 ± 599	6.0 ± 1.9	0.10	9.5
	Composite, WEEE&vehicle[f]	82 ± 21	11 (c)	1334 ± 1145		2.9 ± 0.5	*23 / 29*	964 ± 483	6.7 ± 2.1	0.07	7.9
	All plastic [d]	**482 ± 121**	**8**	1452 ± 617		3.1 ± 0.6	***39 / 43***	1340 ± 669	6.1 ± 2.4	0.09	**8.9**
Combustibles	Coarse	734 ± 183	1 (u)	11		1.0	1 / 3	39 ± 9	6.0 ± 1.8	0.35	6.9
	Fines	183 ± 46	1 (u)	3		0.4	1 / 3	62 ± 20	0.2 ± 0.1	2.45	8.2
	Combustibles[d]	**917 ± 229**	**2 (c)**	9 ± 2		0.9 ± 0.5	**2 / 6**	44 ± 16	3.4 ± 1.3	0.47	**7.5**
Bottom Ash	Coarse		1 (u)	84		1.9	1 / 3	603 ± 95	0.6 ± 0.5	0.72	10.8
	Fine		1 (u)	96		2.0	1 / 3	620 ± 187	1.1 ± 0.1	0.64	10.7
	All bottom ash [d]		**2 (c)**	90 ± 9		2.0 ± 0.0	**2 / 6**	612 ± 133	0.8 ± 0.4	0.68	**10.8**
Flyash			5 (u)	577 ± 438	39 - 1016	2.5 ± 0.6	5 / 18	12 ± 18	0.8 ± 0.4	0.00	12.2
Digestate			2 (u)	3 ± 0	3 - 4	0.5 ± 0.2	2 / 2	8 ± 1	0.6 ± 0.4	0.23	6.9

a) Best estimates of mass flow for various waste fractions in Norway in 2011, with 25% error (Statistics Norway (Statistisk sentralbyrå) for 2011 accessed December 2014); b) number of unique, homogenized samples, with "(u)" indicating if it is a unique waste fraction and "c" if it is a composite of different unique waste fractions; c) total number of samples used in averaging (including replicate analysis of unique samples for each waste fraction) for solid test / leach tests; d) data for combined waste fractions are based on a weighted average by normalizing to $\dot{m}_{waste}$ for the individual subfractions; e) The "WEEE remaining plastic" fraction (i.e. plastics collected from WEEE facilities not from cables or separated because of their Br content) was assumed representative of the "packaging plastic" and "composite other" plastic waste fractions; f) the Composite WEEE&vehicle plastic fraction is average of all WEEE plastics and Vehicle fluff.

Fly ash measurements revealed variable, but potentially high Sb C_{waste} values, ranging from 39 to 1016 mg kg^{-1}. This is in the upper range of previous reported concentration in literature, where fly ash concentrations of 1 – 1000 mg kg^{-1}, and averaging at 349 mg kg^{-1} have been reported.[34, 39, 40] Fly ash is classified as hazardous waste according to the European Waste List (2001/118/EC), because such air pollution control (APC) residues are highly alkaline and often enriched in many toxic elements. Our leaching tests showed low mobility of Sb in the studied fly ash samples. This is in accordance with the literature, where water extraction of fly ash at intrinsic pH showed low solubility,[30] most likely due to a solid solution with ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3*32H_2O$) occurring in the ash. This mineral has been suggested to be a solubility controlling mechanism for Sb, where SO_4^{2-} is replaced by $Sb(OH)_6^-$.[39] Ettringite is stable at pH >10. Furthermore, Ca antimonates (romeites) may be important secondary minerals, due to high concentrations of Ca-bearing minerals.[41, 42]

Bottom ash from waste incineration showed a substantially lower total Sb concentration (90 ± 9 mg kg^{-1}) compared to the fly ash fraction. However, a higher Sb mobility was observed (0.61 ±0.13 mg kg^{-1}) in the leaching test with water, with some replicates exceeding the leaching limit of ordinary waste landfill of 0.7 mg kg^{-1}. Bottom ash is considered as non-hazardous waste according to the Norwegian regulations.[43] Bottom ash concentrations in the literature include solid concentrations 31± 11, 86 ±22 mg kg^{-1} and 133 mg kg^{-1},[31, 44] as well as leached concentrations of 0.17 mg kg^{-1} [31] and 0.14 ± 0.06 mg kg^{-1} [45]. Thus, the values we obtained are within the expected range, though slightly higher than these literature values. The mechanisms responsible for leaching of bottom ash as a function of pH and carbonation have been thoroughly investigated,[31, 46, 47] generally leaching is the lowest at the natural pH of fly ash (10 – 12) and with little carbonation, as Sb tend to reach equilibrium with Ca antimonates.[46]

During incineration approximately 20-40 % of the waste is converted to bottom ash and 2-8 % ends up as fly ash,[42, 48] implying a median bottom ash:fly ash weight ratio of 6. Antimony is relatively volatile,[49] and depending on the type of waste, combustion temperature and occurrence of other elements as chloride (Cl), previous studies have estimated half of the of Sb ends up in bottom ash and the remaining 33 to 74% ends up in the fly ash or is emitted to air.[38, 44, 49] This distribution between fly ash and bottom ash is in agreement with our results, as the concentration in our fly ash is a factor 6.4 times greater than bottom ash, which is close to the median fly ash:bottom ash ratio.

3.2.4. DIGESTATE

Low total Sb concentrations were observed in the sludge digestate fraction, at 3.5 ± 0.2 mg kg^{-1}. Accordingly the leachable Sb fraction was low (0.008 mg kg^{-1}). PNEC values for Sb soil have been reported as 37 mg kg^{-1}.[20] Thus the reuse of measured digestate as a soil amendment in agriculture would not pose a Sb-toxicity risk to soil organisms.

3.2.5. SPECIATION

Chemical speciation analysis showed mainly the less toxic Sb(V) prevailed in all water extracts from the various waste fractions (Figure 2b), with 0.1 % (bottom ash) to 7.6 % (combustibles) of the total Sb occurring as Sb(III). Because Sb is mainly added as Sb(III) (Sb_2O_3) in plastics and glass, a dominance in the leaching of Sb(III) could be expected. However, Sb(III) is generally found to be unstable. Oxidation from Sb(III) to Sb(V) has been found in water extracts in shooting range soil where Sb occur as elementary Sb (Sb^0)[5, 50] and in Sb_2S_3 containing mining soil.[4] A dominance of pentavalent $Sb(OH)_6^-$ in leachate from bottom ash and fly ash is has also been found in with previous studie by Cornelis et al. (2006, 2012)[31, 46] and Okkenhaug et al. (2013).[30] According to thermodynamic data for Sb, the pentavalent $Sb(OH)_6^-$ is stable under oxic conditions and alkaline pH.[51]

The highest Sb(III) percentage was in the digestate waste fraction (7%). Probably due to the reducing conditions during waste treatment process (anaerobic treatment of sewage sludge). However, both total and leachable concentrations were low in this fraction and the possible risk can be considered negligible.

3.3 Waste facility leachate

Leachate concentrations determined with grab sampling, $C_{leachate}$, and DGT sampling, $C_{leachate\text{-}DGT}$, of the various waste handling facilities are presented in Figure 3 and in the ESI Table S2.3, with additional information in the ESI. The variation in $C_{leachate}$ in landfills ranged from 0.5 ±0.3 to 26.0 ±16.1 µg/L, and for WEEE/Vehicle facilities they ranged from 3.3 ±0.2 to 50 ± 0.0 µg/L. All these values are below the suggested PNEC for Sb in fresh water of 113 µg/L,[20] thus these Sb concentrations are not likely to pose an environmental risk to the local environment. Other important parameters analyzed in the leachate water are reported in the ESI.

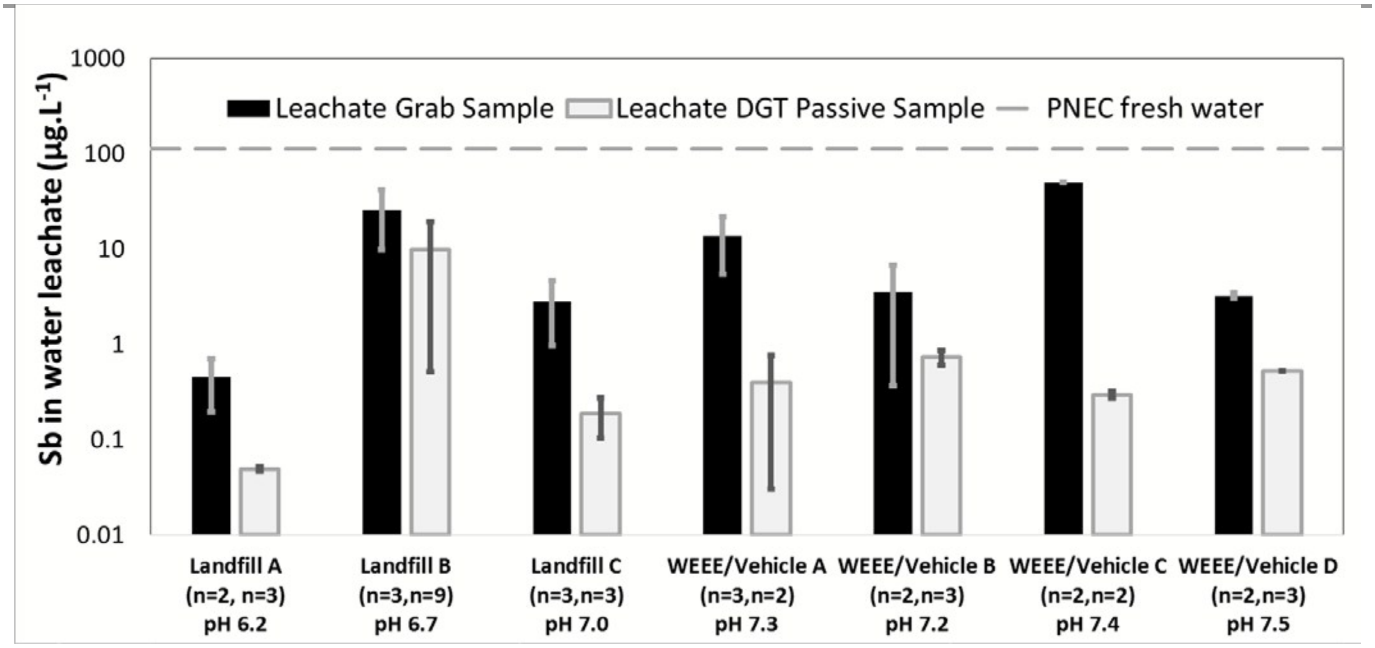

Figure 3 Comparison of Sb concentrations measured in leachate water, $C_{leachate}$, with grab sampling and passive sampling methods. Results are presented according to waste handling facility type and standard deviations are calculated from the average of data collected from sampling campaigns. Also shown is the PNEC value for Sb in fresh water (113 µg L^{-1}).

The Landfill with the largest Sb concentration (Landfill B) is unique in that it contains large quantities of bottom ash, which based on the result of the leaching test may account for the relatively large presence of Sb. Norwegian municipal waste landfills (n=26) in the period (2007 – 2013) reported Sb concentrations of 0.1 - 9 µg/l (average: 1.4 µg/L, n=37),[52] which are within the ranges of Landfills A and C. One review in the literature for municipal waste landfills reported a range in $C_{leachate}$ for Sb of 0 – 3190 µg/L,[53] which indicates that some landfills can have substantially larger Sb than observed here. We would speculate based on the results of the batch test that the presence of plastic and bottom ash would be the most influential waste fractions on leachate concentrations.

3.3.1. MULTIPLE-REGRESSION ANALYSIS WITH WATER PARAMETERS.

Multiple regression analysis were conducted to investigate if any of the water parameters determined (pH, Fe-W DOC, F^-, Cl^-, SO_4^{2-}, ESI Table S2.2) correlated with the grab sample $C_{leachate}$. For this analysis, each individual sample was treated as a separate point. The water parameters that correlated the best and positively with Sb $C_{leachate}$ were F^- and Cl^- followed by Fe: If Landfill C was taken out of the statistic, because it had relatively high Fe concentrations (ranging from 35 to 290 mg L^{-1} (n=6), which is outside the quartile distribution of the median value of 2.5 mg/L (n=37), the resulting correlations for all sites were:

$$\text{Sb } C_{leachate} = 5.78 + 1.64 \text{ Fe } C_{leachate}$$
$$r^2 = 0.43 \text{ (< 0.0001, excluding landfill C)} \quad (2)$$

$$\text{Sb } C_{leachate} = -6.77 + 13.05 \text{ Fe } C_{leachate} + 30.0\, F^- + 0.0014\, Cl^-$$
$$r^2 = 0.89 \text{ (< 0.0001, excluding Landfill C)} \quad (3)$$

The strongest correlating parameter was F^-, explaining 70 % of the variation in leaching, whereas the DOC and pH were not significant. It is likely that the leachate water rich in Cl^- and F^- (environmentally inert and very mobile) also contains higher concentrations of Sb, simply because these are indicators of the amount of dissolving waste present.

3.3.2. GRAB VS DGT SAMPLES

The $C_{leachate,DGT}$ measurements for Sb were consistently lower than the grab samples (Figure 3). The difference is likely due to colloidal or particulate binding of Sb in the leachate water itself, which are too large to diffuse through the hydrated gel of the DGT.

Multiple regression analyses were also performed for $C_{leachate,DGT}$ and the same measured water parameters. $C_{leachate,DGT}$ for Sb was found to correlate with pH, Cl, not with F^-. The concentration of Fe was not significant at all, and thus there were little differences in correlations if Landfill C was included (r^2 = 0.65, p = 0.0002) or not (r^2 = 0.63, p < 0.0014). The best, most significant correlation equation was

$$\text{Sb } C_{leachate,DGT} = -16 + 2.4 \text{ pH} + 0.0006\, Cl^-$$
$$r^2 = 0.64 \text{ (p< 0.0002)} \quad (4)$$

The strongest correlating parameter was Cl^-, explaining 56% of the variation. However, Cl^- is likely correlated with Sb $C_{leachate,DGT}$ only because Cl- is an indicator that many ionic species are present. The weak but positive correlation with pH is expected from previous investigations on the influence of pH on Sb dissolution.[5, 31, 54, 55]

Multiple regression analysis was also performed on the ratio $C_{leachate}/C_{leachate,DGT}$. The variation (excluding the Landfill C data) was, however, only significantly correlated with $Fe_{wat}$by following relationship:

$$\text{Sb } C_{leachate}/C_{leachate,DGT} = -13.1 + 7.7 \text{ Fe } C_{leachate}$$
$$r^2 = 0.66 \text{ (p < 0.0001)} \quad (5)$$

The positive relationship in equation 5 with Fe indicates Sb co-transportation with Fe.

3.4 Air

The air concentrations, C_{air},(ng m^{-3}) and the concentrations in dust itself, C_{dust}, (mg kg^{-1}) are presented in Figure 4 and ESI Table S3.1. Note that C_{air} represents the dust-associated Sb in the air phase, and not volatile Sb. The highest C_{air} were found for emissions from the WEEE/Vehicle facility vent, which were also quite variable, ranging from < 100 to 2200 ng m^{-3}. The maximum concentration in this WEEE/Vehicle facility vent was a factor 10 higher than the maximum concentration in very dusty air surrounding the combustible shredder, which ranged from 25 to 217 ng m^{-3}, it was also than in the vapour emitting from the chimney of the municipal waste incinerator (from < 30 to 100 ng m^{-3}) and much higher than the air in the combustible waste loading dock (9 ng m^{-3}).

In terms of dust concentrations, C_{dust}, the WEEE/Vehicle dust contained <310 to 6816 mg kg^{-1}, which on average is about a factor 3.3 greater than the average observed for C_{waste} of WEEE fractions (ESI Table S3.1). C_{dust} near the combustible shredder ranged from 5 to 44 mg kg^{-1}, which is approximately a factor 2 larger than the average C_{waste} for combustibles. This indicates that the dust fraction of WEEE and combustibles may both be somewhat enriched in Sb compared to the source material. The dust in the combustibles loading dock contained much lower concentrations of Sb (2 mg kg^{-1}), which was 0.2 the C_{waste} value for combustibles. The end-of-chimney C_{dust} value from the incineration plant (<34 to 114 mg kg^{-1}) was only 0.1 the C_{waste} value for fly ash. This is an indication that the ash collecting system is efficient at removing antimony rich ashes before release into the atmosphere.

An important consideration when measuring air-borne Sb data derived from waste-handling facilities is that large, on-site vehicles may emit "brake-dust" that is rich in Sb.[56] For instance, Iijima[40] reported Sb in fly ash to be on average 349 mg kg^{-1} while dust from brake pads contained average concentrations of 146000 mg kg^{-1}. However, the measured C_{dust} of 2 mg kg^{-1} in the combustible loading dock allows the assumption that brake dust did not bias the data; nevertheless, this could be a consideration at other locations.

The larger concentration of Sb in the dust and air from the WEEE/Vehicle shredding corresponds with our general hypothesis that facilities treating plastic rich waste can release more Sb. This was also observed elsewhere. A Chinese study reported Sb in indoor dust from an e-waste village from 6.1 to 232 mg kg^{-1}, which was higher than their reference location of which ranged from 0.66 to 2.45 mg kg^{-1}.[19] Another similar study measured air concentrations in WEEE recycling facilities from 4.2 to 880 ng m^{-3}, which were considerably higher than that measured in offices from 11 to 49 ng m^{-3}.[57] The WEEE/Vehicle concentrations we measured (Figure 4, Table ESI 3.1) overlap but are on the high side of these previous studies. As a basis for comparison, ambient ranges in urban environments in Europe have been reported from 2 to 470 ng m^{-3} and at rural areas locations from 0.0008 to 7 ng m^{-3}.[38]

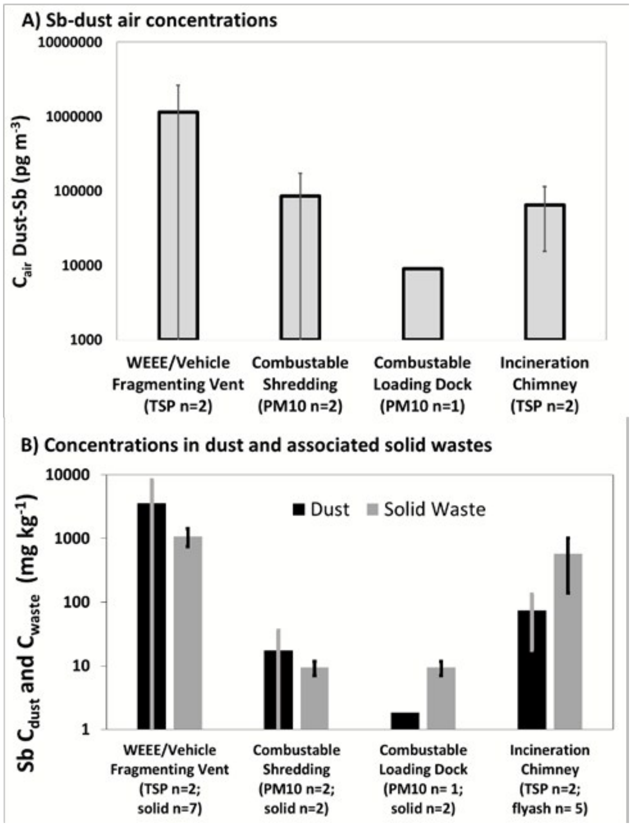

Figure 4. A) Air concentrations of Sb emitting from chimney of a WEEE/Vehicle sorting facility, near the shredder of a combustible sorting facility, the loading dock of a combustible facility, and the chimney of a waste incinerator B) the concentration of Sb in the dust at these facilities compared with the relevant solid waste fraction (WEEE/Vehicle materials, combustibles, and fly ash, respectively).

Conclusions

Plastic rich WEEE and vehicle fluff waste were found to have the highest Sb concentration and to leach more than other waste fractions (Figure 2), supporting the central hypothesis of this study that plastic-rich wastes are the largest potential source of emissions of Sb. Accordingly, water leachate and air concentrations near WEEE/vehicle facilities were elevated in Sb (Figures 3 and 4).

Incineration of waste was found to increase the Sb concentration in the remaining ash residues, with the ratio in fly ash being substantially larger than the bottom ash. However, due to the intrinsic chemistry of these ashes, bottom ash leached Sb more readily than fly ash. As a result landfills rich in bottom ash can also contain leachate with elevated Sb concentrations, similar to those observed near WEEE/Vehicle facilities (e.g Landfill B in Figure 3).

Sb levels in leachate water from waste treatment facilities and landfills were generally below the PNEC for fresh water, and contained predominantly Sb(V) which is less toxic than Sb(III). Thus, the amount of antimony released to water environment from “waste management” appeared to be small in the Norwegian study areas.

The defragmentation and shredding of wastes containing Sb is a major source of Sb in the atmosphere, particularly for WEEE. Here, a gradient in Sb concentrations with distance from the shredder can be expected, as observed in previous studies.

Despite the relatively low levels measured here it is nevertheless worthwhile to include Sb in risk assessments in the vicinity of WEEE, vehicle and bottom ash handling facilities, particularly as other factors could give rise to even higher Sb concentrations than we measured (e.g. larger quantities of Sb-rich plastic, less effective air and leachate cleaning systems, bottom ash deposited in an acidic area, etc.).

An interesting application of this research would be in the area of recycling/reuse of Sb containing waste. Studies on the environmental aspects of Sb leaching related to use of bottom ash or recycled glass for construction material are for instance very scarce. Another interesting application would be in the area of Sb-mineral recovery, especially if Sb increases in economic importance. Waste residues that would be the most suited to Sb-mineral recovery are bottom ashes as well as WEEE/Vehicle plastic fluff, which will increase in their leaching potential with acidification.

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† Electronic Supplementary Information (ESI) available: [extra details regarding field sampling and DGT analysis]. See DOI: 10.1039/b000000x/

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