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ENVIRONMENTAL IMPACT OF RECYCLING AND DUMPING OF WASTE: PCBs, PBDEs, PCDD/Fs, PBDD/Fs, AND PCBDD/Fs AT ZAPALLAL WASTE SITE IN PERU

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Introduction

Urbanisation and industrial growth stimulates the production of hazardous waste. Proper disposal strategies are needed to reduce environmental harm and human health risks associated to waste handling[1]. This is not always common practice, particularly in developing countries[2-4]. Hence, uncontrolled dispose and recycling of waste and waste products has become global environmental issues. In many cases, hazardous waste is neither treated nor separated from the non-hazardous waste fraction, and the dump sites are neither lined nor covered. Local authorities do not necessarily consider environmental impacts of new or existing dump sites. Thus, waste deposits can be allocated to areas without considering the potential distribution of hazardous pollutants in the vicinity, and monitoring and safeties practices, such as covering and fences, are neglected. Inspection of waste before dumping is rare, and therefore illegal dumping of toxic chemicals is common.

Following the global technical development, the production of e-waste is of particular concern. E-waste is today the fastest growing sector of the municipal solid waste stream and currently comprises more than 5% of its total flow, which is equivalent to 20-50 million tonnes a year worldwide[5]. These large quantities in combination with the fact that e-waste contains a wide range of hazardous compounds have turned e-waste into a global environmental issue. In addition, new hazardous compounds, such as dioxins, may be formed as the original e-waste components are degraded. E-waste is often recycled with the aim to take care of its hazardous components and/or to recover its valuable materials. In modern recycling facilities, these two aims are usually combined. In the recycling activities carried out in developing countries, efforts are usually directed towards the valuable materials. Consequently, such activities may result in extensive emissions of hazardous compounds and thereby substantial risks for the recycling workers and the environment.

Compounds of concern at waste sites comprise organic as well as inorganic compounds. The main focus of the current study was to investigate the local environmental impact of open waste handling. We conducted a field study at site in Peru, where wastes and ashes are managed and stored. The levels of a number of well-known persistent organic pollutants (POPs) were measured in ashes and environmental media including locally produced egg. The target compounds included polybrominated diphenyl-ethers (PBDEs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polybrominated DD/Fs (PBDD/Fs), and polychlorinated biphenyls (PCBs).

Materials and methods

The Peruan waste site Zapallal is situated in the Carabayllo district north of Lima on the east side of the Chillon river. The area embraces 440 hectars and is used for dumping and recycling of a wide range of waste types, including urban household waste, industrial waste and hospital waste. The recycling activities at and around the site include e.g. burning of cables and lead batteries and smelting of metals. The methods used include everything from small and partly controlled industrial activities to completely uncontrolled private enterprises. Private activites are carried out by people living in the near vicinity of the waste site, a zone that houses 54 consolidated urban allotments, in which the inhabitants both perform their rudimentary recycling activities and hold animals for egg and meat production, e.g. free range chickens, ducks and pigs. It has been estimated that 30,000 people live in close proximity to the waste site, and may hence be affected by enhanched exposure of environmental pollutants. The climate is extremely arid, and the risk for wind spreading of particles from the ash piles is high. Ashes from the combustion and recycling processes, which generally are dumped directly on the ground in open air or into the nearby Chillon River, are therefore easily spread to the surroundings.

In May 2009, 28 samples of soil, ash, eggs, plants and sediment were collected at the waste site and at places at increasing distance from the site (Table 1). The sampling site furthest away was located >50 km from Zapallal.

Table 1. Samples collected at and in the surroundings of the Zapallal waste site in Peru

Sample	Sample/Site description
Ash 1	Ash from cable burning activities
Ash 2	Ash from a site where plastic film is burned
Ash 3	Ash from a site where lead batteries are burned
Soil 1:1,2,4,5	Soil collected close to the industrial allotments at Zapallal waste site.
Soil 2	Soil collected 200 m from the industrial allotments
Soil 3	Soil collected 300 m from the industrial allotments
Soil 5	Soil collected 1500 m from industrial allotments
Sediment 1	Sediment collected from the Chillon River, 2-3 km south (downstream) of Zapallal
Sediment 2	Sediment collected from the Chillon River, in Trapiche, 50 km upstream Zapallal (reference sample)
Plant 1:1,2,4	Plants collected close to the industrial allotments at Zapallal waste site (at the sample places as the soil samples).
Plant 2	Plant collected 200 m from the industrial allotments
Plant 3	Plant collected 300 m from the industrial allotments
Plant 4	Plant collected 500 m from the industrial allotments
Plant 5	Plant collected 1500 m from the industrial allotments
Plant 6	Plant collected 4000 m from the industrial allotments.
Egg 1	Eggs from free range chicken, 500 m west of industrial allotments
Egg 2	Eggs from free range ducks, 500 m west of industrial allotments
Egg 3	Eggs from free range ducks at the western parts of waste site
Egg 4	Eggs from free range chickens in Trapiche 50 km north of the waste site (reference samples)

The samples were transported to Umeå University, Sweden, where they were analysed using gas chromatography – high resolution mass spectrometry (GC-HRMS).

Results and discussion

The levels of the POPs in ashes and soils are compiled in Table 2. The ash collected at the waste site contained considerable amounts of all contaminants, particularly the ash from the cable burning site that contained 18 µg PCBs (Σ I-PCB), 880 µg PCDD/Fs, 310 µg PBDD/Fs, 94 µg PBCDD/Fs and 11 mg PBDEs per kg dry ash. These levels are comparable to levels found at open e-waste burning sites in Guiyu, China[6-8]. The high levels of PBDEs in the ash can probably be explained by high levels of PBDE containing flame retardants in the cables being burned, which also could explain the high levels of PBDD/Fs and PBCDD/Fs in the ash. The high levels of PCDD/Fs are likely associted to due to presence of PVC-containing cables. The calculated TEQ-values (values not shown) demonstrated that both the PCBs and PBDD/Fs are contributing significantly to the dioxin-like toxicity of the ashes, particularly in the cable ash.

The soil collected in the near vicintity of the waste site (Soil 1:1, 1:2, 1:4, 1:5 and 2) and the downstream sediment contained higher levels of the POPs than the soils collected further away from the site (Soil 3 and 5) and the upstream sediment, respectively (Table 2). This indicates that the environment around the waste site is impacted by the site, even if other urban sources likely also contribute to the elevated levels. The levels were similar to levels found in the rice fields in the Guiyu region in China[7,9], i.e. not hotspot levels but strong

indications of contamination. Accordingly, it appears as the waste site is a significant source of POPs for the surroundings, which was further supported by the PBDD/F-congener pattern found in the samples. As all ash and nearby soil and sediment samples were strongly dominated by PBDFs, it is likley that they all originate from PBDE-mixtures[10]. As for the other contaminants, the highest PBDE-levels in the soil were found close to the waste site.

Table 2. *Total concentrations of I-PCBs, PCDD/Fs, PBDD/Fs, PBCDD/Fs and PBDEs, as well as ratios for PCDDs/PCDFs and PBDDs/PBDFs in various abiotic samples from Zapallal waste site north of Lima in Peru. All concentrations are based on dry weight (d.w.) of the samples.*

	Σ I-PCB (ng kg^{-1} d.w.)	ΣPCDD/F (ng kg^{-1} d.w.)	Ratio PCDD/ PCDF	ΣPBDD/F (ng kg^{-1} d.w.)	Ratio PBDD/ PBDF	ΣPBCDD/F (ng kg^{-1} d.w.)	ΣPBDE (ng kg^{-1} d.w.)
Ash 1	18 000	880 000	0.12	310 000	0.002	94 000	11 000 000
Ash 2	490	3400	0.53	250	0.019	150	1 500
Ash 3	2800	10 000	0.091	50	0.11	160	23 000
Soil 1:1	1000	1000	0.38	78	0.016	36	3500
Soil 1:2	1800	1300	0.38	99	0.015	48	2600
Soil 1:4	1200	1300	0.37	180	0.012	53	51 000
Soil 1:5	640	670	0.42	320	0.007	24	92 000
Soil 2	1800	420	0.41	217	0.008	17	17 000
Soil 3	410	390	0.37	69	0.027	16	3600
Soil 5	120	31	0.43	8.6	0.18	0.58	10 000
Sed. 1	820	170	0.82	74	0.016	15	6100
Sed. 2	120	21	0.49	12*	2.9*	8.1	3700

* The PBDD/F-content in this samples was of unknown reasons completely dominated by 2,3,7,8-TBDD.

All POPs were found in higher concentrations in the eggs collected near the waste site than in the eggs from the reference site (Table 3). The difference was most pronounced for the PCDD/Fs, which were found in 20-70 times higher concentrations close to the waste site than at the reference site, while PCBs, PBDD/Fs and PBDEs were found in 4-5, 1.5-6 and 3-10 times higher levels, respectively. PBCDD/Fs were only detected in eggs from the waste site. In contrast to expectation, eggs from the reference site contained three times as much PBDD/Fs as PCDD/Fs, while a reverse relation was seen in the eggs from the waste site. The contaminant levels in the plants varied, but the levels decreased in general with increasing distance from the waste site (Table 3). However, the contamination levels also appeared to be species-dependent, which made the comparison highly uncertain. For example, levels in Yuccas and the Agave at the waste site differed up to three orders of magnitude.

Table 3. *Total concentrations of I-PCBs, PCDD/Fs, PBDD/Fs, PBCDD/Fs and PBDEs, as well as ratios for PCDDs/PCDFs and PBDDs/PBDFs in eggs and plants from the Zapallal waste site and its surroundings north of Lima in Peru. The concentrations in the eggs are normalized against fat weight and in the plants against wet weight.*

	Σ I-PCB (pg g^{-1} fat / w.w.)	ΣPCDD/F (pg g^{-1} fat / w.w.)	Ratio PCDD/ PCDF	ΣPBDD/F (pg g^{-1} fat / w.w.)	Ratio PBDD/ PBDF	ΣPBCDD/F (pg g^{-1} fat / w.w.)	ΣPBDE (pg g^{-1} fat / w.w.)
Egg 1	2400	92	0.39	19	0.20	37	150 000
Egg 2	3000	140	0.16	79	0.47	57	540 000
Egg 3	2900	290	0.31	76	0.12	34	330 000
Egg 4	640	4.0	0.30	13	0.076	<2	56 000
Plant 1:1	1600	690	0.57	31	0.008	24	14 000
Plant 1:2	640	390	0.44	29	0.008	14	1100
Plant 1:4	14	0.58	0.51	<0.5	-	<2	300

Plant 2	940	340	0.51	14	0.036	19	1700
Plant 3	1200	550	0.46	25	0.028	45	1700
Plant 4	1100	300	0.48	10	0.057	20	1500
Plant 5	660	74	0.56	6.1	-	4.3	950
Plant 6	450	62	0.65	4.4	-	2.2	890

The eggs from the waste site contained 6.1-8.5 pg TEQ g^{-1} fat, with 50-60% contribution from PCDD/Fs, 30-40% from dl-PCBs and 5-10% from PBDD/Fs. These values exceed the EU legislated maximum levels of 3 pg TEQ g^{-1} fat for eggs[11] by 2-3 times.

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