CONCENTRATIONS OF UNINTENTIONAL POPs IN SOILS AND ASHES FROM BENIN, AFRICA

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Abstract
Thirty-three soil and bottom ash samples were collected in Benin and analyzed for unintentional persistent organic pollutants (POPs), namely PCDD/PCDF, dioxin-like PCB, indicator PCB, and hexachlorobenzene as part of their National Implementation Plan to the Stockholm Convention. Of the 33 samples, only four had quantifiable HCB concentrations with the highest value of 2.09 µg/kg dry matter. The concentrations as sum of 7 indicator PCB were low as well with a maximum of 1.23 µg PCB_7/kg in one ash sample. One of the soil samples had 95.4 ng WHO_{1997}-TEQ/kg; for all other soils, PCDD/PCDF ranged from 0.15 ng WHO_{1997}-TEQ/kg to 2.64 ng WHO_{1997}-TEQ/kg. PCDD/PCDF in 19 ash samples ranged 0.43-3.58 ng WHO_{1997}-TEQ/kg but higher concentrations were found in two ashes from uncontrolled burning of biomedical waste in poorly designed furnaces, one ash from aluminium production, and in one ash from the open burning of yam in the field (188 and 264, 249, and 91.1 ng WHO_{1997}-TEQ/kg, respectively). TEQs from dioxin-like PCB were between 1% and 4% of the TEQ from PCDD/PCDF. None of the samples exceeded the "low POP content" of 50 mg/kg for PCB and HCB or 15 µg TEQ/kg for PCDD/PCDF as established in the Basel Technical Guidelines.

Introduction
Polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB), and hexachlorobenzene (HCB) are unintentional chemicals that are formed by a number of industrial and thermal processes where organic carbon, chlorine, and oxygen are present. They are among the twelve initial persistent organic pollutants (POPs) covered by the Stockholm Convention on Persistent Organic Pollutants since they pose serious threats to the environment and to human health. PCDD, PCDF, PCB, and HCB are listed in Annex C of the Stockholm Convention and Article 5 requires that Parties to the Convention shall take measures for "continuing minimization, and where feasible, ultimate elimination" of these POPs. Paragraph (a) of Article 5 of the Stockholm Convention requires the development and implementation of an action plan to "identify, characterize and address the releases of the chemicals listed in Annex C" and subparagraph (i) specifies that the action plan shall include "the development and maintenance of source inventories and release estimates"[1]. In order to fulfill the reporting requirements under the Stockholm Convention, countries that do not have the financial and technical resources to measure releases of PCDD/PCDF have used UNEP's Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases[2]. UNEP is assisting countries in the establishment of their dioxin inventories and together with other implementing agencies is assisting developing countries and countries with economies in transition to address dioxin/furan issues in their National Implementation Plans (NIPs). Within the frame of their NIP and additional funding from the Canada POPs Fund, the Republic of Bénin jointly with UNEP Chemicals collected soil and ash samples and had them analyzed in a laboratory accredited for dioxin/furan analysis, Eurofins-GfA in Germany. The results of this first survey will feed into Benin's NIP and give first indication of unintentional POPs pollution in a Sub-Saharan African country.

Materials and Methods
Sampling protocols were prepared before starting the collection of samples. In brief, soil samples were collected from sites potentially impacted by local industries and other domestic activities covering the whole territory of the Republic of Benin. The site selection was done according to reported activities making them suspect of containing elevated POPs concentrations. At each site five discrete surface soil samples (0-10 cm

depth, vegetation removed) were collected, mixed in a stainless steal bowl, and proportioned into the sampling jars. The sampling sites all had received impacts from discharges of waste or wastewaters. The ash samples were collected from domestic cooking places, from the burning of municipal solid waste and biomedical waste in non-specialized ovens, from open agricultural burning, and from some small informal industries. For each of the ash samples, three sub-samples of bottom ash were taken and put together. The mixed samples were placed into 1 L sterilized glass jars whereby the second served as back-up. Samples of fresh ash were taken after an activity of at least one day of normal operation was accomplished. Unburned residues and visible interfering materials were removed from the sample prior to analysis. The glass jars were wrapped with aluminium foil, placed in plastic bags, and labeled indicating sampling information such as date and time, type, location, sampling personnel, and identification number.

Ten soil and twenty three ash samples were collected and placed into sterilized brown glass jars in March 2006. The samples were shipped *via* express mail to the dioxin laboratory in Germany and analyzed according to EPA Method 1613[3]. The PCDD/PCDF and dl-PCB concentrations are presented in toxic equivalents (TEQ) according to the 1997 WHO-TEF scheme (in WHO_{1997}-TEQ)[4].

Results and Discussion

The numeric results for PCDD/PCDF and dioxin-like PCB in ng WHO_{1997}-TEQ/kg, for the sum of seven indicator PCB and HCB in μg/kg of the soil and ash samples are summarized in Tables 1 and 2. In total, ten soil samples and 23 bottom ash samples were analyzed. It should be noted that for some of the soil samples it was not possible to analyze the second fraction for PCB and HCB. The concentrations presented take into full account the limit of quantification for identified but not quantified congeners. However, it should be noted that for many of the PCB and HCB data, none of the congeners could be quantified; these results with no quantifiable congeners are marked with an asterisk (*).

Of the 33 samples, only four (1 soil sample and 3 ash samples) had quantifiable HCB concentrations; these being close to the limit of quantification. HCB was from non-quantifiable up to 2.09 μg/kg dry matter. In general, also the PCB concentrations (sum of 7 indicator PCB) were low and only one ash sample exceeded a concentration of 1 μg/kg (A22 with 1.23 μg/kg). These concentrations are far below the "low POP content" of 50 mg/kg for PCB and HCB as established in the Basel Technical Guidelines[5].

Similarly, the PCDD/PCDF concentrations in general were low as well. In soils, PCDD/PCDF ranged from 0.15 ng WHO_{1997}-TEQ/kg to 2.64 ng WHO_{1997}-TEQ/kg. However, the one sample that had visible contamination with used oil gave 95.4 ng WHO_{1997}-TEQ/kg. Unfortunately, it was not possible to analyze the PCB and HCB fraction. PCDD/PCDF in 19 ash samples ranged from 0.43 ng WHO_{1997}-TEQ/kg to 3.58 ng WHO_{1997}-TEQ/kg. These included all ashes from cooking places and from the uncontrolled burning of municipal waste. Also, the burned residues from local industries such as burning of sawdust and cotton showed very low values. Two of the three samples from the uncontrolled burning of biomedical waste had high concentrations of PCDD/PCDF: 188 ng WHO_{1997}-TEQ/kg and 264 ng WHO_{1997}-TEQ/kg. A high concentration of 249 ng WHO_{1997}-TEQ/kg was found in the ashes from fusion of aluminum. From the open agricultural burnings, two samples – namely those from the burning of cotton residues and corn – had very low concentrations (0.54 and 0.46 ng WHO_{1997}-TEQ/kg) whereas the ash from the burning of yam in the field gave 91.1 ng WHO_{1997}-TEQ/kg. These four samples with high PCDD/PCDF concentrations also had quantifiable amounts of dioxin-like PCB. However, as expected, the contribution of the dl-PCB to the total TEQ was minor. PCB TEQs were between 1% and 4% of the TEQ from PCDD/PCDF.

The present results are among the first dioxin and PCB data obtained from Africa and present a first orientation as to the contamination of soils and bottom ashes. It is evident that in general the concentrations are low and that as shown for the soil samples, perceived contamination does not necessarily result in high concentrations of unintentional POPs. Nine of the ten soil samples had very low concentrations when compared to datasets obtained elsewhere in Europe, North America or East Asia. However, the soil sample contaminated with waste oil also makes clear the need for improved characterization of the source of contamination and proper management of such waste. The ash samples varied largely. They indicate that the use of typical fuels for domestic cooking and also the burning of "normal" domestic waste does not result in high unintentional POPs pollution in the solid residues. However, some activities could be identified that generated high concentrations in the bottom ashes; especially these would need further investigation to better characterize the local situation and practices – and to finally improve the Toolkit and feed African data into the database – at this stage for solid residues. Future projects should also attempt to sample and analyze flue gases from the combustion processes.

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Table 1: Results of the soil samples. Concentrations include the LOQ for identified but not quantified congeners
Results with no quantifiable congeners are marked *

No	Description	d.m.	PCDD/PCDF (ng TEQ/kg)	dl-PCB (ng TEQ/kg	PCB (ng/kg)	HCB (µg/kg)
S01	Disposal of municipal waste	84.8%	0.53*	0.26*	0.47*	2.50*
S03	Disposal of municipal waste	89.2%	0.50	0.27	0.62	2.50*
S07	Disposal of municipal waste	76.9%	2.76			2.50*
S02	Disposal of wood waste	75.8%	0.15*	0.28*	0.50*	2.50*
S04	Contaminated with used oil	82.2%	95.4			2.50*
S05	Contaminated from cotton industry	94.1%	0.47	0.27	0.85	2.50*
S06	Impact from fish smoking	80.5%	2.64			2.50*
S08	Contaminated after spraying of sludge	88.4%	1.37			2.50*
S09	Contaminated with wastewater from CODA	84.7%	1.30			2.50*
S10	Contaminated with phytopharmaceuticals	86.1%	1.02			2.50

Table 2: Results of the ash samples. Concentrations include the LOQ for identified but not quantified congeners
Results with no quantifiable congeners are marked *

No	Description	d.m.	PCDD/PCDF (ng TEQ/kg)	dl-PCB (ng TEQ/kg	PCB_7 (μg/kg)	HCB (μg/kg)
A03	BCCD – ash domestic cooking	100%	0.46*	2.3	0.2*	0.50*
A04	BCCD – ash domestic cooking	99%	0.45*	0.22*	0.2*	0.50*
A08	BCCD – ash domestic cooking	100%	0.45*	0.22*	0.5*	0.50*
A09	BCCD – ash domestic cooking	99%	0.58	0.22*	0.5*	0.50*
A13	BCCD – ash domestic cooking	95%	0.80	0.23*	0.5*	0.50*
A16	BCCD – ash domestic cooking	100%	0.58	0.22*	0.5	0.50*
A19	BCCD – ash domestic cooking	100%	0.61	0.22*	0.5*	0.50*
A20	BCCD – ash domestic cooking	100%	0.45*	0.22*	0.5*	0.50*
A17	BCCD – ash domestic cooking, smoking of fish	100%	3.58	0.21*	0.5	0.50*
A23	BCCD – ash domestic cooking, smoking of fish	100%	0.99	0.22*	0.5*	
A02	BCDSM – ash from burning of domestic waste	97%	1.21	0.22	0.2*	0.50*
A10	BCDSM – ash from burning of domestic waste	99%	0.46	0.24*	0.5*	0.50*
A14	BCDSM – ash from burning of domestic waste	97%	2.53	0.32	0.6	0.50*
A18	BCDSM – ash from burning of domestic waste	98%	0.56	0.22	0.6	0.50*
A05	BCDBM – ash from biomedical waste incineration	95%	188	7.85	0.5	1.30
A15	BCDBM – ash from biomedical waste incineration	98%	264	10.8	0.5	2.09
A21	BCDBM – ash from biomedical waste incineration	100%	0.52*	0.22*	0.5*	0.50*
A06	BCDI – ash from local industry (burning of sawdust)	94%	1.01	0.27*	0.6*	0.50*
A07	BCDI – ash from local industry (cotton)	100%	0.43*	0.21*	0.5*	0.50*
A22	BCDI – ash from local industry (fusion of aluminum)	99%	249	3.57	1.23	
A01	BCFB – ash from bushfire	99%	0.54	0.22*	0.5	0.50*
A11	BCDA – ash from burning of corn in the field	98%	0.46	0.23*	0.5*	0.50*
A12	BCDRAC – ash from burning of yam in the field	100%	91.1	3.36	0.7	1.93