PCDD/F AND PER- & POLYFLUOROALKYL SUBSTANCES CONTAMINATION IN SELECTED SEWAGE SLUDGES IN NIGERIA

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Introduction

Sewage sludge as solid residues from waste water treatment that contains in addition to nutrients such as phosphorous and nitrogen compounds also a range of toxic by-products[1]. Therefore it is a question if sewage sludges should be applied as bio-solids to agricultural soil or if you should be disposed to landfills or thermally treated. For industrial countries and for economies in transition sewage sludge contain a wide variety of organic pollutants which could have adverse effects on the soils, plant, animals and finally human health if bioaccumulating in the food chain.[1].One class of persistent organic pollutants (POPs) measured in sewage sludge are the polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) which are regulated in some countries in sewage sludge.. A more recent POPs found as contaminant in sewage sludge is PFOS and other per- and polyfluoroalkyl substances (PFASs). PCDD/Fs and PFOS levels in sewage sludge are a subject of concern because they bioaccumulate if e.g. cattle is grazing on pasture contaminated by PCDD/F or PFAS/PFAS, that large amounts of sludges are generated each year, and furthermore one of the alternatives to disposal is the application to agricultural land such as soil conditioners and fertilisers, with the risk that hazardous compounds, such as PCDD/Fs, enter the food chain and bio-accumulate in it[2].

PCDD/F has been included within the dirty dozen as initial POPs in the convention. PFOS and related precursor substances were added in May 2009 as the first fluorinated POPs in the Stockholm Convention[4].

In addition, sewage sludge is an important sink that can lead to the concentration of these persistent organic pollutants (POPs). A range of studies have monitored PCDD/Fs and PFASs in sewage treatment plants in industrialized countries[7,8] and in China[9,10] . For many years, PCDD/PCDF has been reported in sewage sludge of many countries[13]. Decreasing trends have been reported in countries such as Germany and Austria, as well as in Spain[12,13].

For developing and economy in transition countries the monitoring of PCDD/Fs and PFASs is a particular challenge and currently not feasible in almost all developing countries due to the lack of analytical capacity[5,6]. However considering the lack of PCDD/F and PFAS data in most developing countries and the need to understand the fate of these substance classes, data need to be generated in developing county regions such as African countries for a preliminary understanding of the environmental pollution status and fate of PFASs.

It is also important to monitor sewage sludge for chemical pollutants as the purpose of wastewater treatment is to contain and prevent pollutants from being re-released into the environment. The aim of this study was to determine the levels PCDD/Fs and PFASs in sewage sludge from industrial, municipal, and hospital wastewater treatment plants in Nigeria.

Materials and methods

Sampling: Sewage sludge was sampled in three municipal wastewater treatment plants (WWTPs), two industrial effluent treatment plants and one hospital wastewater treatment plant from January – April 2012 at different locations in Lagos, Oyo and Ogun state, all in South West Nigeria.

Extraction and clean up: For PCDD/F the samples were extracted by pressurized Liquid extraction method using two subsequent solvents, toluene and n-hexane, to efficiently recover the target compounds. The sample was spiked with 40 µl each of Internal Standard of PCDD/Fs prior to extraction. The extracts were purified and fractionated on two different open chromatographic columns consisting of multilayered silica and Carbon column. For PFASs, sludge samples were extracted according to an established method[9,14] with a few modifications. The extracts were then dried using a gentle stream of N_2 gas before dilution with HPLC grade water for SPE extraction (using Oasis WAX cartridges (Waters, 6 cc/150 mg)). The elute from SPE was dried by passing a gentle stream of N_2 gas, and subsequently reconstituted using 1:1 volume ratio of MeOH and 4 mM

Ammonium acetate solution to a volume of 200 µL, a procedure which involved addition of recovery internal standard, to make the final volume of 200 µL.

Instrumental analysis: The PCDD/Fs were analyzed by GC/HRMS For PCDD/Fs, a 60 m x 0.25 mm x 0.25 µm J&W Scientific DB 5MS fused silica column (Agilent, Palo Alto, CA, USA) was used for the GC separation with helium carrier gas at 18 psi head pressure. Quantification was done using ^{13}C isotope dilution method.

PFAS were analysed by acquity ultra performance liquid chromatography (UPLC) coupled with Xevo TQS tandem mass spectrometer (MS/MS). For PFASs the chromatographic separation was done by a BEH C18 column. A guard column from Waters Corp. was placed before the main separation column. All compounds were quantified by comparing ratios of native compounds and added ^{13}C-labeled isotopes of the same compounds in the samples and known reference standards, using isotope dilution methodology.

Quality Control/Assurances: To minimize background contamination, all potential sources of instrumental and procedural contamination were eliminated. For PFAS analysis for every batch of 10 samples, 5 blank samples were analyzed and the average concentrations obtained in the blanks was used to correct (subtracted from the analyte sample concentration) all concentration results. The method limit of detection (MLDs) and the method limit of quantification (MLQ) were determined on the basis of a signal-to-noise ratio of three (S/N = 3).

Results and discussion

PCDD/Fs and PFASs were detected in all analyzed Nigerian sewage sludge samples from industrial, domestic, and hospital wastewater treatment plants (Table 1 and 2).

Levels of PCDD/Fs in sewage sludge

Mean total concentrations for PCDDs and PCDFs range from 42.0 to 3206.6 ng/kg dry matter (d.m.) and from 3.2 to 627.6 ng/kg d.w., respectively. The individual results are listed in Tables 1 demonstrate that PCDDs were detected in higher concentration in the sewage sludge compared to PCDFs. Only in the sewage sludge from the waste water plant from the dairy factory the PCDFs levels were higher than the PCDDs (Figure 1). The dominant PCDD congener in most sludges was by far the OCDD with 5 to 15 times higher concentration compared to HpCDD (Figure 1, Table 1). For PCDF in some sludges also the OCDF dominated the PCDF (in particular in the industrial sludge) while for some of the domestic sludges the 1,2,3,4,6,7,8-HpCDF was higher compared to OCDF. The observed patterns of PCDD/Fs in most of the analysed sewage sludges are similar to the profiles reported for sewage around the world with a dominant impact from PCP application the last 60 years[2,3,16].

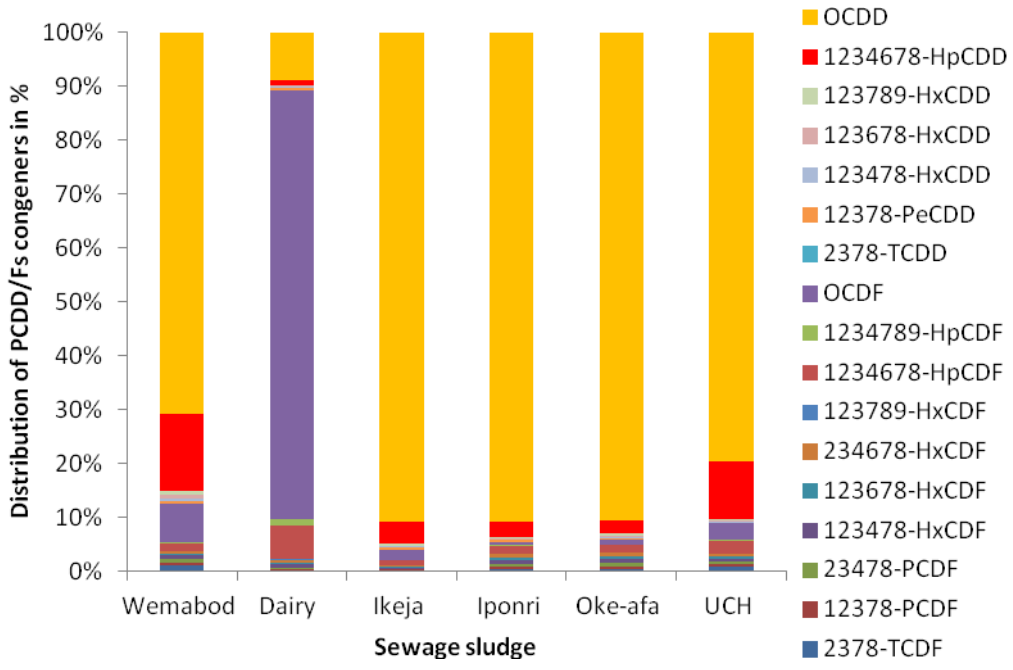

Figure 1: PCDD/Fs congener pattern of sewage sludges from Nigeria

The industrial sewage sludge had the highest concentration of PCDD/Fs (Table 1). This may be due to the use of organochlorine compounds such as PCP or other highly chlorinated aromatic compounds such as Chloranil[18] by e.g. textile industry or leather industries. Further assessments of chemicals used in individual industries are needed to track the pollution source. The industrial use of PCP and sodium-pentachlorophenate where a main contributer to pollution of sewage sludge and the environment[13]. Also the municipal sewage sludge contained measurable concentration of PCDD/Fs and this may be links to the release from household. Horstmann et al.[19] identified that household wastewater was a significant contributor to dioxin-like compounds in sludge and attributed it also to the use of PCP within the textile industry, which is based on the finding that clothing contaminated with dioxin-like compounds can account for the majority of dioxin-like compounds observed in sludge compared to other sources.

The levels in the Nigerian sludge where in the range of the emission factors from the UNEP Dioxin Toolkit20. The domestic sludges, dairy sludge and sludge from hospital were between 6 to 23 ng TEQ/kg d.m. and therefore in the range of the emission factor (EF) of domestic sludge (4 pg TEQ/kg d.m.) and sludge with urban and industrial inputs (EF 20 ng TEQ/kg d.m.). The industrial sludge with 48.2 ng TEQ/kg d.m. were between the EF for urban and industrial inputs and sludge with toolkit EF for specific industrial inputs (200 ng TEQ/kg d.m.).

Table 1: Concentration of PCDD/Fs in sewage sludge sampled in ng/kg dry matter

	Sewage Sludge Concentration in ng/kg dry matter					
	Wemabod Industrial Sludge	**Dairy Sludge**	**Ikeja domestic sludge**	**Iponri domestic sludge**	**Oke-afa domestic sludge**	**UCH Hospital sludge**
2378-TeCDF	39.7	1.9	3.6	14.1	7.9	10.0
12378-PeCDF	15.7	1.0	2.2	12.2	7.5	3.8
23478-PeCDF	25.8	1.2	2.6	12.5	8.5	6.4
123478-HxCDF	25.8	5.6	3.4	18.7	11.1	6.0
123678-HxCDF	14.7	2.0	3.2	13.7	8.7	4.2
234678-HxCDF	11.5	3.0	5.3	19.9	9.1	4.8
123789-HxCDF	7.1	1.6	1.4	5.0	2.8	1.8
1234678-HpCDF	47.6	44.0	14.5	39.8	19.8	26.0
1234789-HpCDF	10.5	7.2	3.6	3.4	1.8	1.0
OCDF	258	560	33.7	17.3	14.2	34.0
PCDFs	**456**	**6278**	**73.3**	**157**	**91.4**	**98.0**
2378-TeCDD	0.400	0.4	1.5	0.4	0.4	0.5
12378-PeCDD	15.5	3.0	4.8	8.0	3.8	1.6
123478-HxCDD	15.7	0.60	5.3	3.4	3.6	1.2
123678-HxCDD	33.7	1.80	2.8	7.4	4.7	4.4
123789-HxCDD	23.8	0.80	5.5	5.8	5.7	2.4
1234678-HpCDD	516	7.20	77.2	79.7	37.5	118
OCDD	258	62.0	1660	2590	1400	880
PCDDs	**3180**	**75.8**	**1760**	**2690**	**1460**	**1010**
PCDD/Fs	**3640**	**703**	**1830**	**2850**	**1550**	**1110**
WHO (2005) TEQ	**48.2**	**6.29**	**11.6**	**23.3**	**13.3**	**9.41**

Levels of PFOS and PFCs in Nigerian sewage sludge[21]

PFOS was the most dominant and detected PFASs in all sludge samples analyzed in this study with quantified concentration range from 100 ng/kg to 540 ng/kg with a mean concentration of 273 ng/kg. Only in a water treatment plant receiving waste water from a diary production, PFOS not detected (<4 ng/kg). Levels of PFBS (maximum 138 ng/kg) and PFHxS (maximum 42 ng/kg) were detected at lower levels. Furthermore PFHxS was only above the detection limit in two plants and PFBS was detected in 5 from the 10 plants studied (Table 2).

This indicate that these two PFOS alternatives were present only in minor concentration in releases from the Nigerian society and is therefore currently not used in significant amounts in the country. The concentrations of the individual PFAAs in the sludge samples ranged from <10 ng/kg to 597 ng/kg for PFDA in one sample (see Table 2). PFOA were detected in all samples in the concentration range of 19–416 ng/kg, with a mean concentration of 90 ng/kg. In general, the long chain PFAAs were present in most sludge samples analyzed. This is interesting as longer chain PFAAs (e.g carboxylates with P8 perfluorinated carbons are known to be bioaccumulative)[11]. The waste water treatment sludge from the Brewery had the highest PFAS levels from all measured sludges. In contrast, lower concentrations were detected in sludge from waste water treatment from the dairy industry with total of approximately 250 pg total PFASs with a major contribution from PFOA (146 ng/kg) and PFOS below detection limit (<10 ng/kg).

In the four sludges from municipal WWTPs from Lagos, PFOS was the dominating PFAS and contamination levels were similar (less than a factor of three) for all four plants: Abesan (276 ng/kg), Ikeja (240 ng/kg), Oke Afa (110 ng/kg) and Iponri (101 ng/kg). Also PFOA (19–42 ng/kg) and PFDA (23–63 ng/kg) was detected in all four municipal WWTP samples in consistent concentrations. The highest PFOS concentration (540 ng/kg) was detected in the sludge of the hospital WWTP. The elevated PFOS levels might stem from the use of PFOS in specific medical devices or from medical clothes using PFC impregnation for protection against blood.

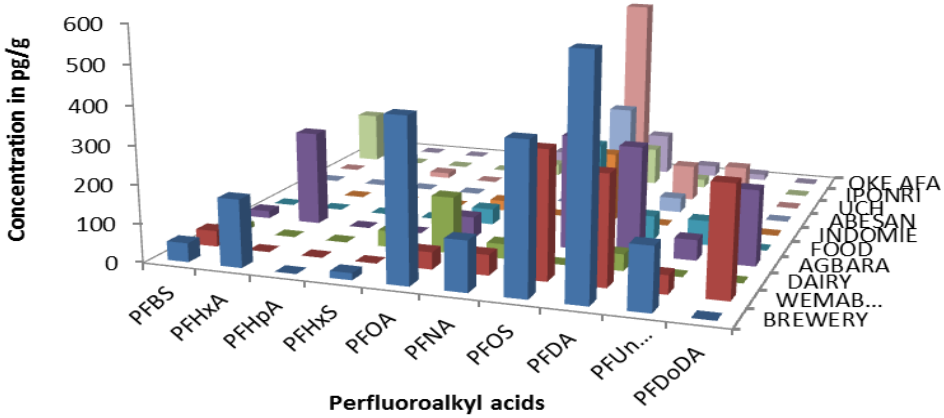

Figure 2: Distribution of PFAS contaminants in Nigerian sewage sludge from municipal and industrial waste water treatment plants.

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