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Concentrations and risks of polychlorinated biphenyls (PCBs) in transformer oils and the environment of a power plant in the Niger Delta, Nigeria



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ABSTRACT

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The concentrations of Σ 14 PCBs were determined, with the aid of gas chromatography-mass spectrometry (GC–MS), in transformer/turbine oils, soils, groundwater, and drainage water collected within a power plant in the Niger Delta of Nigeria. The Σ 14 PCB concentrations in the transformer oils, drainage water, groundwater and soils ranged from 484 to 48506 mg kg⁻¹, 0.99 to 2.95 mg L⁻¹, 0.16 to 0.56 mg L⁻¹ and from 8.4 to 510 mg kg⁻¹ respectively. The congener distribution patterns in these samples indicate the dominance of highly chlorinated homologues (hepta- and octa-PCBs). The Σ 14 PCB concentrations in the transformer oils were above the provisional definition of low persistent organic pollutant (POP) content for PCBs of 50 mg kg⁻¹ as defined in the guidelines on the management of POP waste of the Basel Convention. The concentrations of Σ 14 PCBs in the soils were above the Dutch guideline value of 1000 µg kg⁻¹ and the estimated incremental lifetime cancer risks relating to exposure of humans to PCBs in soils indicate serious health risks. There is therefore a need to implement a surveillance programme in the vicinity of power plants to determine the impacts on the adjacent ecosystem.

1. Introduction

Polychlorinated biphenyls (PCBs) were among the first twelve compounds included in the list of persistent organic pollutants (POPs) in May 2001 by the Stockholm Convection on POPs. They are derived from biphenyl in which between one and ten hydrogen atoms are replaced by chlorine atoms. This gives rise to 209 possible congeners but only about 130 of these are found in commercial products [1]. They are man-made organic compounds that are inert, semi-volatile, resistant to alkalis, acids and oxidising agents, thermally stable, poorly water soluble, lipophilic, and resistant to photodegradation. PCBs have many applications including their use as additives in paints, and as coolants and insulating liquids in power capacitors and transformers [2]. In addition, PCBs have been used as pesticide extenders, hydraulic fluids, flame retardants, cutting oils, in carbonless copy paper, as stabilizing additives in PVC coatings, adhesives, sealants, wood floor finishes, and casting agents [3,4].

Their physicochemical properties cause them to be persistent in the environment, and to exhibit tendencies for bioaccumulation and biomagnification, and long-range transport and deposition in places far removed from emission sources. In addition, they cause chronic toxicity and are ubiquitous in ecosystems and humans [5,6]. The adverse effects of PCBs on humans include impaired reproduction, cancer, neuro-developmental effects in infants, endocrine disruption, and immunotoxicity [5]. The dioxin-like PCBs cause the activation of the arylhydrocarbon receptor which induces the multiplication of genes including xenobotic metabolizing enzymes such as cytochrome P450 (CYPs) and anti-oxidant proteins, e.g paraoxonases and metallothioneins. In addition, exposure to dioxin-like PCBs is known to cause adverse changes in hepatic micronutrient homeostasis. These changes exacerbate severe liver damage [7]. The hepatotoxicity of PCBs in animals is associated with the blockage of the autophagic flux [8] and aggravated loss of clearance capacity and activation of apoptosis [9]. PCBs stimulate changes in the DNA sequence [10] and oxidative stress [11]. For these reasons, the production and use of PCBs has been banned globally, but large quantities of these compounds are still found in old power capacitors and transformers [12,13]. PCBs from these sources can be released into the environment through runoff, volatilization, oil leakage, waste discharges, and dry and wet deposition, thus causing pervasive environmental effects [12,14].

As at 2016, the PCB Elimination Network (http://www.pops.int/ Implementation/IndustrialPOPs/PCB/Guidance/tabid/665/ctl/

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Download/mid/4238/Default.aspx?id = 11&ObjID = 22585) reports that Nigeria could have at least 341 transformers with oil containing PCBs that are still in service. Yet, a review of the literature indicates that there are no published works on the PCB concentrations in the environments of power plants in Nigeria. The present work was aimed at determining the concentrations of PCBs in transformer/capacitor oils, and in soils, groundwater, drainage water and effluent, in the immediate vicinity of a power plant in the Niger Delta of Nigeria. We believe that this is the first work that reports PCB concentrations in these media in Nigeria.

2. Materials and methods

2.1. Study area, sample collection and pretreatment

The study was conducted at the Transcorp Power Station, which is a gas-fired thermal plant, located at Kilometer 20 Ughelli-Patani Road, Ughelli in Ughelli North Local Government of Delta State, Nigeria. The power plant was built in 1964 with an installed capacity of 2×36 MW or 72 MW from two Stal-Laval gas turbines but, today, the Transcorp Power Station stands at 972 MW of electricity with all gas turbines running at full capacity. It is the largest fossil fuel-based generating station in Nigeria and has the capacity of generating 2500 GW h of electricity annually [15].

Four groundwater samples (GW1-GW4), two drainage water samples (DRA1-DRA2), one containment pond water (Effluent), five samples of soil (SL1-SL5) and nine samples of transformer/turbine/compressor oil (T1 to T4 were used transformer oils, FTraO was fresh transformer oil, FTurO was fresh turbine oil, UTB was used turbine oil, UCO was used compressor oil, and USO2 was fresh compressor oil) were collected within the power plant. The oil samples were collected from transformers, turbines and compressors that were in use as well as fresh oil from their spare parts store. The samples were collected in amber-coloured sample bottles, stored in a cooler box containing ice, and conveyed to the laboratory for PCB analysis. The soil samples were air-dried and passed through a 2 mm mesh sieve.

2.2. Chemicals and reagents

A standard PCB mixture containing 14 PCB congeners (PCB-18, PCB-28, PCB-29, PCB-43, PCB-52, PCB-101, PCB-118, PCB-138, PCB-142, PCB-153, PCB-170, PCB-180, PCB-194 and PCB-209) was obtained from Supelco Inc. (Bellefonte, PA, USA), while a mixed standard containing six isotopically labelled ¹³C₁₂PCBs (13 C₁₂PCB-28, 52, 118, 153, 180 and 209) was obtained from Cambridge Isotope Laboratories, Inc. (USA). The PCB congener choice covered the seven indicator PCBs. *n*-Hexane, dichloromethane (DCM) and acetone (pesticide grade) were obtained from BDH, Poole, UK, while anhydrous sodium sulfate, copper powder, Florisil and silica gel were purchased from Merck (Darmstadt, Germany).

2.3. Extraction and clean-up

2.3.1. Soil

A mass of 10 g of each soil sample was spiked with a mixed standard containing the surrogate PCBs and transferred into a Whatman Soxhlet cellulose thimble (previously extracted with DCM). The sample-standard mixture was subjected to Soxhlet extraction for 18 h with 50 mL of DCM/n-hexane (1:1 v/v). The extract was concentrated to 1 mL by rotary evaporation. The concentrated extract was purified on a column packed from bottom to top with 1 g each of anhydrous Na₂SO₄, Florisil, acidified silica gel and copper powder. Elution with 50 mL of hexane provided the PCB fraction. The eluate was subsequently evaporated to 1 mL under a slow flowing stream of pure nitrogen gas.

2.3.2. Transformer oil

The preparation of transformer oil for PCB analysis was carried out following the procedure described by Shin and Kim [16] with slight modifications. Briefly, a 5 g sample of the transformer oil was refluxed for 1 h with 50 mL of 1 M ethanolic potassium hydroxide solution and cooled to room temperature. The PCBs were extracted from the alkalitreated solution by ultra-sonication for 10 min with 30 mL of hexaneacetone (1:1 v/v), washed twice with 100 mL of water, and the extract reduced in volume to about 5 mL by rotary evaporation. Approximately 30–50 mL of concentrated H_2SO_4 was added and the addition repeated until the sulfuric acid phase was clean. A volume of 10 mL of water was used to wash the solution, and the washing process was carried out three times with fresh 10 mL portions of water used each time. The washed extract was concentrated to approximately 1 mL and was purified as described for soil.

2.3.3. Drainage water and groundwater

The drainage water and groundwater samples were prepared for PCB analysis following the procedure described by Sichilongo and Banda [17] with slight modifications. A 50 mL aliquot of the water sample was measured into a 100 mL separating funnel, 10 mL of 1:1 (v/ v) DCM/*n*-hexane was added, and the mixture was subjected to ultrasonication for 15 min. The organic layer was drained into a 250 mL beaker. The extraction process was repeated three times on the aqueous layer with fresh 10 mL aliquots of 1:1 DCM/*n*-hexane each time. The organic layer in each repeated extraction was drained and combined with the first aliquot. The combined extracts were rotary evaporated to 2 mL and cleaned-up as described in the case of the soil samples.

2.4. Instrumental analysis

A gas chromatograph (Agilent Model 7890A) coupled to a mass selective detector (Agilent 5972) (GC-MS) was used to quantify the PCB concentrations in the samples. The column type used for the separations was a HP-5 fused silica capillary column (5% phenyl-95% dimethyl polysiloxane) (30 m length \times 0.25 mm i.d. \times 0.25 μ m film thickness). The initial column temperature was set at 120 °C (holding time 1 min), and was increased to 190 °C at 20 °C min⁻¹, followed by a further increase to 230 $^\circ C$ at 5 $^\circ C$ min $^{-1},$ and finally to 300 $^\circ C$ at a rate of 25 $^\circ C$ \min^{-1} (holding time 10 min). The temperatures of the injector and transfer line were set at 280 and 300 °C, respectively. High purity helium with a constant flow rate of 0.8 mL min⁻¹ was used as the carrier gas. The sample injection volume was 1 µL, injected into the GC-MS in splitless mode. The mode of operation of the mass spectrometer was electron impact ionization (EI) by using automatic gain control. The storage window was programmed at full scan mode in the range of m/z200-500, and the selected ion monitoring (SIM) mode was used for data acquisition. The retention times of the authentic PCB standards alongside the abundance of the quantification and confirmation ions were used to resolve the identities of the PCBs in the samples (Table 1).

2.5. Statistical analysis/quality assurance

All statistical calculations were performed by using Microsoft Excel (Microsoft Inc., USA) and SPSS 16.0 (SPSS Inc., Chicago, IL, USA). The surrogate standard consisting of the ¹³C₁₂-labelled PCBs was used to evaluate the extraction efficiency for the target PCB congeners. The surrogate PCBs were added prior to the extraction processes and the average recoveries of these standards from the different environmental matrices ranged from 89.7 to 103%. Calibration was performed by injections of standard solutions containing a mixture of PCBs at six concentration levels. The R² values for the calibration lines of the PCB congeners are given in Table 1. The blanks were clear of all the investigated PCBs. The limits of detection (LODs) and quantification (LOQs) were determined as the concentrations that produce a signal-tonoise ratio of 3 and 10 respectively (see Table 1).

Table 1

Validation parameters of the GC-MS method for the PCB analytes.

PCB Congener	Retention time/min	Quantification ion	Confirmation ion	LOD/mg kg ⁻¹	LOQ/mg kg ⁻¹	\mathbb{R}^2
PCB-18	8.91	256	258	0.003	0.01	0.9994
PCB-28	9.83	258	260	0.003	0.01	0.9997
PCB-29	10.7	292	294	0.003	0.01	0.9996
PCB-43	11.2	292	294	0.003	0.01	0.9991
PCB-52	12.4	336	338	0.003	0.01	0.9996
PCB-101	13.7	360	362	0.003	0.01	0.9998
PCB-118	13.9	326	338	0.006	0.02	0.9998
PCB-138	14.1	360	362	0.003	0.01	0.9995
PCB-142	14.7	360	362	0.003	0.01	0.9999
PCB-153	16.3	394	396	0.013	0.04	0.9994
PCB-170	16.8	394	396	0.006	0.02	0.9991
PCB-180	17.7	428	430	0.006	0.02	0.9992
PCB-194	18.8	438	440	0.003	0.01	0.9996
PCB-209	21.2	441	443	0.003	0.01	0.9999

2.6. Incremental lifetime cancer risk assessment

The model equations and conditions stated by the US EPA [18,19] were used to estimate the incremental lifetime cancer risk (ILCR) for human exposure to PCBs through dermal contact, accidental ingestion, and inhalation of soil particles. The total carcinogenic risk was evaluated by adding up the risks arising from these three exposure pathways [14].

$$ILCR_{ing} = \frac{C_{soil} \times IngR \times EF \times ED \times CF \times SFO}{BW \times AT}$$
(1)

ILCR_{derm}

$$=\frac{C_{soil} \times SA \times AF_{soil} \times ABS \times EF \times ED \times CF \times SFO \times GIABS}{BW \times AT}$$
(2)

$$ILCR_{inh} = \frac{C_{soil} \times InhR \times EF \times ET \times ED \times IUR}{PEF \times AT^*}$$
(3)

where ILCRing, ILCRderm, and ILCRinh are the ILCR via unconscious ingestion, dermal contact and inhalation of soil particles, C_{soil} represents the measured concentration of PCBs in soil (mg kg $^{-1}$), *IngR* represents the ingestion rate of soil (100 mg d^{-1} for an adult), *EF* represents the exposure frequency (350 days/year, excluding 15 days of holidays), ED represents the exposure duration (52 years was used based on the average life expectancy of a Nigerian), CF is the conversion factor (1×10^{-6}) , SFO signifies the oral slope factor (2.0 mg kg⁻¹ d⁻¹), BW is the average body weight (65 kg), AT represents the averaging time for carcinogens (days) estimated as $52 \times 365 = 25,550$ days, SA represents the surface area of the skin in contact with soil (3300 cm²) including exposed hands and arms, AFsoil represents the skin adherence factor for soil (0.2 mg cm⁻²), *InhR* is the inhalation rate which is 15.8 m³ d⁻¹ for adults, ABS and GIABS depict the dermal absorption factor (0.1) and gastrointestinal absorption factor (1) respectively. ET, PEF and IUR represent the exposure time (8 h d^{-1}), soil to air particle emission $(1.36 \times 10^9 \,\mathrm{m}^3 \,\mathrm{kg}^{-1}),$ and inhalation unit factor $(5.7 \times 10^{-1} \,\mu g \,m^{-3})$ respectively [20,21].

Eq. (1) was adopted for the estimation of the ILCR associated with drinking of water sourced from the boreholes within the power plant premises. Since the recommended daily intake of water is 2 L d⁻¹, a consumption rate of 667 mL per 8 h working period was assumed. The quantitative categorization of cancer risk is as follows: $\leq 10^{-6}$ = very low; 10^{-6} to $\leq 10^{-4}$ = low; 10^{-4} to $\leq 10^{-3}$ = moderate; 10^{-3} to $\leq 10^{-1}$ = high and $\geq 10^{-1}$ = very high [22].

3. Results and discussion

3.1. Concentrations and distribution patterns of PCBs

The Σ 14 PCB concentrations in the transformer oils, and groundwater, drainage water and soils from the power plant are displayed in Tables 2–4. The concentrations of the Σ 14 PCBs ranged from 0.16 to 0.56 mg L⁻¹ in the groundwater samples, 0.99 to 2.95 mg L⁻¹ in the drainage and containment pond waters, 484 to 48,506 mg kg⁻¹ in transformer/turbine and compressor oils, and from 8.4 to 510 mg kg⁻¹ in the soils. The Σ 14 PCB concentrations in the soils and drainage water were higher than those of the groundwater samples. However, the concentrations of the Σ 14 PCBs in the transformer and compressor oils were several thousand-fold higher than the measured concentrations in the other environmental matrices around the power plant.

Table 2

Concentrations	of	PCBs	(mg	L-	· ')	in	water	sam	oles
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	GW1	GW2	GW3	GW4	DRA1	DRA2	Effluent
PCB-18	< 0.01	< 0.01	< 0.01	< 0.01	0.15	0.02	0.11
PCB-28	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01
PCB-29	< 0.01	< 0.01	< 0.01	< 0.01	0.04	0.05	0.01
PCB-43	< 0.01	< 0.01	< 0.01	< 0.01	0.03	0.12	0.1
PCB-52	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.04	0.1
PCB-101	< 0.01	< 0.01	< 0.01	< 0.01	0.03	< 0.01	0.31
PCB-118	< 0.01	< 0.01	< 0.01	< 0.01	0.06	0.08	0.04
PCB-138	< 0.01	< 0.01	< 0.01	< 0.01	0.06	0.02	0.01
PCB-142	< 0.01	< 0.01	< 0.01	< 0.01	0.21	0.02	0.07
PCB-153	< 0.01	< 0.01	< 0.01	< 0.01	0.04	< 0.01	0.08
PCB-170	< 0.01	< 0.01	< 0.01	< 0.01	0.08	0.07	0.09
PCB-180	0.43	0.1	0.13	0.14	0.27	0.42	0.26
PCB-194	0.11	0.04	0.25	0.08	0.07	0.13	0.31
PCB-209	0.01	0.02	0.01	0.01	1.89	0.01	0.09
TOTAL	0.56	0.16	0.39	0.23	2.95	0.99	1.59
Tri-PCBs	< 0.01	< 0.01	< 0.01	< 0.01	0.19	0.08	0.13
Tetra-PCBs	0.01	< 0.01	< 0.01	< 0.01	0.05	0.16	0.2
Penta-PCBs	< 0.01	< 0.01	< 0.01	< 0.01	0.09	0.08	0.35
Hexa-PCBs	< 0.01	< 0.01	< 0.01	< 0.01	0.31	0.04	0.16
Hepta-PCBs	0.43	0.1	0.13	0.14	0.35	0.49	0.35
Octa-PCBs	0.11	0.04	0.25	0.08	0.07	0.13	0.31
Deca-PCBs	0.01	0.02	0.01	0.01	1.89	0.01	0.09
Indicator	0.43	0.10	0.13	0.14	0.48	0.57	0.81
PCBs							

Tri-PCBs = PCB-18 + PCB-28 + PCB-29

Tetra-PCBs = PCB-43 + PCB-52

Penta-PCBs = PCB-101 + PCB-118

Hexa-PCBs = PCB-138 + PCB-142 + PCB-153

Hepta-PCBs = PCB-170 + PCB-180

Octa-PCBs = PCB-194

Deca-PCBs = PCB-209

Indicator PCBs = PCB-28 + PCB-52 + PCB-101 + PCB-118 + PCB-138 +

PCB-153 + PCB-180

Concentrations of PCBs (mg kg^{-1}) in transformer oil samples.

			1						
	T1	T2	T3	T4	FTraO	FTurO	UTB	UCO	USO2
PCB-18	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-28	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-29	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-43	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-52	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-101	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-118	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-138	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-142	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-153	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-170	164	370	< 0.01	< 0.01	173	80.3	< 0.01	< 0.01	< 0.01
PCB-180	617	3412	97.0	247	3042	1099	1019	48004	2320
PCB-194	62.4	419	387	26384	285	256	374	502	160
PCB-209	84.5	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
TOTAL	927.9	4201	484	26,631	3500	1435.3	1393	48,506	2480
Tri-PCBs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Tetra-PCBs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Penta-PCBs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Hexa-PCBs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Hepta-PCBs	781	3782	97	247	3215	1179.3	1019	48004	2320
Octa-PCBs	62.4	419	387	26384	285	256	374	502	160
Deca-PCBs	84.5	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Indicator PCBs	617	3412	97.0	247	3042	1099	1019	40008	2320

Tri-PCBs = PCB-18 + PCB-28 + PCB-29

Tetra-PCBs = PCB-43 + PCB-52

Penta-PCBs = PCB-101 + PCB-118

Hexa-PCBs = PCB-138 + PCB-142 + PCB-153

Hepta-PCBs = PCB-170 + PCB-180

Octa-PCBs = PCB-194

Deca-PCBs = PCB-209

Indicator PCBs = PCB-28 + PCB-52 + PCB-101 + PCB-118 + PCB-138 + PCB-153 + PCB-180

 Table 4

 Concentrations of PCBs (mg kg⁻¹) in soil samples.

	SL1	SL2	SL3	SL4	SL5
PCB-18	0.95	5.65	< 0.01	< 0.01	< 0.01
PCB-28	0.09	< 0.01	< 0.01	< 0.01	< 0.01
PCB-29	1.15	0.27	< 0.01	< 0.01	< 0.01
PCB-43	2.13	1.19	< 0.01	< 0.01	< 0.01
PCB-52	1.04	0.32	0.42	< 0.01	0.41
PCB-101	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-118	3.94	< 0.01	0.52	< 0.01	0.77
PCB-138	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB-142	1.73	< 0.01	< 0.01	< 0.01	< 0.01
PCB-153	3.34	< 0.01	< 0.01	< 0.01	< 0.01
PCB-170	2.62	20.5	0.8	< 0.01	< 0.01
PCB-180	12.8	4.4	505	13.6	4.38
PCB-194	3.67	19.6	3.31	27.4	2.82
PCB-209	0.49	8.16	< 0.01	< 0.01	< 0.01
TOTAL	33.95	60.09	510.05	41.0	8.38
Tri-PCBs	2.19	5.92	< 0.01	< 0.01	< 0.01
Tetra-PCBs	3.17	1.51	0.42	< 0.01	0.41
Penta-PCBs	3.94	< 0.01	0.52	< 0.01	0.77
Hexa-PCBs	5.07	< 0.01	< 0.01	< 0.01	< 0.01
Hepta-PCBs	15.42	24.9	505.8	13.6	4.38
Octa-PCBs	3.67	19.6	3.31	27.4	2.82
Deca-PCBs	0.49	8.16	< 0.01	< 0.01	< 0.01
Indicator PCBs	21.2	4.72	506	13.6	5.60

Tri-PCBs = PCB-18 + PCB-28 + PCB-29Tetra-PCBs = PCB-43 + PCB-52

Penta-PCBs = PCB-101 + PCB-118

Hexa-PCBs = PCB-138 + PCB-142 + PCB-153

Hepta-PCBs = PCB-170 + PCB-180

Octa-PCBs = PCB-194

Deca-PCBs = PCB-209

Indicator PCBs = PCB-28 + PCB-52 + PCB-101 + PCB-118 + PCB-138 + PCB-153 + PCB-180

The $\Sigma 14$ PCB concentrations in the soil samples were above the $60 \,\mu g \, kg^{-1}$ value set as the regulatory limit for PCBs in ambient soil by the defunct USSR Ministry of Health in 1991 [23]. The Σ 14 PCB concentrations in the soil samples also exceeded some international regulatory limits such as the Dutch action intervention values, the Australian and New Zealand ecological investigation levels (1000 $\mu g \; kg^{-1)}$ [24,25], and the Canadian soil guideline for residential areas $(1300 \,\mu g$ kg^{-1}) [26]. A comparison of the measured concentrations of PCBs with those reported in other studies is usually complex because of the variations in the selected congeners and related statistics. However, the levels of $\Sigma 14$ PCBs in soils from the power plant were comparable to the total PCBs (120,000 µg kg⁻¹) around a former telecommunication manufacturing site in south west England [27] and a PCB production site in Sauget, USA (150-27,000 μ g kg⁻¹) [28], but were higher than the total PCB concentrations found around an electrical transformer in Ghana [29], a chemical factory [30], rural/urban soils [31-36], soils around e-waste recycling sites [37-41], mountain soils [42], and soils around industrial sites [1]. The Σ 14 PCB concentrations in the transformer oils were higher than those $(nd-48.33 \text{ mg kg}^{-1})$ found in transformer oils from Korea [16]. The Basel Convention set 50 mg kg⁻¹ as the acceptable limit for the classification of waste in the POPs regulation [43]. The levels of PCBs in the analyzed transformer oil samples exceeded this limit and also that of the Republic of Korea Ministry of the Environment limit which is 2 mg kg^{-1} [44].

3.2. PCB profiles

Generally, the hepta-PCBs constituted significant proportions (0.9–99.2%) of the Σ 14 PCBs in these samples (Figs. 1–3), which indicates that the use of PCBs in the power plant is the major source of contamination. Tri-, tetra-, penta-and hexa-PCBs were less than the limit of quantification in most of the samples, except for soils and drainage water/containment pond water samples. The occurrence of





Fig. 3. PCB profiles in soil samples.

other PCB homologues in the drainage water and soil samples may be related to microbial transformation, and weathering of higher chlorinated PCBs into less chlorinated PCBs. The tri-PCBs constituted less than 10% of the Σ 14 PCBs in the drainage water and soil samples (Fig. 1 and Fig. 3).

There are similarities in the compositions of PCBs in the soils collected in the vicinity of the power plant. The hepta-PCBs are the major PCB homologues and constituted 33.2–99.2% of the Σ 14 PCBs in these soil samples, while the octa-PCBs constituted 0.6–66.8% of the Σ 14 PCBs in these soil samples. The tri-, tetra-, penta and hexa-PCBs were found in one to four out of the five soil samples investigated. The tri-, tetra- and penta-PCBs were detected at levels less than 6.0 mg kg⁻¹ in these soils. PCB-180 was the main determinant of the hepta-PCB concentrations in these soils except for SL2 where PCB-170 constituted

34% of the Σ 14 PCBs.

Of the 14 PCB congeners investigated, only PCB-180, PCB-194 and PCB-209 were detected in the groundwater samples. PCB-180 constituted the major proportion of the Σ 14 PCBs (33.3–76.8%) in the groundwater samples except for GW-3 where PCB-194 constituted 64.1% of the Σ 14 PCBs. In the groundwater samples, the hepta-PCBs constituted 33.3–76.8% of the Σ 14 PCBs, whereas the octa-PCBs constituted 19.6–64.1% of the Σ 14 PCBs. The congener distribution patterns in the drainage water are entirely different from those observed in the soil, groundwater and transformer/turbine oils. The majority of the 14 PCB congeners were found in the drainage water samples except for a few cases. The dominant PCB homologues in the drainage water samples were hepta-PCBs except in the case of DRA1 that had a higher concentration of deca-PCBs (PCB-209). Results from earlier reports suggest that high concentrations of PCB-209 found in wastewater treatment plants might have originated from industrial sources (although the kind of industries is yet to be known) [13,45,46].

The hepta- and octa-PCBs were the only PCB homologues found in the transformer, compressor and turbine oils investigated. PCB-180 was the dominant PCB congener in these oil samples except in the case of T3 and T4 that had higher concentrations of PCB-194. PCB-170 was detected in four of the oil samples investigated and constituted 4.9-17.7% of the $\Sigma 14$ PCBs in these oil samples. The PCB homologue profile in these transformer oils was different from that of Chinese transformer oil. For example, the PCB homologue profile of Chinese transformer oil followed the order: tri-PCBs (63%) > tetra-PCBs (24%) > di-PCBs (9%), and Σ PCBs in the oil contained 42.9% chlorine [47]. PCBs were usually applied as technical mixtures and not as individual compounds, and 70% of the PCBs manufactured globally were tri-to-penta-chlorinated PCBs, with trichlorinated ones as the dominant homologues [31,48]. Aroclors are PCB mixtures produced from approximately 1930 to 1979, and are potential sources of PCBs in the environment. Of the nine Aroclors, Aroclor 1016, 1242, 1248, 1252 and 1260 are the most commonly used. The PCB profiles in the oils, soils and other environmental matrices within the power plant consist of mainly hepta- and octa-PCBs and point to the fact that Aroclor 1252 and 1260 are still in use in this area.

3.3. Risk assessment

The total risk is related to the exposure from all possible routes (dietary consumption included) and the aggregated exposure should ideally be considered [49,50]. In addition, risk can be higher as real exposure is related to chemical mixtures of many more chemicals which manifest the same toxicities at low doses. Their effects and possible interactions can manifest at the concentrations of the individual components, which when tested alone, cannot be measurable by the available conventional testing methods. Therefore, there is a need to develop sensitive methods that account for multiple adverse outcomes, which is similar to what occurs in human conditions [51,52]. In this study, the risk assessment was based on human exposure to PCBs in soils around the power plant through dermal contact, inhalation and unconscious ingestion of soil particles during working hours. We did not incorporate other possible sources of exposure to PCBs such as those arising from inhalation, food consumption, drinking water at home, and exposure to outdoor and indoor dusts, etc. The estimated cancer risk

Soil Samples RISK _{ING} RISK _{INH}	RISK _{DERM}	Total Cancer Risk	Water Samples	Daily Intake/ μ g kg ⁻¹ bw d ⁻¹	Total Cancer Risk
$ \begin{array}{cccc} SL1 & 6.26 \times 10^1 & 1.24 \times 10^- \\ SL2 & 1.11 \times 10^2 & 2.20 \times 10^- \\ SL3 & 9.41 \times 10^2 & 1.87 \times 10^- \\ SL4 & 7.56 \times 10^1 & 1.50 \times 10^- \\ SL5 & 1.55 \times 10^1 & 3.07 \times 10^- \end{array} $	$\begin{array}{ccc} 7 & 2.50 \times 10^{-1} \\ 7 & 4.42 \times 10^{-1} \\ 6 & 3.75 \\ 7 & 3.02 \times 10^{-1} \\ 8 & 6.17 \times 10^{-2} \end{array}$	$\begin{array}{l} 6.29 \times 10^{1} \\ 1.11 \times 10^{2} \\ 9.44 \times 10^{2} \\ 7.59 \times 10^{1} \\ 1.55 \times 10^{1} \end{array}$	GW1 GW2 GW3 GW4	6.23 1.78 4.34 2.56	6.89 1.97 4.80 2.83

values associated with exposure of humans to PCBs in the soil through dermal contact, unconscious ingestion, and inhalation are given in Table 5. The risk of PCB exposure from the ingestion pathway exceeded that from dermal contact and inhalation. The total cancer risk values for human exposure to PCBs in the soil ranged from 15.5 to 944 which suggest a very high risk. The estimated probabilistic cancer risk is by far greater than the acceptable risk of one chance in a million of equally exposed persons to suffer the risk of cancer or cancer-linked illness. The dietary intakes of PCBs from drinking water sourced from the boreholes on the premises of the power plant ranged from 1.78-6.23 μ g kg $^{-1}$ bw d $^{-1}$ which exceeds the tolerable intake value. As given in Table 5, the total cancer risk (1.97–6.89) associated with drinking the water from the boreholes suggests serious adverse effects arising from these compounds.

4. Conclusion

The congener distribution patterns in these samples indicate the dominance of highly chlorinated homologues (hepta- and octa-PCBs). The PCB concentrations in transformer oils exceeded the Basel Convention guideline value of 50 mg kg^{-1} generally accepted as the limit for waste classification in the POPs regulation. The $\Sigma 14$ PCB concentrations in the soils were above the Dutch guideline value of 1000 µg kg⁻¹ and the estimated incremental cancer risks associated with human exposure to PCBs in soils indicate a very high risk. It is therefore imperative to carry out constant and systematic surveillance of PCB concentrations in order to elucidate the long-term trends and impacts of the power plant on the surrounding ecosystem. Therefore, further studies on PCB concentrations and those of other halogenated hydrocarbon contaminants in the biota, soils, surface water and sediments around the power plant are required so as to provide a detailed and complete appraisal of the impacts of the power plant on the adjacent ecosystem.

Declaration of Competing Interest

The authors declare no conflict of interest.

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