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Research

Persistent organic pollutants in sediment of a tropical river: the case of N'djili River in Kinshasa (Democratic Republic of the Congo)

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Abstract

Surface sediments collected in several areas along the N'djili River, in the Kinshasa Province, Democratic Republic of the Congo, were analyzed for persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), organochlorine, polycyclic aromatic hydrocarbons (PAHs), and also organophosphorus and pyrethroid (PYR) pesticides. High values of POPs were determined in the DIGUE area of the river reaching 710 µg kg^{-1} for Σ_{12} PCBs, 397 µg kg^{-1} for Σ_6 DDTs, 1138 µg kg^{-1} for Σ_{16} PAHs, and 23 µg kg^{-1} for Σ_6 PBDEs. Regarding toxic effects on aquatic biota, the Total PCBs ($\Sigma_{7\times4.3}$) were above the Threshold Effect Level (TEL) value of 34.1 µg kg^{-1} and above the Probable Effect Level (PEL) value of 277 µg kg^{-1} in most sampling sites. Σ_{16} PAHs values were, in general, below the TEL value of 610 µg kg^{-1}, but with exceptions for several sampling sites where values exceeded the TEL value. The Σ_6 DDTs in all sampling sites were higher than both TEL and PEL values of 6.15 and 20.03 µg kg^{-1}, respectively. These values above TEL and PEL indicate potential adverse effects on benthic organisms. In general, the ratio values of (DDD + DDE)/DDT were higher than 0.5 reflecting past DDT use mostly, and Fluo/(Fluo + Pyr), IDP/(IDP + BghiP) and BaA/(BaA + Chry) ratios indicated several PAHs origins including petrogenic and pyrolytic sources, petroleum, grass, wood and coal combustion. Globally, the results of this research showed high contamination of N´djili River sediments by a plethora of organic pollutants and at toxic levels to the aquatic biota. Furthermore, the river water quality might be not suitable for human consumption.

Article highlights

- Persistent Organic Pollutant (POPs) concentrations were assessed in sediments from N'djili River using gas chromatography.
- Found an extensive contamination by pesticides, hydrocarbons, polychlorinated biphenyls, polybrominated diphenyl ethers.
- Various sources of polycyclic aromatic hydrocarbons, including pyrolytic, grass, wood and coal combustion.

Keywords Persistent organic pollutants · GC–MS/MS · River sediments · Ecotoxicity

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1 Introduction

Contamination of surface waters by persistent organic pollutants (POPs) is nowadays very widespread and became a major concern worldwide. POPs are a group of organic compounds that have toxic properties, persist in the environment, accumulate in food chains and pose a threat to human health and the environment. POPs include several classes of chemical compounds, such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCs), polycyclic aromatic hydrocarbons (PAHs), and polybrominated diphenyl ethers (PBDEs) [1]. In general, POPs are hydrophobic compounds, with high octanol–water partition coefficients (K_{ow}) and, once released into the environment they easily bind to organic matter. Many of these contaminants are not readily degraded and persist long time in the environment which facilitates their environmental levels to increase [2]. Furthermore, these contaminants can be concentrated by biota and transferred in food webs, posing toxic hazards to environmental and human health [2–6]. As the dispersion of such chemicals poses a hazard to public health, persisting with environmental contamination is not a sustainable way of life.

POPs are present in discharges of untreated urban sewage and in agricultural and industrial effluents and these are the main sources of environmental contamination. Currently, this is a major problem in developing countries in Africa and elsewhere, and frequently it still is overlooked [7–11]. In the Democratic Republic of the Congo (DRC), due to the lack of suitable regulations on agrochemicals and poor law enforcement, POPs are often handled and applied in a careless manner in rural and urban environments. In addition, PCBs, PAHs, OCs, PBDEs have high chemical stability and once released into the environment may be transported by water and atmospheric processes to locations far away from their application zone [2, 12].

Due to their environmental persistence and risks to human health, the ban on the use of POPs was agreed at international level [1]. Nevertheless, due to the low cost of these chemicals some, such as the OC pesticides, are still used in developing countries. Among the OCs, DDTs are used for sanitary purposes in many regions [4, 13–17]. In view of the above, the assessment of concentrations and spatial distribution of POPs is needed to evaluate the status of the environment and the ecological and public health risks posed by these compounds [11].

Few studies on POPs have been conducted in the Congo River Basin [8, 14, 18, 19]. The N´djili River is a major tributary to the Congo River, flowing through heavily populated areas in the Kinshasa Province and it is also the source of drinking water to the capital city of DR Congo. The current study focused on the assessment of the contamination of N'djili River by a wide range of persistent organic pollutants.

2 Materials and methods

2.1 Study area and sediment sampling

The N'djili River is a tributary to the Congo River crossing Kinshasa, the capital city of the Democratic Republic of the Congo with a population of about 15 million inhabitants. The N'djili River flows from south to north through Kinshasa urban areas and receives discharges of anthropogenic pollutants from several sources, such as untreated urban sewage and industrial and agricultural effluents [20–22]. This river is also a fishing ground, a source of irrigation water, and a main source of the drinking water supply to the population of Kinshasa.

The region has a tropical climate with a rainy and dry season, and the average rainfall is 1400 mm per year. With increasing deforestation for installation of new settlements and coal production, the erosion of soil by rainwater has increased and, consequently, the turbidity of river water increased as well. The surface runoff also enhanced the carriage of litter and chemical contaminants into the rivers [23–25].

Sediment samples were collected at 12 sites along the Ndjili River (Fig. 1 and Table 1). The sampling sites were located in four areas, namely, CECOMAF (n = 3 sites, labelled as 1A, 1B, 1C), CAPT (n = 3 sites, labelled as 2A, 2B, 2C), MTT (n = 3 sites, labelled as 3A, 3B, 3C) and DIGUE (n = 3 sites, labeled as 4A, 4B, 4C). All these sites are characterized by intensive human activities leading to uncontrolled domestic waste landfills, household effluent discharges, and direct discharges of untreated effluents from farms, industries, and septic tanks into the river (Fig. 2).

The acronym CECOMAF stands for "Centre de Commercialisation des Produits Maraîchers et Fruitiers", in French). Several human activities take place in this area, including fishing and agriculture as described by Lundemi et al. [20]. CAPT comes from the word "captage" (in French). At this place, the national water treatment and distribution agency called "Régie de Distribution d'Eau" (in French) collects the N'djili River water to supply Kinshasa with drinking water. MTT is

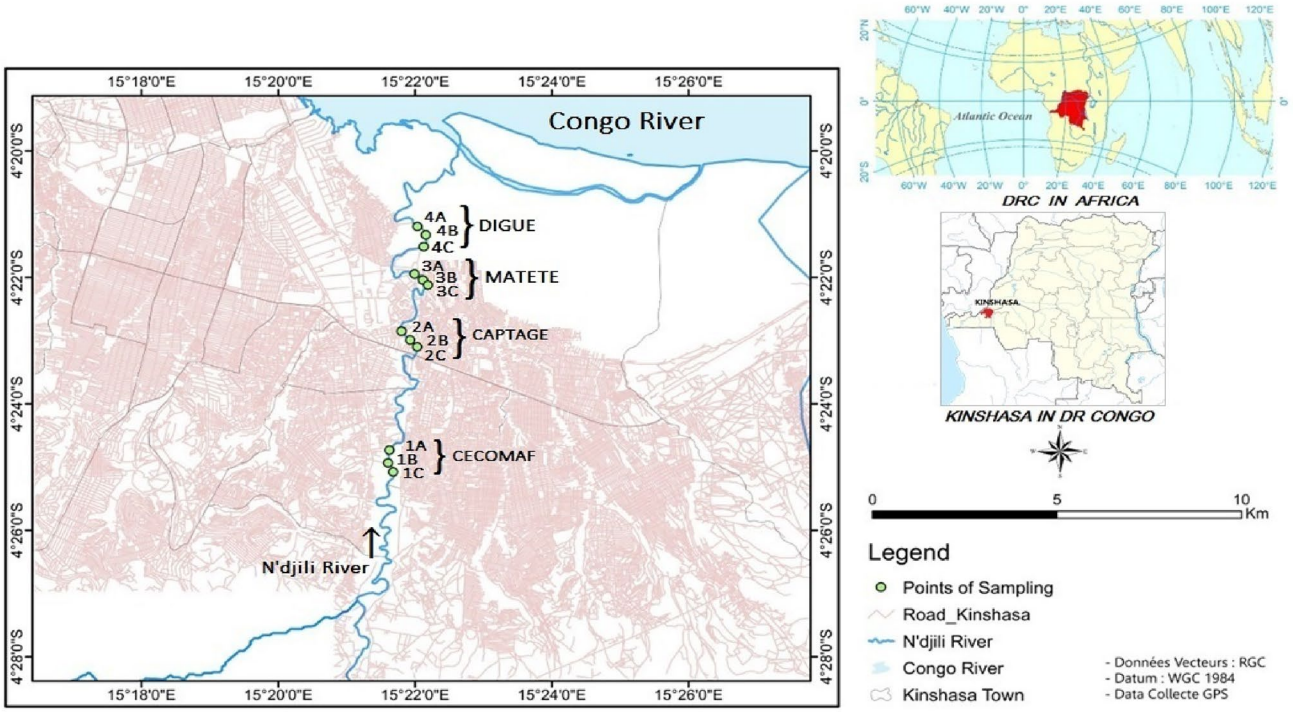

Fig. 1 Study areas and location of sampling points along the N´djili River

Table 1 GPS coordinates of sampling points and sediment physicochemical characteristics

Sampling areas	Sample	Latitude (S) Longitude (E)	Clay	Silt	Sand	Textural class	WC (%)	OM (%)	$CaCO_3$ (%)
	1A	4°25′36.9 ″ 015°21′40.04 ″	6.70	23.26	70.04	Silty sand	49.68	11.16	2.62
CECOMAF	1B	4°25 ′37.07 ″ 015°21′41.01″	7.38	21.55	71.07	Sandy silt	52.08	10.05	2.83
	1C	4°25 ′37.63 ″ 015°21′53.32 ″	6.80	21.1	72.1	Silty sand	50.07	10.64	1.97
	2A	4°23 ′17.05 ″ 015°21′58.08 ″	0.90	49.61	49.49	Sandy silt	54.77	5.95	0.83
CAPT	2B	4°23 ′17.08 ″ 015°21′57.04 ″	0.97	49.05	49.98	Sandy silt	50.12	4.75	0.96
	2C	4°23 ′17.11 ″ 015°21′57.10 ″	1.09	48.04	50.87	Sandy silt	52.13	5.42	0.88
	3A	4°22 ′45.08 ″ 015°21′4.74 ″	0.91	8.14	90.95	Sand	16.43	1.48	0.34
MTT	3B	4°22 ′45.17 ″ 015°21′4.95 ″	0.97	9.01	90.02	Silty sand	17.39	1.75	0.55
	3C	4°22 ′45.23 ″ 015°21′5.05 ″	0.86	8.05	91.09	Sand	18.44	2.05	0.43
	4A	4°22 ′01.06 ″ 015°21′43.04 ″	1.40	34.66	63.94	Sandy silt	23.69	3.07	0.58
DIGUE	4B	4°22 ′01.18 ″ 015°21′43.42 ″	1.12	33.93	64.95	Sandy silt	24.36	3.19	0.67
	4C	4°22 ′01.22 ″ 015°21′43.86 ″	1.07	31.24	67.69	Sandy silt	21.19	2.85	0.53

Fig. 2 N'djili River. **A** Uncontrolled waste pile on the river bank, **B** Industrial effluent discharge into the river, **C** Uncontrolled landfill and waste discharge by surface runoff into the river

used as the diminutive of the Matete municipality. DIGUE (meaning dam in English) is the N'djili River sampling area located in the Limete municipality and characterized by the presence of a dike built to protect riparian fields from floods.

The surface sediment samples (the 0–5 cm sediment top layer) were collected in June 2021 using a hand operated stainless-steel grab sampler. Triplicate samples of surface sediment were taken at each site and combined in one pooled sample with approximately 100–200 g per site. The sediment samples from the 12 sites were kept in autoclaved jars. The sediment containing jars were stored in an icebox at 4°C and transported to the "Ecole Polytechnique Fédérale de Lausanne", Switzerland, for analysis of organic contaminants.

2.2 Sediment characterization

After homogenization of samples, sediment aliquots were taken for physical and chemical analyses. Sediment particle grain size, including percentages of clay, silt, and sand were determined in fresh sediment using a Laser Coulter® LS-100 diffractometer (Beckman Coulter, Fullerton, CA, USA), following 5 min ultrasonic dispersal in deionized water as described in Loizeau et al. [26].

The water content (WC) was evaluated by the sediment weight loss following oven drying at 60 °C during 24 h. The organic matter (OM) and carbonate ($CaCO_3$) content were determined by the dry sediment weight loss on ignition at 550 °C and 1000 °C, respectively, after 1 h burning the sediment aliquots in a muffle furnace (Salvis AG, Luzern, Switzerland) at each temperature [27].

2.3 Analyses of POPs

Analyses of persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs), organochlorine pesticides (OCs), polycyclic aromatic hydrocarbons (PAHs), and polybrominated diphenyl ethers (PBDEs) were performed according to the methods described by Thevenon et al. [28] and Suami et al. [6]**.** A few other compounds, namely organophosphorus pesticides (OPs) and pyrethroid pesticides (PYR) were analysed also. Procedures used are briefly described below.

All glassware was rinsed with acetone and hexane for decontamination and tested before use. Procedural blanks did not display any quantifiable amount of contaminants or interfering compounds. Aliquots of sediment samples with approximately 5 g of dry sediment were accurately weighed and analytical internal standards (^{13}C-labeled for all halogenated compounds and deuterated labeled compounds for all PAHs) added. Analytical standards and all chemical reagents used were purchased from Sigma-Aldrich (Switzerland).

Samples were extracted with a mixture of 20% acetone in 80% hexane (v/v) for 4 h into a Soxhlet system (Buchi B-811, Flawil, Switzerland). Interfering sulfur compounds were removed by addition of activated copper to the extract. Next, the organic extract was concentrated to 1 mL in a vacuum rotary evaporator (Buchi Rotavapor, Flawil, Switzerland). The extract was further submitted to fractionation and clean-up over a chromatographic column containing 3 g of Silica gel

eluted with the solvents hexane and dichloromethane. Three fractions from the eluate were collected separately: the first 16 mL of hexane, the next 35 mL of hexane, and finally 50 mL of hexane: dichloromethane (v/v, 1:1). The first two fractions did contain PCBs and PBDEs, respectively. PAHs and chlorinated pesticides were distributed in the 3 fractions. After a new reduction of the solvent volume to 1 mL, chemicals were determined by gas chromatography with triple mass spectrometry detection (GC–MS/MS, Thermo Scientific, TSQ Quantum XLS Ultra, Waltham, MA, USA). Two columns with different polarities, a ZB-5 ms column (60 m × 0.25 mm × 0.25 µm) and one ZB-XLB column (20 m × 0.18 mm × 0.18 µm), were used for separation and identification of the several compounds. The chromatography column selection for identification of compounds is specified in Tables 3.

The following PCB congeners (IUPAC numbers) were investigated: CB-28 (2,4,4′-trichlorobiphenyl), CB-52 (2,5,2′,5′-tetrachlorobiphenyl), CB-101 (2,4,5,2′,5′-pentachlorobiphenyl), CB-105 (2,3,4,3′,4′-pentachlorobiphenyl), CB-118 (2,4,5,3′,4′-pentachlorobiphenyl), CB-128 (2,3,4,2′,3′,4′-hexachlorobiphenyl), CB-138 (2,3,4,2′,4′,5′- hexachlorobiphenyl), CB-149 (2,3,6,2′,4′,5′-hexachlorobiphenyl), CB-153 (2,4,5,2′,4′,5′-hexachlorobiphenyl), CB-156 (2,3,4,5,3′,4′- hexachlorobiphenyl), CB-170 (2,3,4,5,2′,3′,4′-heptachlorobiphenyl) and CB-180 (2,3,4,5,2′,4′,5′- heptachlorobiphenyl). Results were expressed as Σ12PCBs (meaning the sum of all CBs quantified in the sample) and also as "Total PCBs" (meaning the sum of a selection of 7 CBs, namely CBs number 28, 52, 101, 118, 138, 153 and 180) multiplied by a correction factor of 4.3 [29]. However, these ∑7 PCB values are important because the toxicity parameters TEL and PEL were defined as a function of ∑7 PCBs.

The chlorinated pesticides determined in sediments were: hexachlorocyclohexane (HCH) (isomers alpha, beta & gamma), heptachlor, cis-heptachlorepoxyde, trans-heptachlorepoxyde, hexachlorobenzene, aldrin, dieldrin, endrin, oxy-chlordane, alpha-chlordane, gamma-chlordane, cis-nonachlor, trans-nonachlor, o,p′-DDE (dichloro diphenyl dichlorethylene), p,p′-DDE (dichloro diphenyl dichlorethylene), o,p′-DDD (dichloro diphenyl dichlorethane), p,p′-DDD (dichloro diphenyl dichlorethane), o,p′-DDT (dichloro diphenyl trichlorethane), p,p′-DDT (dichloro diphenyl trichlorethane), mirex (dodecachlorooctahydro-1H-1,3,4-(epimethanetriyl) cyclobuta[cd]pentalene), methoxychlor, endosulfan I, II and endosulfan-sulfate, endrin-aldehyde, endrin-ketone and acetochlor (herbicide). Additionally, the organosphosphorus pesticides (OPs) chlorpyrifos-methyl and chlorpyrifos-ethyl, and the pyrethroids (PYR), cyhalothrin-λ, cypermethrin-α, cypermethrin–β, and deltamethrin were determined also. In the present work, results for DDT related compounds were given as ΣDDT, i.e., the sum of DDT and DDT metabolites.

Among PAHs, the following compounds were determined: naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k) fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3c,d)pyrene. Results were expressed as ΣPAHs, meaning the sum of all 16 PAHs determined. This set of PAHs is similar to those proposed by US EPA to be measured in sediment samples, with exception of benzo(e)pyrene and addition of acenaphtylene [30].

Among PBDEs, the following congeners (IUPAC numbers) were determined: BDE-17 (2,2′,4-tribromodiphenyl ether), BDE-28 (2,4,4′-tribromodiphenyl ether), BDE-47 (2,2′,4,4′-tetrabromodiphenyl ether), BDE-66 (2,3′,4,4′-tetrabromodiphenyl ether), BDE-85 (2,2′,3,4,4′-pentabromodiphenyl ether), BDE-99 (2,2′,4,4′,5-pentabromodiphenyl ether), BDE-100 (2,2′,4,4′,6 pentabromodiphenyl ether), BDE-138 (2,2′,3,4,4′,5′ hexabromodiphenyl ether), BDE-153 (2,2′,4,4′,5,5′-hexabromodiphenyl ether), BDE-154 (2,2′,4,4′,5,6′-hexabromodiphenyl ether), BDE-183 (2,2′,3,4,4′,5′,6-heptabromodiphenyl ether), BDE-190 (2,3,3′,4,4′,5,6-heptabromodiphenyl ether). BDE-209 (decabrominated) was not analyzed. Results are expressed as the ΣPBDEs, meaning the sum of all PBDEs determined.

The concentrations of all organic contaminants were expressed in µg kg^{-1} sediment dry weight. The limit of quantification (LOQ) of individual chemical compounds was defined as 10 times the baseline noise and, for the entire list of organic compounds analyzed, LOQs were comprised between 0.02 ng g^{-1} (for p,p′-DDE) and 0.15 ng g^{-1} (for BDE-190) dry weight.

2.4 Analytical quality assurance

Quality control and quality assurance (QC/QA) were implemented to evaluate the efficiency of the analytical procedure and trueness of results, as detailed in previous reports [6, 21, 28]. Briefly, to evaluate the efficiency of the analytical procedure, recovery assays were conducted using certified reference materials with similar matrices. The recovery yield values were satisfactorily high and ranged from 80 to 105% for all POPs targeted in this study.

Additional quality control was implemented through the use of internal tracers, 14C–labeled for all halogenated compounds and deuterated labeled compounds for all PAHs, added to each sample in order to compute the recovery yield and correct analytical results sample by sample, instead of using average recovery yields.

Blank samples were run for the entire analytical procedures. Blanks samples did not show any quantifiable amount of contaminants or interfering compounds.

The limit of detection (LOD) and limit of quantification (LOQ) for target analytes were defined as the analyte concentration producing a peak with a signal-to-noise ratio of 3 and 10, respectively. LOD and LOQ have been determined experimentally by measuring the coincident instrumental response of standard POPs solutions and procedural blank for all analytes targeted.

2.5 Statistical analysis

Triplicate measurements were performed for all analytes. Percent standard deviation of triplicate measurements were within ± 10% of the mean value. Statistical data treatment was made using SigmaStat 12.5 (Systat Software, Inc., USA).

3 Results and discussion

3.1 Physical–chemical characteristics of sediments

The results of physical–chemical analysis of sediment samples, including the determination of particle grain size (clay, silt, and sand), water content (WC), organic matter (OM) and carbonate ($CaCO_3$) are shown in Table 1. Results of particle grain size analyses indicated that all sediment samples were sandy, with sand percentages varying from 49.49% to 91.09%, and with minor contributions of silt (8.14–49.61%) and clay (0.86–7.38%). The highest percentage of sand was recorded in the MTT samples (87.05–91.09%), followed by CECOMAF (69.07–72.10%), DIGUE (58.75–63.94%) and finally CAPT samples (48.16–51-55%).

The water content (WC) of sediment samples varied according to sampling sites. It was noted that the WC was negatively correlated with the sand content ($R^2 = (-)\ 0.713$, $p < 0.05$) while it was positively correlated with the silt content ($R^2 = 0.713$, $p < 0.05$), OM ($R^2 = 0.804$, $p < 0.05$) and $CaCO_3$ ($R^2 = 0.776$, $p < 0.05$). The OM content of sediments from N'djili River varied from 1.48 to 11.16%. The OM was positively correlated with clay content ($R^2 = 0.641$, $p < 0.05$) and $CaCO_3$ ($R^2 = 0.930$, $p < 0.05$). The $CaCO_3$ percentage varied from 0.35 to 2.83. A strong and positive correlation was observed between the $CaCO_3$ and the clay content ($R^2 = 0.711$, $p < 0.05$).

3.2 Concentrations of organic pollutants in sediments

The results of Persistent Organic Pollutants (POPs) analysis, including polychlorinated biphenyls (PCBs), pesticides (OCs, OPs, PYR), polycyclic aromatic hydrocarbons (PAHs), and polybrominated diphenyl ethers (PBDEs) in surface sediments from the N'djili River are shown in Tables 2, 3, 4 and 5.

3.2.1 Concentrations of polychlorinated biphenyls (PCBs)

PCBs belong to a broad family of synthetic organic chemicals known as chlorinated hydrocarbons. These substances vary in consistency and have a wide range of toxicity. Due to their non-flammability, chemical stability, high boiling point and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications including electrical, heat transfer and hydraulic equipment, plasticizers in paints, plastics and rubber products, pigments, dyes and carbonless copy paper [32].

PCBs were detected in all sediment samples (Table 2). The sum of 12 PCB congeners (chlorobiphenyl (CB) congeners number 28, 52, 101, 105, 118, 128, 138, 149, 153, 156, 170 and 180) ranged between 116.69 (in sample 1A) to 709.61 µg kg^{-1} (in sample 4B) with a mean value of 407.89 µg kg^{-1}. The higher ∑12 PCB congener concentrations were observed in DIGUE area (709.61 µg kg^{-1}), followed by MTT (667.72 µg kg^{-1}), CAPT (188 µg kg^{-1}) and CECOMAF (137.56 µg kg^{-1}). The predominance of PCB congeners in terms of total concentration and by decreasing order was as follows: CB 101 (20.3%), 153 (19.9%), 149 (18.9%), 180 (17%), 138 (16.9%), 170 (16.5%), 128 (16.2%), 52 (13.3%), 118 (12.7%), 105 (6.5%), 156 (5.9%) and 28 (3%).

The concentration of the sum of 12 PCBs in N´djili River sediments was higher than values previously reported for the Congo River [4, 19] and comparable or lower than those reported for the Atlantic coast of DRC [6], indicating that environmental contamination by PCBs is widespread in this region. The high PCB concentrations in N´djili River pointed out to the urban areas of Kinshasa as the main source of these chemicals. Furthermore, the PCB concentrations in N´djili

Table 2 Concentrations of polychlorinated biphenyl (PCBs) in sediment samples from N'djili River

		CECOMAF (1)			CAPT (2)			MTT (3)			DIGUE (4)		
PCBs (µg kg^{-1} dry weight)	LOQ	1A	1B	1C	2A	2B	2C	3A	3B	3C	4A	4B	4C
28	0.03	1.74	2.64	0.35	1.51	0.68	0.70	10.65	8.55	15.27	11.65	14.86	19.92
52	0.05	12.90	12.86	23.29	12.99	21.02	30.97	45.47	42.65	48.68	42.82	46.76	49.89
101	0.10	11.84	14.39	13.17	17.36	18.64	32.35	83.56	75.95	74.24	98.26	81.66	72.56
105	0.05	6.79	8.02	9.63	9.57	11.23	11.96	19.45	18.08	34.90	19.28	21.63	18.63
118	0.10	9.42	8.76	7.74	4.29	5.29	6.49	31.64	35.65	36.77	75.34	72.22	76.83
128	0.05	6.73	7.68	9.13	7.27	11.64	12.84	73.46	73.23	71.68	68.25	69.23	63.07
138	0.05	6.65	7.38	8.58	8.84	9.80	11.92	76.76	71.28	77.91	68.32	76.65	71.33
149	0.10	7.72	13.86	12.56	13.89	15.86	16.52	66.64	67.81	65.86	84.28	91.63	97.63
153	0.05	11.47	10.89	14.52	17.88	19.91	23.40	73.64	71.46	70.83	87.73	87.51	94.36
156	0.05	2.58	2.69	3.17	3.60	3.86	5.49	19.35	16.90	18.92	27.13	33.52	35.47
170	0.05	12.49	13.46	11.67	12.81	14.79	13.94	82.24	80.38	83.20	44.62	52.61	61.48
180	0.05	26.36	21.45	23.75	24.74	21.63	21.42	74.37	70.84	69.46	37.22	61.33	45.84
Total PCBs (∑ 7 × 4.3)		80.38	78.37	91.4	87.61	96.97	127.25	396.09	376.38	393.16	421.34	440.99	430.73
∑ 12 PCBs		116.69	124.08	137.56	134.75	154.35	188	657.23	632.78	667.72	664.9	709.61	707.01
TEL[a] (∑7 PCBs) 34.1													
PEL[b] (∑7 PCBs) 277													

[a]Threshold effect levels (TELs) (µg kg^{-1} dry weight) and [b]Probable effect levels (PELs) (µg kg^{-1} dry weight) [54]

River sediments showed a clear increasing trend from South to North, towards the Congo River, reflecting the cumulative effect of discharges from urban areas along the N´djili river.

PCBs were, and still are used in the region in transformers and capacitors and old electrical devices. With an improper scrap metal retrieval and lack of urban waste management in the country, PCB leaks from dismantling old equipment does occur. Kinshasa province is well known for its many informal scrap metal yards and many repair workshops that likely are PCB sources..

The chlorobiphenyl congeners detected in N'Djili River sediments indicate the use of old PCB mixtures containing penta, hexa, and hepta chlorobiphenyls, which have been banned from international marketing in the 1980s. Globally, these results imply that several PCB mixtures have been used in the region overtime.

PCBs such as congeners 138, 153 and 180 are among the most persistent in the environment and these congeners were present in N'Djili River sediments [1].

Regarding the sum of 7 PCBs congeners (28, 52, 101, 118, 138, 153, 180) the concentrations ranged from 78.37–91.4 µg kg^{-1}; 87.61–127.25 µg kg^{-1}; 376.38–396.09 µg kg^{-1}; 421.34–440.99 µg kg^{-1} respectively for CECOMAF, CAPT, MTT and DIGUE areas. The results for the ∑7 PCB congeners were systematically lower than ∑12 PCB results despite the correction factor used as recommended in the literature [29]. As mentioned above, these ∑7 PCB values are important because the toxicity parameters TEL and PEL were defined as a function of ∑7 PCBs (Table 2).

In the CECOMAF and CAPT samples the sum of 7 PCB congeners exceeded the TEL value of 34.1 µg kg^{-1}, while MTT and DIGUE values were already higher than PEL value of 277 µg kg^{-1}. These elevated concentration values indicate that current PCB levels in N'Djili River sediments reached toxic levels to the aquatic organisms [33].

3.2.2 Concentrations of polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a class of chemicals that naturally occur in coal, crude oil, and gasoline. PAHs spread in the environment from the burning of coal, oil, gasoline, wood, garbage, and tobacco. PAHs can bind to, or form small particles in the air. High heat when cooking meat and other foods will form PAHs also. PAH_S are widespread in the environment and their inhalation and ingestion is harmful to humans [34].

Sixteen PAH compounds were identified and quantified in all sediment samples (Table 3). These PAHs included the carcinogens benzo(a)anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BbF), and the $\sum_{16}$ PAH congeners. The following decreasing trend of concentrations was observed across the sampling sites for the compounds: phenanthrene > pyrene > naphthalene > fluoranthene > benzo(b)fluoranthene > benzo(g,h,i)perylene > indeno(1,2,3c.d)

Table 3 Concentrations of polycyclic aromatic hydrocarbons (PAHs) in sediment samples from N'djili River

		CECOMAF(1)			CAPT(2)			MTT(3)			DIGUE(4)		
PAHs (μg kg^{-1} dry weight)	LOQ	1A	1B	1C	2A	2B	2C	3A	3B	3C	4A	4B	4C
Naphthalene (Naph)	0.50	44.46	32.53	112.02	82.50	20.5	58.03	32.56	28.73	112.74	97.16	91.66	106.58
Acenaphthylene (Acy)	0.50	5.90	12.23	2.41	3.79	12.30	3.49	2.16	3.37	6.32	5.36	7.18	8.57
Acenaphthene (Ace)	0.50	3.30	2.21	4.50	5.17	5.67	17.27	3.59	6.12	19.17	22.46	9.17	26.47
Fluorene	0.50	11.40	23.43	9.23	15.36	3.73	34.27	4.53	5.33	43.37	13.58	19.53	36.15
Phenanthrene	0.50	68.47	70.08	57.67	94.67	16.52	134.21	41.53	26.34	140.23	57.17	64.57	183.17
Anthracene	0.50	3.37	10.22	15.14	12.52	13.24	16.85	12.35	11.81	21.78	15.46	11.24	17.42
Fluoranthene	1.00	39.39	61.82	37.49	29.12	3.57	102.54	26.18	61.18	88.26	32.49	112.12	143.70
Pyrene	1.00	51.37	63.79	43.19	57.37	4.97	155.67	22.29	22.10	118.61	103.19	129.39	174.81
Benzo (a) Anthracene	1.00	9.82	17.23	10.87	38.47	2.57	36.34	14.14	8.64	32.82	12.67	28.47	39.35
Chrysene	1.00	33.13	33.23	26.11	36.34	2.56	36.86	16.91	23.64	34.25	31.51	37.12	42.57
Benzo(b)Fluoranthene	1.00	29.15	41.59	17.57	61.37	14.38	96.79	16.62	19.35	44.13	35.36	25.77	84.28
Benzo (k) Fluoranthene	1.00	5.49	14.23	17.17	22.15	5.63	37.71	12.63	8.36	32.19	17.17	19.15	38.40
Benzo (a) Pyrene	1.00	14.31	16.62	14.30	26.73	21.32	58.36	15.37	15.22	34.08	24.66	26.28	59.81
Dibenz (a.h) Anthracene[a],*	1.00	4.13	5.26	2.82	3.29	1.30	32.75	12.32	7.89	5.21	23.51	27.21	36.47
Benzo (g.h.i) Perylene*	1.00	27.12	27.27	17.75	38.91	3.49	48.53	13.23	19.64	31.19	33.75	35.39	72.27
Indeno (1.2.3c.d) pyrene[a],*	1.00	15.28	22.36	15.67	25.24	6.54	67.12	36.31	13.73	26.38	23.46	42.24	67.55
∑16 PAHs congeners		366.09	454.1	403.91	553	138.29	936.79	282.72	281.45	790.73	548.96	686.49	1137.57
TELs[b] (∑13 PAHs) 610													
PELs[b] (∑13 PA Hs) 22,800													
Fluo/ (Fluo + Pyr)		0.18	0.27	0.18	0.21	0.43	0.18	0.17	0.19	0.27	0.12	0.13	0.17
IDP/ (IDP + BghiP)		0.4	0.5	0.5	0.4	0.7	0.6	0.7	0.4	0.5	0.4	0.5	0.5
BaA/ (BaA + Chry)		0.2	0.3	0.3	0.5	0.5	0.5	0.5	0.3	0.5	0.3	0.4	0.5
LMW/HMW[c]		0.6	0.5	1.1	0.7	1.2	0.4	0.6	0.4	0.8	0.7	0.5	0.5

[a]Chromatographic separation on a ZB-XLB column. All remaining compounds on a ZB-5 ms column

[b]Threshold effect levels (TELs) and Probable effect levels (PELs) (μg kg^{-1} dry weight) [54]. Canadian sediment quality guidelines for the protection of aquatic life. Canadian Council of Ministers of the Environment[54]

[c]LMW/HMW: Ratio of low molecular weight (LMW) PAHs (i.e. Naphthalene (Naph), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Fl), Phenanthrene (Phen), Anthracene (Anthr) to high molecular weight (HMW) PAHs (i.e. fluoranthene (Fluo), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IDP), dibenz[a,h]anthracene (DahA),and benzo[g,h,i]perylene (BghiP)

*Not included in the sum of (∑13 PAHs)

pyrene > chrysene > Benzo(a)pyrene > benzo(a)anthracene > benzo(k)fluoranthene > fluorene > dibenz(a.h) anthracene > anthracene > acenaphthene > acenaphthylene.

The $\sum_{16}$ PAHs congener concentrations spread over wide ranges: from 366.09 to 454.1 μg kg^{-1} in CECOMAF area, 138.29–936.79 μg kg^{-1} in CAPT, 281.45–790.73 μg kg^{-1} in MTT and 548.96–1137.57 μg kg^{-1} in DIGUE area. In average, these concentrations displayed a trend increasing along the N'djili River towards the Congo River, showing a cumulative effect of PAH discharges from the urban areas crossed by the river.

The ranges of $\sum_{16}$ PAH concentrations in sediments from N´djili River were much higher than values reported for sediments from other rivers in the same region (Kinshasa, DR Congo), namely Congo River (at Maluku, Mongole and Chanic area) and "Lake Ma Vallée" by Mwanamoki et al. [19] **(**63.89 μg kg^{-1}**)** but were still in the range of values reported for sediment collected from Makelele, Kalamu and Nsanga Rivers by Kilunga et al. [4] (22.56–951.13 μg kg^{-1}), which indicated that contamination by PAHs is widespread and at similar levels in other aquatic environments of this region.

As proposed in the literature, the PAH pollution levels can be classified as: (a) low pollution level (< 100 μg kg^{-1}), (b) moderately polluted (101–1000 μg kg^{-1}), (c) highly polluted (1001–5000 μg kg^{-1}), and (d) very highly polluted (> 5000 μg kg^{-1}) [35]. According to this classification scale, the majority of samples from the N'Djili River may be classified as "moderately polluted" for PAHs, except for the sample 4C which was "highly polluted".

Table 4 Concentrations of organochlorine pesticides (OCs), organophosphorus pesticides (OPs), and pyrethroid pesticides (PYR) in sediment samples from N'djili River

Compounds (µg kg-1 dry weight)	LOQ	CECOMAF (1)			CAPT(2)			MTT(3)			DIGUE(4)		
		1A	1B	1C	2A	2B	2C	3A	3B	3C	4A	4B	4C
Hexachlorobenzene (OC)	0.05	< 0.05	**0.79**	< 0.05	**0.23**	**0.78**	**0.82**	**1.24**	**1.87**	**1.41**	**1.61**	**1.73**	**1.86**
alpha-HCH (OC)	0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
beta-HCH (OC)	0.05	< 0.05	< 0.05	**0.12**	< 0.05	< 0.05	< 0.05	**0.20**	**0.40**	**0.54**	**0.58**	**0.61**	**0.75**
gamma-HCH (OC)	0.10	< 0.10	**0.18**	**0.62**	< 0.10	< 0.10	< 0.10	**2.63**	**3.03**	**4.27**	**3.27**	**6.25**	**5.04**
delta-HCH (OC)	0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30
gamma-Chlordane (OC)	0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30
alpha-Chlordane (OC)	0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30
oxy-Chlordane (OC)	0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30
Dieldrin (OC)	0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30
Endrin (OC)	0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Heptachlor (OC)	0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Aldrin (OC)	0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Heptachlor epoxid A (OC)	0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30
Heptachlor epoxid B (OC)	0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30
Endosulfan I (OC)	1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00
Endosulfan II (OC)	1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00
Endosulfan sulfate (OC)	0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Endrin aldehyde (OC)	0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Endrin ketone (OC)	0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Methoxychlor (OC)	0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30
Acetochlor (OC)	1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00
trans-Nonachlor (OC)	0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	**0.20**	**1.44**	**1.44**	**1.44**
Mirex (OC)	0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30
Chlorpyrifos-methyl (OP)	1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00
Chlorpyrifos-ethyl (OP)	0.50	**2.84**	**2.26**	**3.85**	**4.82**	**3.79**	**8.36**	**10.63**	**12.30**	**26.33**	**29.10**	**27.98**	**22.80**
Cyhalothrin-λ (lambda) (PYR)	1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	**4.89**	**5.36**	**17.82**	**22.78**	**25.66**	**23.87**
Cypermethrin a (PYR)	8.00	< 8.00	< 8.0	< 8.0	< 8.0	< 8.0	< 8.0	**33.27**	**23.42**	**36.45**	**44.49**	**38.62**	**42.63**
Cypermethrin b (PYR)	8.00	< 8.00	< 8.0	< 8.0	< 8.0	< 8.0	**9.70**	**23.36**	**36.79**	**29.72**	**21.35**	**25.15**	**19.40**
Deltamethrin (PYR)	8.00	**12.68**	**17.33**	**26.73**	**32.46**	**57.94**	**59.82**	**61.10**	**72.31**	**87.19**	**182.19**	**198.57**	**208.67**
DDTs (µg kg^{-1})	LOQ	1A	1B	1C	2A	2B	2C	3A	3B	3C	4A	4B	4C
p.p'-DDE	0.10	**19.12**	**17.88**	**13.08**	**18.15**	**20.67**	**19.63**	**152.79**	**138.99**	**166.22**	**181.29**	**134.23**	**124.38**
o.p'-DDE	0.10	**1.45**	**1.49**	**3.63**	**3.67**	**3.29**	**6.76**	**17.28**	**28.26**	**29.72**	**27.57**	**21.67**	**24.94**
p.p'-DDD	0.10	**3.85**	**8.90**	**6.47**	**11.80**	**8.33**	**7.74**	**46.78**	**55.84**	**59.64**	**41.22**	**63.82**	**57.72**
o.p'-DDD	0.10	**2.64**	**5.37**	**8.38**	**7.33**	**19.75**	**17.57**	**27.67**	**3.68**	**29.66**	**31.67**	**54.72**	**63.83**

Table 4 (continued)

DDTs (µg kg^{-1})	LOQ	1A	1B	1C	2A	2B	2C	3A	3B	3C	4A	4B	4C
p.p′-DDT	0.10	**8.89**	**3.62**	**4.58**	**13.68**	**5.27**	**23.85**	**39.33**	**4.80**	**47.63**	**48.27**	**32.49**	**52.83**
o.p′-DDT	0.10	**13.54**	**6.70**	**32.65**	**6.79**	**21.54**	**23.17**	**33.56**	**28.35**	**25.65**	**45.43**	**61.26**	**73.75**
∑ DDTs		49.49	43.94	68.79	61.41	78.84	98.71	317.41	259.90	358.52	375.46	368.19	397.45
TEL[b](∑6DDTs) 6.15													
PEL[b] (∑6DDTs) 20.03													
(p,p′-DDE + p,p′-DDD)/p,p′-DDT		2.6	7.4	4.3	2.2	5.5	1.1	5.1	40.6	4.7	4.6	6.1	3.4
(o,p′-DDE + o,p′-DDD)/o,p′DDT		0.3	1	0.4	1.6	1.1	1.1	1.3	1.1	2.3	1.3	1.2	1.2

[a]Federal Environmental quality guidelines Polybrominated Diphenyl Ethers (PBDEs) in sediments (https://www.canada.ca/content/dam/eccc/migration/ese-ees/05df7a37-60ff-403f-bb37-0cc697dbd9a3/feqg_pbde_en.pdf)

[b]Threshold effect levels (TELs)/Probable effect levels (PELs) (dry weights). Canadian sediment quality guidelines for the protection of aquatic life. Canadian Council of Ministers of the Environment [54].

Table 5 Concentrations of polybrominated diphenyl ethers (PBDEs) in sediment samples from N'djili River

PBDEs[a] (µg kg^{-1} dry weight)	LOQ	CECOMAF (1)			CAPT (2)			MTT (3)			DIGUE (4)		
		1A	1B	1C	2A	2B	2C	3A	3B	3C	4A	4B	4C
BDE28	0.15	< 0.15	0.19	< 0.15	0.16	< 0.15	< 0.15	< 0.15	0.18	0.16	0.79	0.16	0.88
BDE47	0.10	1.38	2.09	0.75	3.08	2.20	4.93	1.73	2.59	3.82	7.09	4.38	9.81
BDE100	0.10	0.96	0.67	0.53	0.71	0.99	3.18	3.18	1.77	2.71	1.18	1.84	2.80
BDE99	0.10	2.73	3.63	1.37	3.41	2.28	4.16	1.78	3.46	4.33	2.72	4.39	6.88
BDE154	0.15	0.24	0.38	0.79	0.65	0.77	2.21	1.65	1.43	2.17	0.92	0.93	1.84
BDE153	0.15	0.42	0.69	0.19	0.47	0.96	0.94	0.98	1.78	1.92	2.07	0.73	0.88
∑6 PBDEs		5.7	7.6	3.6	8.5	7.2	15.4	9.3	11.2	15.1	14.8	12.4	23.1

[a]Federal Environmental quality guidelines Polybrominated Diphenyl Ethers (PBDEs) in sediments (Https://www.ec.gc.ca/ese-ees/)

Regarding potential ecotoxicity of sediments with the current PAH levels in N´djili River, the values for Σ_{16} PAHs congeners were higher than the TEL (Σ_{13} PAHs) of 610 µg kg^{-1} in samples 2C (936.79 µg kg^{-1}), 3C (790.73 µg kg^{-1}), 4B (686.49 µg kg^{-1}) and 4C (1137.57 µg kg^{-1}), although below the PEL value, but nevertheless indicating the potential occurrence of toxic effects caused by PAHs on benthic organisms [30, 33] (Table 3).

The ratio of certain PAH concentrations has been used to diagnose the origin of compounds and apportioning them to either natural or anthropogenic sources [4]. Four PAH ratios can be used for this purpose. The ratio values Fluo/(Fluo + Pyr) or IDP/(IDP + BghiP) allow determining whether PAHs are from petrogenic (when the ratio is < 0.4) or pyrogenic origin (> 0.4). Furthermore, when the ratio is between 0.4 and 0.5 this indicates a petroleum combustion source, and if it is > 0.5, the source is grass, wood, or coal combustion [36, 37]. The ratio IDP/(IDP + BghiP) < 0.2 indicates the petrogenic source; a ratio ranged from 0.2–0.5 corresponds to a petroleum combustion, and a ratio > 5 indicates grass, wood, or coal combustion [36]. If the ratio BaA/(BaA + Chry) is less than 0.2 indicates a petroleum source, a ratio between 0.2 and 0.35 means a petroleum or combustion source, and a ratio greater than 0.35 indicates pyrolytic origin [36]. The ratio of Low Molecular Weight / High Molecular Weight compounds (LMW/HMW) was proposed also as an indicator of the PAH sources and LMW/HMW < 1 indicates a petrogenic source, while LMW/HMW > 1 indicates a pyrogenic source [38]. Using the ratios introduced above, the results for N'Djili River sediment samples indicated several PAH origins, namely petrogenic and pyrolytic sources, petroleum, grass, wood and coal combustion. Actually, in Kinshasa city, over 70% of the inhabitants use coal and wood to cook [4]. This coal and wood combustion are certainly a major source of the PAHs along N'djili River, but contributions from petrogenic sources are likely present too. Definitively, the high PAH concentrations determined in N´djili River sediments were from anthropogenic sources.

3.2.3 Concentrations of organochlorine, organophosphorus and pyrethroid pesticides

Agrochemicals, from a list of 35 compounds including organochlorine pesticides (OCs), organophosphorus compounds (OPs), and synthetic pyrethroids (PYR) which are used as insecticides and herbicides or are metabolites from them, were searched in the sediment samples. The results of analyses are reported in Table 4.

In general, the concentrations of these organic compounds were under the LOQ values in many sediment samples indicating that they were not present in significant amounts. There were exceptions, namely of hexachlorobenzene, beta-HCH, gamma-HCH, chlorpyrifos-ethyl, trans-nonachlor, cyhalothrin-λ, cypermethrin-α, cypermethrin-β, and deltamethrin which were detected in many samples.

Organochlorine pesticides, such as hexachlorobenzene (HCB), hexachlorocyclohexane (HCHs), aldrin, endrin, dieldrin and hepthachlor are old pesticides which were banned and their production discontinued several decades ago. International regulations such as those from USA and European Union have certainly made difficult the trade and import of such compounds into DRC. Therefore, it is unlikely that they have been used in recent years in DRC. Furthermore, the HCB and HCHs detected in sediments displayed low concentrations and, likely, these were residues from past applications. The long environmental half-lives of these OC chemicals, particularly when bound to soils and sediments, may explain the presence of these long-lasting residues [39–42]**.** HCB, HCHs and endosulfan compounds were present in N´djili sediments but in low concentrations which were generally comparable to levels reported for other regions in the world (Table 6).

DDT and DDT metabolites are also environmentally persistent organochlorine compounds and p.p'-DDE, o.p'-DDE, p.p'-DDD, o.p'-DDD, p.p'-DDT and o.p'-DDT were detected in all samples (Table 4). However, their concentrations in

Table 6 Concentrations of organic contaminants in sediments (μg kg^{-1} dry weight) reported for aquatic systems (mean and range of values)

Compounds	Coastal lagoons Pacific coast NW Mexico (a)	Terminus Lagoon Caribbean Sea, Mexico (b)	Coastal lagoons Nicaragua (c)	Mekong River delta, Vietnam (d)	Red River Hanoi, Vietnam (e)	Manila Bay Philippines (f)	Rivers and estuaries, Portugal (g)	Other rivers in the world	Congo River (Upper reach by Kisangani (l)	N´djili River DRCongo This study
∑ 12 PCBs	Nd	0.148 (0.016–0.356)	9.5 * (0.2–37)	0.49 (0.11–2.0)	10.98- (0.97–33.68)	0.69 (0.10–1.47)	(0.19–4.23)	Nd	0.87	408 (117–709.6)
∑HCHs	0.9 (0.01–4)	0.003 (0–0.005)	0.256 (0.005–1.31)	0.14 (nd-0.89)	0.83 (0.07–3.12)	0.03 (0.05–0.11)	(0.326–52.3)	Nd	0.056	< 0.30–6.86
∑ DDTs	13 (0.6–45)	0.19 (0.008–0.631)	66 (2–321)	6.3 (0.32–67)	30.55 (7.40–80.55)	0.53 (0.20–1.04)	(0.06–15.5)	Nd	0.042	(49–397)
∑Endosulfans	5.4 (0.4–26)	0.013 (0.00–0.05)	0.35 (< 0.01–0.67)	0.073 (nd-0.49)	(nd-0.03)	(0.04–0.084)	Nd	Nd	Nd	< 1
∑PAHs	Nd	Nd	Nd	Nd	Nd	Nd	(3.71–17.73)	7763 (5940–9724) (h)	Nd	548 (281–1137)
∑PBDEs	Nd	Nd	Nd	Nd	Nd	Nd	Nd	15.8 (Nd-28700) (i)	0.49	11.2 (3.6–23.1)
HCB	0.1 (0.05–0.1)	(0.008–0.055)	(0.005–0.25)	(0.03–6.9)	(Nd-0.13)	(0.007–0.016)	(0.04–0.06)	Nd	Nd	Nd
Heptachlor	0.004 (0.0–0.02)	Nd	(nd-0.059)	< 0.002	Nd	< 0.004	Nd	Nd	Nd	Nd
Chlopyrifos	1 (0.4–8)	Nd	(nd—1.2)	Nd	Nd	Nd	Nd	Nd-40 (j)	Nd	12.92 (2.26–29.1)
Cypermethrin	Nd	Nd	(0.22–20.4)	Nd	Nd	Nd	Nd	Nd	Nd	< 8–36.79
Deltametrin	Nd	Nd	(Nd-1.29)	Nd	Nd	Nd	Nd	(Nd-3.1) (k)	Nd	85 (12.68–208.67)

(a) [41]; (b) [51]**;** [53]; (c) [42]; (d) [52]; (e) [53]; (f) [49]; (g) Data selected from several rivers and estuaries in Portugal, [9]; (h) Euphrates River, [54]; (i) Chinese rivers, [55]; (j) Rivers in Spain, [56]; (k) Orange County, Southern California, [57]; (l) [14]. *Reported as araclor1254

sediments were 2–3 orders of magnitude higher than other OCs, and reached values as high as 397.45 µg kg^{-1} for Σ6 DDTs (Table 4). Again, there was a trend of increasing concentrations along the N´djili River from South to North, towards the Congo River, with the lowest concentrations of Σ6 DDTs (43.94–68.79 µg kg^{-1}) at the CECOMAF area, followed by concentrations in CAPT area (61.41–98.71 µg kg^{-1}) and MTT area (259.9–358.52 µg kg^{-1}), and then by the DIGUE area (375.46–397.45 µg kg^{-1}).

High concentrations of DDE and DDD were detected in sediments. Indeed, DDT can be converted into DDE or DDD by biodegradation under aerobic conditions via dehydrochlorination and oxidation process such as those, for example, induced by the metabolism of molluscs [40] or by reductive dechlorination under anaerobic conditions in sediments [43, 44].

Using the ratio (DDD + DDE)/DDT it is possible to clarify whether DDT input was historic or from recent applications [45]. Ratios > 0.5 indicate a past application of DDT, and ratios < 0.5 indicate recent DDT application. In this study, the (DDD + DDE)/DDT values ranged from 0.3 to 7.4; 1.1 to 5.5; 1.1 to 40.6 and 1.2 to 6.1 for CECOMAF, CAPT, MTT and DIGUE sites, respectively (Table 4). These results suggest a recent input of DDT in the CEFOMAF area and historical inputs in the other areas. These DDTs may come from domestic applications and agricultural misuse. A WHO report pointed out that in fighting against the malaria vectors in Congo, DDTs have been authorized for household applications [46]. Many hospitals located near the river also use insecticides for disinfestation purposes and discharge their untreated effluents into waterways. This may explain the high level of DDTs along the watershed of N´djili River. The values of Σ_6 DDTs in sediments from N´djili River were higher than both the TEL and PEL values indicating that the current levels of DDTs are a threat to aquatic biota.

Pyrethroid compounds, such as cypermethrin and deltamethrin, displayed high concentrations from 9.70 to 44.49 µg kg^{-1} and from 12.68 to 208.67 µg kg^{-1}, respectively, in the N´djili River sediments (Table 4). Chlorpyrifos, an organophosphorus pesticide known to have a much shorter environmental half-life than OCs, displayed also high concentrations in N´djili River sediments and these were originated from recent chlorpyrifos applications [2].

The presence of these modern compounds in relatively high concentrations in sediments testified their intensive use in the region nowadays. Following the authorization of their import by the Minister of Agriculture in 2013, these insecticides are presently used in the regional agriculture [48].

3.2.4 Concentrations of polybrominated diphenyl ethers (PBDEs)

Polybrominated diphenyl ethers (PBDEs) belong to a class of chemicals that are added to certain manufactured products as fire retardants, i.e., to reduce the chances that the products will catch on fire. Finished products that may contain PBDEs are furniture foam padding, wire insulation, rugs, draperies, upholstery and plastic cabinets for televisions, personal computers, and small appliances. These chemicals can leak from products that contain them or escape when the products that contain them break down. They do not dissolve easily in water. Instead, they stick to particles and settle to the bottom of rivers or lakes. Some PBDEs can build up in certain fish and mammals when they eat contaminated food or water [47].

The concentrations of polybrominated diphenyl ethers (PBDEs) in sediments from N'djili River are shown in Table 5. The Σ6 PBDEs concentration ranged from 3.6–7.6 µg kg^{-1}, 7.2–15.4 µg kg^{-1}, 9.3–15.1 µg kg^{-1} and 12.4–23.1 µg kg^{-1} for CECOMAF, CAPT, MTT and DIGUE areas, with a clear increasing trend from South to the North. The order of PBDE concentrations was: BDE47 > BDE99 > BDE100 > BDE154 > BDE153 > BDE28. Substantial differences between samples highlighted the variability of PBDE load and congener mixture in the sediment. However, at all sites in N´djili River, the BDE99 and BDE100 concentrations exceeded the threshold value (0.4 µg kg^{-1}) recommended by the Canadian Federal Environmental Quality Guidelines [48].

3.3 Comparison of the contamination of N´djili River sediments with other regions

For a better framing and understanding of the contamination of N´djili River, the concentrations of contaminants can be compared with contamination levels in aquatic ecosystems in other tropical regions and in non-tropical regions (Table 6). Some of these aquatic ecosystems are located in coastal areas and surrounded by extensive agriculture fields, such as the lagoons at the northwest of Mexico and the coastal lagoons at the Pacific coast of Nicaragua [42, 49, 50, 53]. Other aquatic ecosystems are located near highly populated urban areas such as the Red River by Hanoi, in Vietnam, and the Manila Bay in Philippines. Manila Bay is of particular interest as a comparison because this bay receives the discharge of several rivers crossing agriculture fields and urban areas of the Metropolitan Manila with above 14 million inhabitants.

In the African continent significant contamination by organochlorine pesticides has been reported for other rivers, such as the Niger River in Nigeria and the Ga-Selati River in South Africa [58, 59].

PCB concentrations in the N´djili River ranked very high in comparison with other regions worldwide and revealed an extreme contamination by these organic contaminants (Table 6). This calls for an urgent control of PCB sources in the Kinshasa region.

Most of the classic OC pesticides, such as endrin, dieldrin, heptachlor, and chlordane, were not detected in N´djili river sediments indicating that they were either not much used in the region or were degraded already to very low levels. Some among the OC pesticides, such as HCB, HCHs, and endosulfan were quantified in the N´djili River sediments but were present in low concentrations which are comparable to concentrations measured in other regions (Table 6). This indicates that these compounds have not been used in Kinshasa region for a long time and their levels followed the worldwide decreasing trend after the ban of POPs. Furthermore, this clarifies that old pesticides donated to African countries after becoming disused in developed countries, which have been a concern because of potential unsecure application, did not show up in environmental samples in this region.

The case of DDT compounds was very different from other OCs, and their average concentrations in the N'djili River ranked extremely high even in comparison with regions with known intensive past use of DDT, such as Nicaragua and Vietnam (Table 6). This extreme contamination of N´djili River by DDT may deserve consideration by authorities as it seems likely that under the legal exception for DDT use for sanitary purposes, large amounts of DDT might have been used in agriculture.

The classic OC pesticides, once intensively used, have been gradually replaced by OPs and Pyrethroids with shorter environmental half-lives. However, many among these modern chemicals are also bioaccumulative and toxic to aquatic biota, particularly the OPs such as chlorpyrifos [2]. The concentrations of chlorpyrifos, cypermethrin and deltametrin in N´djili River sediments were already elevated and comparable to other regions worldwide with noticeable contamination with residues from these chemicals. As these compounds were recently introduced in the DRC, such level of contamination was attained in a short time and this indicated that these compounds were used in very liberal amounts.

The PAH and PBDE levels determined in N´djili River were comparable to levels reported from other rivers in Asia and considered highly contaminated (Table 6).

Pollutant levels may vary among regions due to many reasons, including the amounts of chemicals applied in the region and waste management procedures. Nevertheless, the organic contaminant levels measured in N´djili river sediments globally ranked very high in comparison with other worldwide regions receiving also high loads of contaminants (Table 6).

The concentrations of pollutants in N´djili River sediments by Kinshasa may also be compared with concentrations determined in sediments from the upper reaches of Congo River by Kisangani, reported by Verhaert et al. [14] (Table 6). The concentrations in the upper Congo River were generally one to three orders of magnitude lower than in the N´djili River, indicating that the contamination of N´djili River originated in pollutant discharges from the Kinshasa area which, in turn, contributes to enhance the contamination of Congo River.

4 Conclusion

An extensive assessment of the concentration and distribution of persistent organic pollutants was carried out in N'djili River sediments. The results indicated extensive contamination of the river by POPs in all areas investigated. In the river sediments, concentrations of ∑12 PCBs reached 710 µg kg^{-1}, PAHs reached 1138 µg kg^{-1}, ∑6 DDT reached 397 µg kg^{-1} and ∑6 PBDE reached 23 µg $kg.^{-1}$

For several chemical groups, the concentrations in sediments exceeded sediment quality guidelines. For example, the ∑6 DDT compounds at all sampling sites exceeded both the TEL and PEL values of 6.15 and 20.03 µg kg^{-1}, respectively, indicating that the current levels of these pesticides in sediments are able to induce toxic effects on benthic organisms. Furthermore, although DDTs in sediments seemed to be from past applications there were evidence for recent DDT applications in some areas as well.

The Fluo/(Fluo + Pyr), IDP/(IDP + BghiP) and BaA/(BaA + Chry) ratios indicated several PAH origins including petrogenic and pyrolytic sources, petroleum, grass, wood and coal combustion. This result was not surprising because of the presence of oil exploitation and widespread use of coal in cooking, which are known PAH sources. Current levels of PAHs in sediments also exceeded the TEL values from sediment quality guidelines.

PBDEs, which are used as fire retardants, were detected in all samples of river sediments and exceeded sediment quality guidelines adopted by the Canadian government.

Other agrochemicals more recently introduced in the market, such as chlorpyrifos and several pyrethroids which are less persistent than OC pesticides, were already present in N´djili River sediments in non-negligible concentrations which indicated their intensive use in the region and discharge into aquatic ecosystems.

The research on the contamination of N´djili River provided first-hand information on POPs and several other organic contaminants in an important African river flowing through the capital of DRC and supplying drinking water to the population. Unambiguously, results indicated that the N'Djili River is highly contaminated by many persistent organic pollutants including old and modern agrochemicals. These pollutants were accumulated in sediments and several groups of chemicals reached concentration levels that are toxic to aquatic biota. Synergistic effects of all these chemicals on biota are unpredictable and may bring about even more disastrous consequences to the aquatic ecosystem.

The chemical contaminants found in river sediments are expected to be present also in river water, although at lower concentrations and depending upon the octanol–water partitioning coefficient (K_{ow}) of each compound. As the K_{ow} for POPs are generally high, the concentrations of the chemicals dissolved in river water probably will range from nanogram to microgram per Liter levels (e.g. [41]). Eventually, this may allow for chemical contaminants in water to exceed safety limits in drinking water [46]. Therefore, the current results which primarily revealed that sediments in N'djili River were highly polluted by several classes of organic chemicals toxic to aquatic biota, also indicated that residues dissolved in the water may represent a public health hazard. As the N'djili River supplies drinking water to the population, the contamination of the river is a critical issue to public health and the current situation is not sustainable. Therefore, measures to control the use of chemicals and waste water discharges into the river seem urgently needed.

River water and water supplied for human consumption were not directly analyzed. A further step in research, required for the full assessment of public health risks, would be the analysis of water for human consumption. This is in the prospects for future work.

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Declarations

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