Accumulation of toxic metals and organic micro-pollutants in
sediments from tropical urban rivers, Kinshasa, Democratic Republic
of the Congo

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Abstract

The increasing contamination of fresh water resource by toxic metals and Persistence Organic Pollutants (POPs) is a major environmental concern globally. In the present investigation, surface sediments collected from three main rivers named, Makelele, Kalamu and Nsanga, draining through the city of Kinshasa, Democratic Republic of the Congo, were characterized for grain size, organic matter, toxic metals, POPs (including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs)), and polycyclic aromatic hydrocarbons (PAHs). Furthermore, enrichment factor (EF) and geoaccumulation index (*I_{geo}*) were performed to determine metal source and pollution status. The results highlighted high concentration of toxic metals in all sediment samples, reaching the values (mg kg^{-1}) of 325 (Cu), 549 (Zn), 165 (Pb) and 1.5 (Cd). High values of PCBs and OCPs were detected in sediment samples, e.g. in Makelele rivers, PCB values ranged from 0.9-10.9 with total PCBs ($\sum 7 \text{ PCBs} \times 4.3$): $169.3 \mu\text{g kg}^{-1}$; OCPs from 21.6-146.8 with $\sum \text{OCPs}$: $270.6 \mu\text{g kg}^{-1}$. The PBDEs concentrations were higher in investigated rivers comparatively with values detected in many rivers from Sub-Saharan Africa. The $\sum \text{PAHs}$ value ranged from 22.6 to $1011.9 \mu\text{g kg}^{-1}$. River contamination may be explained by local intense domestic activities, urban and agricultural runoff, industrial and hospital wastewaters discharge into the rivers without prior treatment. This research provides not only a first baseline information on the extent of contamination in this tropical ecosystem but also represents useful tools incorporated to evaluate sediment quality in the river receiving systems which can be applied to similar aquatic environments.

Keywords: Urban rivers; sediments; toxic metals; POPs; PAHs; tropical conditions

1. Introduction

The water resource contamination by toxic metals and POPs is a worldwide problem because these chemicals are not degradable in the environment and can persist in sediments for decades or even centuries. Most of them are characterized by long-term stability and can have high toxic effects on aquatic living organisms (Wildi et al., 2004; Ghrefat and Yusuf, 2006; Thevenon et al., 2012; Mwanamoki et al., 2014b). Previous studies have highlighted that sediment as recipients and reservoirs of toxic heavy metals (Pote et al., 2008; Varol, 2011). In addition, accumulated toxic elements and POPs in sediments over the period of time serve as important indicators to assess and reevaluate the pollution history (Mwanamoki et al., 2014a; Devarajan et al., 2015b; Doong et al., 2008). On the other hand, polluted sediments represent a significant source of contamination in freshwater organisms and have long-term implications for human health (Thevenon et al., 2013; Raghunath et al., 1999). The discharge of untreated urban effluents into river environments is a major concern in developing countries. Given this fact, in recent years accumulation of heavy metals in river sediments from developing countries have been reported with more attention (Mubedi et al., 2013; Devarajan et al., 2015b; Tamim et al., 2016; Laffite et al., 2016). Hydrophobic organic compounds (HOCs), such as PAHs, PCBs, and OCPs have been identified as environmental pollutants in all environmental compartments (Wu et al., 1999). Due to their high persistence and low solubility in water, HOCs can accumulate in sediments (Poté et al., 2008). European Union (EU) and the US Environmental Protection Agency (USEPA) highlighted that PAHs are of significant concern with regard to human health as having carcinogenic properties and bioavailability with water, soil, and sediments (Sindermann, 2006; Zhang et al., 2012). PCBs, PAHs, OCPs, and PBDEs are known to have extraordinary stability, high toxicity, extremely high long-range atmospheric transportability, and potential threats to human health and environmental ecosystems (Cui et al., 2016; Poto et al., 2012). Heavy metals, POPs and PHAs could be accumulated in aquatic organisms and eventually may transfer to higher order

organisms including humans (Pardos et al., 2004; Huang et al., 2006; Díez et al., 2009). Therefore, it is important to assess the accumulation of toxic heavy metals and POPs in the environmental compartments to evaluate the ecological risk.

Kinshasa is the capital and largest city of the Democratic Republic of the Congo (DRC) and has an estimated population of more than 13 million. In Congo DR urban rivers are specially considered as several sources of pollution including sanitary landfills, mining activities, discharge of effluents from industries, hospitals, and urban activities. The Makelele, Kalamu, and Nsanga Rivers are the main rivers and tributaries of Congo River that drain the capital city of Kinshasa (Tshibanda et al., 2014; Mwanamoki et al., 2015). These rivers serve as sources of recreational use, bathing, drinking water supply and irrigation for urban agriculture. A very few comprehensive studies of heavy metals, pesticides and POPs in Congo River Basin have been conducted (Verhaert et al., 2013; Mwanamoki et al. 2014b; 2015; Laffite et al., 2016). These studies recommended further researches in the urban river receiving systems in studied area to evaluate the quality of the aquatic ecosystem. The levels of toxic metals, persistent organic pollutants (POPs: including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated biphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs) in sediments are good indicators to evaluate the environmental quality of aquatic systems. Therefore, the objective of the present study was to discuss the occurrence and spatial distribution of toxic metals, POPs and PAHs in sediments from three of main rivers draining the capital city of Kinshasa. Sediment analyses were performed for the physicochemical characterization including sediment grain-size, total organic matter (loss on ignition), total carbon (TC), total phosphorus (TP), metals including Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Sb, and Pb, and persistent organic pollutants (including OCPs, PCBs, PBDEs) and PAHs. In addition, the degree of sediment pollution by

heavy metals was evaluated using geo-accumulation index (*I_{geo}*) and enrichment factor (EF) calculation.

2. Material and methods

2.1. Study sites and sampling procedure

Three rivers named Makelele, Kalamu and Nsanga draining the capital city of Kinshasa (Fig. 1), DRC were selected in this study according to the recommendations of our previous studies (Mubedi et al., 2013; Tshibanda et al., 2014; Mwanamoki et al., 2014ab; 2015). Sampling took place in January 2016. The surface sediments (0-4 cm layer) were collected from (i) Makelele River (R1, n=3, labelled: R1A, R1B, R1C), (ii) Kalamu River (R2, n=4, labelled: R2A, R2B, R2C, R2D) and Nsanga River (R3, n=2, labelled: R3A, R3B). GPS location of sampling site is presented in Table-1.

Approximately 400-500 g of sediments were taken from each site in triplicate. The surface sediments from all sites were collected manually at about 0.3-1 m water depth. Sediment samples were kept in autoclaved glasses for POPs and PHAs analysis and in polyethylene bottles for other analyses. All samples were stored in an icebox at 4 °C that were transported to the laboratory for different treatments within 24 h. After preliminary treatments, the samples were sent to the Department F.-A. Forel, the University of Geneva for analysis.

2.2. Sediment grain size and organic matter, total organic carbon, total nitrogen and phosphorus analysis

The particle grain size was measured in fresh sediment with a Laser Coulter® LS-100 diffractometer (Beckman Coulter, Fullerton, CA, USA), following 5 min ultrasonic dispersal in deionized water. The sediment total organic matter content was estimated from mass loss on ignition, at 550°C during 1 hour in a Salvis oven (Salvis AG, Luzern, Switzerland).

The percentage of TC and Total Nitrogen (TN) was measured with an Elemental Analyser (Perkin Elmer CHNS/O PE 2400 Series II, Waltham, MA, USA) by the following conditions: Combustion Temperature: 975°C, Reduction Temperature: 500°C, Detection Oven: 82.2 °C, Pressure: 514.0 mm Hg.

The TP was measured with a spectrophotometer (Helios Gamma UV-Vis, Thermo scientific, Waltham, USA) at 850 nm. Fifty milligrams of dry sediments were diluted in 5 mL 1N HCl in centrifuge tubes and ultrasonicated (at ambient temperature) for 16 h and then centrifuged at 4000 rpm for 20 min. The supernatant was mineralized for 45 min at 130°C after addition of 5 % K₂S₂O₈ solution. The TP concentration was determined by measuring the absorbance of the blue complex obtained after reduction of molybdophosphoric acid according to the method described by Poté et al. (2008).

2.3. *Metal analysis in sediment samples*

Before analysis, the sediment samples were lyophilized, grounded into a fine homogenized, and sieved through a 63 µm mesh size sieve and digested according to the previous method as described by Poté et al. (2008). The digested samples were subjected to analysis by Inductive Coupled Plasma-Mass Spectroscopy (Agilent 7700x series ICP-MS developed for complex matrix analysis, Santa Clara, CA, USA). A collision/reaction cell (Helium mode) and interference equations were utilized to remove spectral interferences that might otherwise bias results. This is sufficient for many routine applications. Multi-element standard solutions at different concentrations (0, 0.02, 1, 5, 20, 100 and 200 µg L⁻¹) were used for calibration. The certified sediment reference materials LKSD-2 and LKSD4 were used for lake and river sediment analysis in order to verify the sensibility of the instrument and the reliability of the results, respectively. Concentrations are in mg kg⁻¹ (ppm) dry weight. The standard deviations

of 3 replicate measurements were below 5 %, and chemical blanks for the procedure were less than 1 % of the sample signal.

2.4 Geoaccumulation index and enrichment factor

The enrichment factor (EF) and geo accumulation index (*I_{geo}*) in sediment samples were calculated as described by Maanan et al. (2004), Varol (2011) and Thevenon et al. (2012, 2013). The *I_{geo}* accumulation index is defined by the following equation:

$$I_{geo} = \log_2 (C_n) / 1.5 (B_n)$$

C_n: concentration of metals (n) examined in the sediment samples

B_n: concentration of the metal (n) geochemical background

1.5: lithospheric effect background correlation matrix factor

Enrichment factor is a useful tool to determine the degree of anthropogenic heavy metal pollution. EF is calculated using the following equation, and according to our previous study, Scandium (Sc) was used for the geochemical normalization (Mwanamoki 2014b).

$$EF = (\text{metal/Sc})_{\text{sample}} / (\text{metal/Sc})_{\text{background}}$$

2.5. Chlorinated pesticides, PCBs, PAHs and PBDEs analysis

Chlorinated pesticides, PCBs, PAHs and PBDEs analysis was performed according to our previous paper as described by Mwanamoki et al. (2014b) and Thevenon et al. (2013). Briefly: all glassware was rinsed with acetone and hexane and tested before using. Blanks do not present any quantifiable amount of contaminants or interfering compounds. After addition of surrogate standards (¹³C-labeled for all halogenated compounds and deuterated-labeled compounds for all PAHs), about 5 g of dry sediment were extracted with a mixture of 20 % of

acetone in 80 % of hexane (v/v) for 4 hours into a Soxhlet system (Buchi B-811, Flawil, Switzerland). Interfering sulfur compounds were removed by addition of activated copper to the extract. Then, 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 Silicagel, according to de Boer et al. (2001). Three separated fractions were collected: first with 16 mL of hexane, then 35 mL of hexane, and finally 50 mL of hexane: dichloromethane (v/v, 1:1). The first two fractions should contain respectively PCBs and PBDEs. PAHs and chlorinated pesticides are distributed on the 3 fractions. After a new reduction of the volume, chemicals were measured 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-5ms column (60m x 0.25mm x 0.25 μ m) and one ZB-XLB column (20m x 0.18mm x 0.18 μ m), were used for separation and identification of the different compounds. The choice of the column for the identification of a specific compounds is mentioned on table 4a and 4b. *Chlorinated pesticides* analyzed in sediment were: Hexachlorocyclohexane (HCH) (isomers alpha, beta & gamma) Heptachlor, Heptachlorepoxyde cis, Heptachlorepoxyde trans, hexachlorobenzene, Aldrin, Dieldrin, Endrin, Oxy-chlordane, Alpha-chlordane, Gamma-chlordane, Cis-nanochlor, 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) and Mirex. In the present work, results for DDT compounds are given as Σ DDT, meaning the sum of the DDT and metabolites. These pesticides are included in the Second Round of UNEP-coordinated Global Interlaboratory Assessment 2012/2013 (UNEP-POPs, 2012). Selected congeners of PCBs searched were

186 IUPAC numbers: CB-28 (2,4,4'-trichlorobiphenyl), CB-52 (2,5,2',5'- tetrachlorobiphenyl),
187 CB-101 (2,4,5,2',5'-pentachlorobiphenyl), CB-149 (2,3,6,2',4',5'-hexachlorobiphenyl), CB-
188 118 (2,4,5,3',4'-pentachlorobiphenyl), CB-153 (2,4,5,2',4',5'-hexachlorobiphenyl), CB-105
189 (2,3,4,3',4'- pentachlorobiphenyl), CB-138 (2,3,4,2',4',5'- hexachlorobiphenyl), CB-128
190 (2,3,4,2',3',4'-hexachlorobiphenyl), CB-156 (2,3,4,5,3',4'- hexachlorobiphenyl), CB-180
191 (2,3,4,5,2',4',5'- heptachlorobiphenyl) and CB-170 (2,3,4,5,2',3',4'- heptachlorobiphenyl).
192 These CBs were used for certification purposes by the former Community Bureau of
193 Reference (BCR) of the European Union (Wells et al., 1992). Results are given as $\Sigma 12\text{PCBs}$
194 meaning the sum of all CBs measured in a sample and also as "Total PCBs" meaning the sum
195 of 7 selected CBs (28, 52, 101, 118, 138, 153 and 180) multiplied by a correction factor of 4.3
196 (FOEN, 1998).

197 *PBDEs*: Selected congeners were IUPAC numbers: BDE-17 (2,2',4-tribromodiphenyl ether),
198 BDE-28 (2,4,4'-tribromodiphenyl ether), BDE-47 (2,2',4,4'-tetrabromodiphenyl ether), BDE-
199 66 (2,3',4,4'-tetrabromodiphenyl ether), BDE-85 (2,2',3,4,4'-pentabromodiphenyl ether),
200 BDE-99 (2,2',4,4',5-pentabromodiphenyl ether), BDE-100 (2,2',4,4',6-pentabromodiphenyl
201 ether), BDE-138 (2,2',3,4,4',5'-hexabromodiphenyl ether), BDE-153 (2,2',4,4',5,5'-
202 hexabromodiphenyl ether), BDE-154 (2,2',4,4',5,6'-hexabromodiphenyl ether), BDE-183
203 (2,2',3,4,4',5',6-heptabromodiphenyl ether), BDE-190 (2,3,3',4,4',5,6-heptabromodiphenyl
204 ether). BDE-209 (decabrominated) was not analysed. ΣPBDEs is the sum of all studied
205 PBDEs. These PBDEs are included in the Second Round of UNEP-coordinated Global
206 Interlaboratory Assessment 2012/2013 (UNEP-POPs, 2012).

207 Quantitation limits (LOQ) defined as 10 times baseline noise, were comprised between 0.02
208 ng/g (p,p'-DDE) and 0.15 ng/g for BDE-190 dry weight.

209 *PAHs*: Naphthalene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene,
210 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, Σ PAHs means the sum of all 16 studied PAHs. These PAHs are similar to those proposed by US EPA to be measured in sediment samples, with exception of Benzo(e)Pyrene and addition of Acenaphthylene.

The results for POPs and PAHs analysis are expressed in $\mu\text{g kg}^{-1}$ dry weight.

2.6. Data analysis

Triplicate measurements were performed for all the analyses. Statistical treatment of data (Spearman's rank order correlation) has been realized using SigmaStat 12.5 (Systat Software, Inc., USA). Principal Component Analysis (PCA), a multivariate statistical analysis was performed using R (R Core Team, 2015) in order to understand relationship among analyzed compound and their potential sources. Prior to performing PCA analysis, data were centered in order to maximize the dispersion.

3. Results and discussion

3.1. Physicochemical characteristics of sediments

Sediment characteristics including particle grain size, OM, TC, TN, and TP are shown in Table 1. The total OM in sediments ranged from 5.3 to 9.2, 7.2-12.6 and 1.7-13.4% for the sites R1, R2, and R3, respectively. There was no significant difference in total OM among all samples (triplicate) from the same site. According to the results of our previous studies (Poté et al., 2008; Haller et al., 2009; Mubedi et al., 2013), the organic matter in non-contaminated freshwater sediments varied from 0.1-6.0%. The results of this study indicated that the sediment from studied sites can be considered as polluted/moderately polluted by organic

matter. For example, OM can reach more than 30% in sediments contaminated by the municipal WWTP effluent waters (Poté et al. 2008; Devarajan et al., 2015a).

Surface sediments of rivers in all studied sites are generally sandy-silt. For all samples, the sand values ranged from 61.0-95.0% and silt from 5.8-39.0%. The maximum value of clay was observed at the site R2A (1.5%). The sediment median grain size varied substantially internally within the sampling sites ($p < 0.05$). The values ranged from 46.8-105.3, 32.9-195.9 and 79.5-225.3 μm for R1, R2 and R3 respectively. In accordance with our previous report, the percentage of grain size in sediments observed in this study could probably be responsible for high porosity and high permeability, and further flexible transportation of the sediment downstream (Wildi et al., 2004; Thevenon et al., 2011; Bartoli et al., 2012). The values of TC content varied from 1.7-4.8, 2.1-7.2 and 1.7-2.4 % for R1, R2, and R3, respectively. The TN exhibited relatively low concentrations and a limited variability in sediments. The values ranged from 2.6-6.3, 2.8-3.6 and 1.8-4.2 mg kg^{-1} for the sites R1, R2, and R3, respectively. The total phosphorous contents of the sediments varied considerably with sampling sites ($p < 0.05$). The values ranged from 92.6-242.7, 76.5-163.2, 67.4-89.8 mg kg^{-1} for the sites R1, R2, and R3, respectively. The results obtained are in agreement with our previous studies, which demonstrated that there are large variations in the distribution of TC, TN, TP and grain size in sediments from some urban rivers located in the city of Kinshasa (Mubedi et al., 2013; Tshibanda et al., 2014; Kilunga et al., 2016; Laffite et al., 2016).

3.2. *Metal concentrations in the surface sediments*

The results of the heavy metals analysis are presented in Table 2. It is noted that the concentrations of four heavy metals including Cu, Zn, Cd and Pb were found considerably higher in most of the sediment samples. The concentration of Zn was found to be higher than the threshold level in all sediment samples and the value ranged from 128.1-549.6 mg kg^{-1} .

The concentration of Pb was found to be in the range of 24.6-165.3 mg kg⁻¹. It was observed that the concentration of Pb generally high in all sediments except for the site R2B. The highest concentration of Cu was recorded at the site R3B with the value of 325.14 mg kg⁻¹. Similarly, for Cd at 1.5 mg kg⁻¹ and Pb at 165.30 mg kg⁻¹ in the same site. The concentration of heavy metals including Cu, Zn, Cd and Pb recorded in this study were primarily compared with the Sediment Quality Guidelines for the Protection of Aquatic Life (CCME EPC-98E 1999). The evaluation of the potentially deleterious effects of the metals towards benthic fauna, which is based on consensus-based guidelines for the sediment quality (MacDonald et al., 2000a; Long et al., 2006), can give an estimate of the hazard that the sediments may represent for the local biota. Authors proposed (MacDonald et al., 2000a; Long et al., 2006) for specific metals a “threshold effect concentration” (TEC), a level above which some effect (or response) will be produced in an organism and below which it will not, and a “probable effect concentration” (PEC), a contaminant level that is likely to cause an adverse effect on biota. Though distribution of heavy metals varied among all sampling sites, the concentration of Cu, Zn, Cd, and Pb is generally higher than the threshold level. Surprisingly, the concentrations of Zn, Pb and Cd are higher than that of the Congo River (Mwanamoki et al., 2014b; Mwanamoki et al., 2015). The results of the present stud show that the higher concentrations of Cu, Ni, Zn, and Pb are likely to have a harmful effect on aquatic organisms. Therefore, the sediments from Makelele, Kalamu and Nsanga Rivers can be considered as highly polluted by heavy metals and this could be explained by various industrial sources and urban discharge into the rivers. Urban rivers in Kinshasa seem to be under high threat and stretch of the river running through urban areas is extremely polluted due to open drains, sewage inflow and landfills. (Mavakala et al., 2016; Mwanamoki et al., 2015, Mubedi et al., 2013). However, the presence of other non-identified sources (such as artisanal activities) and untreated hospital effluent water discharge cannot be excluded (Laffite et al., 2016).

3.3. *Enrichment factor (EF) and Geoaccumulation index (Igeo)*

EF and *Igeo* values for selected metals in sediment samples from rivers are presented in Table 3. The EF and *Igeo* indices are important in discriminating between anthropogenic metals and provide a quantitative criterion for characterizing the sediment according to the degree of metal pollution (Adamo et al., 2005). According to the *Igeo* values, pollution of toxic metals in studied sites was classified in the order of Zn > Pb > and Cu. The *Igeo* classification of “extremely polluted” was observed for Zn in samples from the sites R2C and R3B, and “heavily polluted” were observed in samples from R1A, R1B, and R2A. Other sites are “moderately to heavily polluted” level for Zn. For Pb, “moderately to heavily polluted” level was observed for all samples for the river R1, while the site R2C and R3B present “heavily polluted” level. Cu, *Igeo* values were ranged from -0.40 to 2.63 and the high *Igeo* value was observed in the site R3A. Based on the *Igeo* values of Cu, except for the sites R2B and R2C, other sites were not polluted by Cu.

The enrichment results were interpreted according to previous studies (e.g. Sakan et al., 2009; Mavakala et al., 2016). The EF values for Cu was ranged from 1.28 to 51.15, indicating “minor to extreme enrichment”. For Cu the highest EF value was recorded at site R2A and R2B, indicating “extreme enrichment”. Whereas, three sites (R2D, R3A, and R3B) for Cu showed lesser values of EF (1.28 to 1.58), implied that there were minor enrichments of Cu. The EF values for Zn ranged from 15.70 to 135.26, indicating “severe to extremely severe enrichment”. Intriguingly, Zn showed the highest EF values among the toxic metals investigated. The EF values of Zn for the sites R1A (88.43), R1B (79.69), R1C (92.49), R2A (84.80), R2B (68.38) and R2C (135.26) indicated “extreme enrichment”. It was observed that the EF values of Pb ranged from 7.70 to 128.81, which indicated that “moderately severe to extremely severe enrichment”. Furthermore, the EF values of Pb revealed “extreme

enrichment” for the sites R1C (78.35) and R3A (128.81) and very “severe enrichment” for the sites R1A (42.78), R1B (38.88), R2A (43.64) and R2B (29.52). The results suggested that Zn and Pb could be originated from anthropogenic sources. Whereas Cu might have originated both from natural and anthropogenic sources (Mavakala et al., 2006; Mwanamoki et al., 2015).

3.4. *Spatial distribution of persistent organic pollutants in sediments*

The concentration of persistent organic pollutants (POPs) including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and polycyclic aromatic hydrocarbons (PAHs) in surface sediments from river Makelele (R1), Kalamu (R2) and Nsanga (R3) are shown in Table 4a and 4b. All results are reported to dry weight. PCBs were detected in most surface sediment samples. In the current study 12 PCB congeners (PCBs 28, 52, 101, 105, 118, 128, 138, 149, 153, 156, 170 and 180) were detected. The sum of 12 PCBs ($\sum 12$ PCBs) ranged between 3.46 to 52.94 $\mu\text{g kg}^{-1}$. Comparison of the ($\sum 7$ PCBs $\times 4.3$) PCBs for surface sediment samples at the nine sampling sites in three different rivers revealed the maximum concentration for site R1C (169.29 $\mu\text{g kg}^{-1}$), followed by R2D (83.24 $\mu\text{g kg}^{-1}$) and R3B (35.90 $\mu\text{g kg}^{-1}$). Concentrations increase from upper stream to downstream in all rivers, confirming the enrichment of PCBs coming from more heavily populated areas. In all sediments, the most abundant congeners were in order 153>138>180>149> 101, penta and hepta chlorobiphenyls. These congeners are reflecting historic use of PCB mixtures containing penta, hexa and hepta chlorobiphenyls. This pattern is somewhat different from Verhaert, et.al. (2013) who found a PCB pattern indicating dominant use of Arochlor 1254. PCB 138, 153 and 180 are among the most persistent PCB congeners, and have long half-life. As the use of commercial PCBs was forbidden in the 1980s, what we find here are a number of the most persistent PCB congeners, in this case in

aquatic sediment environment. Fair enough, the pattern of PCB is reflecting historic use of commercial mixtures but it is also important to stress that the pattern found in this study reflects high persistence (long half-life) (Stockholm Convention, 2017). MacDonald et al. (2000b) proposed values for TEL ($59.8 \mu\text{g kg}^{-1}$) and PEC ($676 \mu\text{g kg}^{-1}$) for “total PCBs”, that we can compare with our $\sum 7 \text{ PCBs} \times 4.3$. Site R1C (Makelele River) and all sites (R2A, R2B, R2C and R2D) from Kalamu River presented higher concentrations than PEL value. To understand the degree of contamination, the concentrations of PCBs in sediments from Rivers Makelele, Kalamu and Nsanga were compared with PCB levels recorded in previous studies in Congo DR and on other tropical developing countries.

The contents of ($\sum 7 \text{ PCBs} \times 4.3$) PCBs were higher than those reported for the Congo river basins (Verhaert et al., 2013; Mwanamoki et al., 2014b) and a similar site, Yamuna River in Delhi in India (Kumar et al., 2013). However, concentrations of PCBs were lower as compared to reported by Malik et al. (2014) from the sediment of Soan River, Pakistan ($27.9\text{--}116 \mu\text{g kg}^{-1}$). In order to investigate potential PCBs sources, PCA was performed (Fig. 2a). The active variable was composed of the congeners composition of PCBs at different sampling sites. The first component was mainly influenced (94.5%) by the PCBs load. The second component explains the relative congener composition in samples. Based on the loading plot of the PCA, strong differences in PCBs load and relative congener pattern was observed among the different R1, R2, and R3 sampling sites. Furthermore, all the PCBs were correlated with each other ($R > 0.77$, $p < 0.05$) but three cluster of highly strong correlation between PCB congeners can be seen: 101-105-118 ($0.99 < R < 1$, $p < 0.001$), 138-149-153-156 ($0.99 < R < 1$, $p < 0.001$) and 170-180 ($R = 1$, $p < 0.001$). These observations suggest that river water quality in Kinshasa has been hugely impacted by a multi-diffuse direct discharge of industrial (artisanal activities included) and urban waste water. Therefore, we suggest that the urban and industrial untreated effluents and runoff water (one important source of PCBs being

the atmospheric fallout), could be the on-going source of the contaminations of the presented PCBs in sediments of three rivers.

For the 35 OCPs targeted in this study, only 14 were detected i.e. hexachlorobenzene, β - and γ -HCH, chlorpyrifos-ethyl, trans-nonachlor, p,p'- and o,p'-DDE, p,p'- and o,p'-DDD, p,p'- and o,p'-DDT, cyhalothrin- λ , cypermethrin a, cypermethrin b and deltamethrin. None of the OCPs α - and δ -HCH, chlorpyrifos-methyl, α -, γ - and oxy-chlordane, dieldrin, endrin, endrin aldehyde and ketone, heptachlor, heptachlor epoxid A and B, aldrin, endosulfan I and II, endosulfan sulfate, methoxychlor, acetochlor and Mirex were detected. The non-detection of these OCPs may be due to their regulation and/or banishment by US EPA and European directives. Figure 2b shows the results of PCA analysis for OCPs. The first and second components explained 59.7% and 27.5% of the total variance. The first component was mainly influenced by the quantity of OCPs while the second component was influenced by congeners composition. All sites are grouped in the same cluster in reason of a similar OCPs mixture, but R1A and R1C differ from the other sites because of their strong contamination by DDT and its derivatives at R1A site and chlorpyrifos-ethyl & deltamethrin at the R1C site.

Pyrethroids pesticides like cypermethrin, cyhalothrin and deltamethrin have all neurotoxic effects and may cause adverse health effects in humans. Cypermethrin and deltamethrin are highly toxic to aquatic life, especially fish. The concentration of deltamethrin ranged from 27.3 to 227.5, 32.2-97.3 and 12.5-69.1 $\mu\text{g kg}^{-1}$ for the River Makelele, Kalamu and Nsanga respectively. Since the year 2013, the Ministry of Agriculture of DRC has approved the import, sale, and use of deltamethrin and chlorpyrifos for insecticidal applications in agriculture (M.A.P., 2016). As a result, the above - mentioned chlorinated pesticides has been intensively used regularly in urban agriculture. Furthermore, many hospitals nearby urban river sites have been using insecticides for cleaning purposes. On other hand, the agricultural runoff and untreated hospital effluent waters are discharged into the

river receiving systems without regulation. These aspects might have attributed to the high concentration of deltamethrin and other chlorinated pesticides at the studied sites, mainly in the site R1C (Makelele River) located near a great hospital discharging the effluent waters without previous treatment.

OCPs including p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT and o,p'-DDT were detected in all sediments as shown in Table 4. In all sediments, the most dominant isomers were in order p,p'-DDE > p,p'-DDD > p,p'-DDT > o,p'-DDT > o,p'-DDD and o,p'-DDE. The highest concentrations of $\sum 6$ DDTs were recorded in the sediments from the Makelele River for site R1A ($270.61 \mu\text{g kg}^{-1}$), whereas the lowest values detected at the site R3A ($1.23 \mu\text{g kg}^{-1}$), Nsanga River. The fluctuations observed in the total concentrations of $\sum 6$ DDTs suggest different emission sources on river basins or a dilution by clean sediments. The total concentrations of DDTs in all sediments was found to be higher than the TEL and PEL values except for the site R3A. A previous study reported that DDT could be converted into DDE by biodegradation under aerobic conditions via dehydrochlorination and oxidation process, and into DDD involving reductive dechlorination under anaerobic conditions (Syed et al., 2014). Similarly, our results showed elevated concentrations of DDE and DDD. The total concentrations of $\sum 6$ DDTs detected in surface sediments in this study present an extreme increase in comparison to those previously detected in Congo River (Verhaert et al., 2013; Mwanamoki et al., 2014b). According to Li et al. (2016), it is possible to establish if DDTs input is historic or recent origin using the ratio between the concentrations of $(\text{DDD} + \text{DDE})/\text{DDT}$. If the ratio is greater than 0.5 in the first case, indicates historic and less than 0.5 indicates recent input. The values of $(\text{DDD} + \text{DDE})/\text{DDT}$ ranged from 2.7 to 6.12, 2.2-8.9 and 2.2- 4.1 for the River Makelele, Kalamu, and Nsanga, respectively. These results suggest that the rivers have been exposed to DDT from historic use, but may also be derived from indoor household appliances and agricultural misuse. DDTs are one of the important OCPs in

409 connection with human and aquatic organism's health. According to WHO report, DDTs have
 410 been permitted for indoor household appliances in Congo DR for fighting against malaria
 411 vector (WHO, 2011). This could also possibly responsible for the elevated level of DDTs
 412 along the river basins.

413 $\sum 6$ -PBDEs concentration ranged from 1.5-27.9 $\mu\text{g kg}^{-1}$. BDE-47 and BDE-99 were the most
 414 abundant in all sites. We observe a concentration enrichment from upper stream to
 415 downstream in R1 and R2 rivers. Figure 2c represent the results of PCA analysis for PBDEs.
 416 The PCA first component explained 98.3% of the total variance and was mainly influenced by
 417 contamination level. Only 1% of the total variance was explained by the second component.
 418 The different sites showed substantial differences between each other, highlighting the
 419 variability of PBDEs load and congener mixture in the sediment. Canadian Federal
 420 Environmental Quality Guidelines (FEQGs, 2013) recommended the threshold level of 44,
 421 39, 0.4, 440, 5600 and 19 $\mu\text{g kg}^{-1}$ dw in sediment for tri, tetra, penta, hexa, octa, and deca –
 422 BDEs respectively. The BDE99 concentrations at all sites exceed the recommended value of
 423 0.4 $\mu\text{g kg}^{-1}$ dw. The BDE100 concentrations were found higher than the threshold level of 0.4
 424 $\mu\text{g kg}^{-1}$ dw for most of the sediment samples. Coal combustion, urban sewage, the oil spill
 425 from the pirate garages and electronic wastes along the river basins were probably the
 426 possible sources of PBDEs in sediments. It should also be noted that the concentrations are
 427 much higher than in a previous work on Congo River Basin, DR Congo, where Verhaert et al.
 428 (2013) measured between below limits of quantification and 1.9 $\mu\text{g kg}^{-1}$ dw for the sum of 8
 429 BDEs, the same than in our case, more BDE-183 and BDE-209. BDE-209 represents near 90
 430 % of $\sum 8$ -BDEs, followed by BDE-47 and BDE-99, 5 % and 3 % respectively. In another
 431 study on sediments from 6 rivers from Gauteng, South Africa, Olukunle et al. (2015)
 432 measured similar concentrations than in our study, values ranged from 0.82 $\mu\text{g kg}^{-1}$ and 44 μg
 433 kg^{-1} for the sum of 8 PBDEs congeners, including BDE-209. Here, BDE-100, BDE-99 and

BDE-47 were the most abundant congeners. In their study on 4 sampling sites from Murchison Bay of Lake Victoria, Uganda et al. (2012) measured concentrations ranged from 0.060 and 0.179 $\mu\text{g kg}^{-1}$ for the sum of 11 PBDE congeners.

The concentrations of individual PAHs investigated in the current study are presented in Table 4a. All investigated PAHs were detected in most sediments. The concentrations of $\Sigma 16$ PAHs in surface sediments ranged from 22.56-1011.94 $\mu\text{g kg}^{-1}$. Based on PCA loading plot (Fig. 2d), we observed a strong correlation among all the congeners ($R > 0.83$, $p < 0.01$) except for naphthalene ($0.40 < R < 0.74$). The first component, which explains 93.3% of the total variance, was mainly influenced by the PAHs concentration in the sediment and the second component (4.9% of the total variance) was influenced by the PAHs mixture composition. PCA results showed that the composition of PAHs mixture differs substantially from site to site. The highest concentration for $\Sigma 16$ PAHs was observed at R1C, while the lowest was recorded at R3A. Again, concentrations are higher downstream in R1 and R2 rivers, confirming the enrichment of PAHs across the more populated areas. As for Σ PCBs, Σ DDT, sampling point R1C on Makelele River is the most contaminated one. The results indicate that moderate to heavy contamination of sediments by PAHs. According to MacDonald et al. (2000b), proposed values for TEL were (1 610 $\mu\text{g kg}^{-1}$) and PEL (22 800 $\mu\text{g kg}^{-1}$) for the sum of 13 PAHs (the 16 PAHs analyzed in this work with exception of: Dibenzo (a,h) Anthracene, Benzo (g,h,i) Perylene and Indeno (1,2,3c,d) Pyrene). In general, the detection level of the sum of Phenanthrene concentrations in all 9 sediments (635.24 $\mu\text{g kg}^{-1}$) and of Pyrene (550.36 $\mu\text{g kg}^{-1}$) were found to be the most dominant PAHs among all sediments, followed by those of Naphthalene (457.86 $\mu\text{g kg}^{-1}$) and those of Fluoranthene (410.79 $\mu\text{g kg}^{-1}$). The detection level of the sum of Acenaphthylene in all sediments was the lowest (34.24 $\mu\text{g kg}^{-1}$) among the 16 PAHs investigated in this study. As shown in Table 4, the high molecular weight (HMW, 4–6 aromatic rings) PAHs were predominant in surface

sediments. The total concentrations of ($\Sigma 13$ PAHs) in all sediments was found to be lower than the TEL value except for the sites R1C and R2B. However, the total concentrations of 13 PAHs in all sediments was found be lower than the PEL ($22800 \mu\text{g kg}^{-1}$, dw). Yang et al. (2013) reported that soils and sediments are the primary steady sinks for PAHs in the environmental compartments. A similar trend was observed in surface sediments of the current study. Furthermore, the results were in similar to that previously reported for rivers (Kanzari et al., 2014). However, it was noted that the concentrations of PAHs were higher than our previous study (Mwanamoki et al., 2014b) from the sediment of Congo River basins (34.48 to $63.89 \mu\text{g kg}^{-1}$).

Yunker et al. (2002) reported that PAHs can originate from natural or anthropogenic processes. To better understand the potential source of PAHs, four diagnostic ratios were calculated in this study. According to Yunker et al. (2002) and Manneh et al. (1997), it is possible to establish if PAHs are from petrogenic or pyrogenic origin using the ratio between the concentrations of Fluo/(Fluo + Pyr) or IDP/(IDP + BghiP). If the ratio is < 0.4 in the first case, the source is petrogenic, when it is between 0.4 and 0.5 the source is petroleum combustion, and when it is >0.5 , the source is grass, wood, or coal combustion. The ratio of IDP/(IDP + BghiP) smaller than 0.2 indicates the source is petrogenic; a ratio ranged from 0.2 to 0.5 is considered as the source of petroleum combustion, a ratio greater than 5 indicates grass, wood, or coal combustion (Manneh et al., 2016). Furthermore, the ratio of BaA/(BaA+Chry) smaller than 0.2 is generally considered as petroleum source, a ratio between 0.2 and 0.35 indicates either a petroleum or combustion source and a ratio greater than 0.35 indicates pyrolytic origin (Manneh et al., 2016). In addition, Budzinski et al., (1997) propose that if the LMW/HMW ratio is smaller than 1 , the source is petrogenic, when it is higher than 1 , the source is pyrogenic. According to ratio as explained above, the results for sediment samples from Makelele and Nsanga Rivers suggested that the PAHs probably have

originated from petrogenic processes and/or petroleum combustion (Table 5). The PAHs pollution in Kalamu River were probably originated from petrogenic and pyrogenic sources (combustion of fossil fuel). However, it should be noticed that the studied rivers take their sources upstream, in the savannas region, before arriving in the city. People leaving in the savannas burn the forest and the herbs for their crops without any regulation. Also in the city of Kinshasa, over 70% of the inhabitants use coal and wood to cook. This combustion of coal and wood could explain the origin of some PAHs along these rivers.

For more than 45 years, PAHs, PCBs, OCPs, and PBDEs have been of great environmental concern. Consequently, several studies have been performed to assess their levels and potential risk in air, soil, and surface sediments of rivers and lakes from Europe and the United States (e.g. Degrendele., 2016; Kanzari et al., 2014; Thevenon et al., 2013; Desmet et al., 2012; Echols et al., 2012; Poté et al., 2008). In many cases, the levels of PCBs in sediments are higher than those detected in this study. However, the PAHs concentration presented in this study were higher than those observed in our previous study in sediments from Swiss Lakes (Pardos et al., 2004; Poté et al., 2008; Thevenon et al., 2013).

3.5. *Correlation between parameters*

The Spearman's rank-order correlation values are presented in Table 6. The results showed a significant positive correlation among the metals Zn, Pb, and Cd. Zn showed strong positive correlation with Cd ($r = 0.917$, $p < 0.05$, $n = 9$) and Pb ($r = 0.9$, $p < 0.05$, $n = 9$). Cd also displayed positive correlation with Pb ($r = 0.733$, $p < 0.05$, $n = 9$). These results indicated that these metals could have originated from common sources with a similar transport pathway (runoff and streams) (Poté et al., 2008; Haller et al., 2009). The negative correlation between total organic carbon and Cd indicating a possible multiple sources and transport pathway, which may be the discharge of domestic wastes from the urban population. On the

whole, the results suggested that these toxic metals could have originated from multiple sources into the river receiving systems. Total organic matter displayed positive correlation with PAHs ($r = 0.733$, $p < 0.05$, $n = 9$) and PBDEs ($r = 0.767$, $p < 0.05$, $n = 9$) indicating that probably had a similar source such as from point source of dumping of urban waste and industrial activities on the river basins and combustion of coal, wood and fossil fuel. The negative correlative between grain size and PBDEs indicating that the diverse pollution source, possibly from electronic waste. PCBs showed strong positive correlation with TC, indicating PCBs were more likely come from urban surface runoff. In addition, DDTs showed strong positive correlation with TP, indicating that the DDTs accumulation in the sediments could be attributed to urban activities, pesticide abuse, and household runoff. Furthermore, a positive correlation was observed between PCBs and PAHs. This result suggested that PCBs and PAHs might have had common sources and transport pathway like an urban runoff. Consequently, it becomes clear that industrial wastewater, urban effluents, artisanal activities, dumping the huge amount of urban waste and combustion of coal, wood, and fossil fuel were the main contribution sources of toxic metals and micro pollutants in the studied areas.

4. Conclusion

This study provides an extensive data on heavy metals, POPs and PAHs contamination level in Makelele, Kalamu and Nsanga Rivers in Congo DR. The results indicated that four toxic heavy metals including Cu, Zn, Cd and Pb were predominantly detected in most of the sediments and the contamination level was higher than other Congo River basins. Makelele River is the most contaminated in comparison with two others investigated rivers in the present study. In addition, the concentration levels of PCBs, DDTs and PAHs were generally high in Makelele River and it warrants the important steps on limit the input sources to prevent further food web contamination. The PBDEs concentrations were higher in investigated rivers comparatively with some values detected in many rivers from Sub-Saharan

Africa. It was also noted that PAHs represented the highest contributor of organic micro-pollutants pollution in these rivers. Our findings suggest that these rivers were heavily polluted and may pose a great risk to human health and aquatic environment. Further research in aquatic organisms such as fish from these rivers may provide more comprehensive information on contaminants with regard to the aquatic life and human health. Industrial effluents, untreated urban effluents, automobile exhaust, e-waste, improper incineration of urban waste in landfills, run off, petroleum combustion and pyrogenic activities could be the major contributors for the investigated contaminants for the studied sites. Our study will be useful for the establishment of effective water management strategies in urban river ecosystems in Congo DR, which can be applied in similar aquatic environment.

Acknowledgements

We are grateful to financial support from the Swiss National Science Foundation (grant no. 31003A_150163/1). Authors thank Profs. Marie Besse and Patrycja Paruch, and Mme Brigitte Mantilleri, Service égalité – UNIGE for financial support to Pitchouna Kilunga during her training at University of Geneva. Periyasamy Sivalingam is a Postdoctoral fellow supported by Swiss Government Excellence Scholarship for Foreign Scholars. This study presents a collaboration between University of Geneva (Forel Department) and University of Kinshasa (Democratic Republic of the Congo).

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774 Tables

775 Table 1. GPS location of sampling sites and physico-chemical parameters of surface
776 sediments from Makelele, Kalamu and Nsanga Rivers

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site	Sample	Longitude	Latitude	OM (%)	Median grain size (μm)	Clay (%)	Silt (%)	Sand (%)	TC (%)	TN (mg kg^{-1})	TP (mg kg^{-1})
R1	R1A	15°16'28.0''	4°19'95''	9.15	105.3	2.06	29.7	68.24	1.65	2.56	141.80
	R1B	15°16'24.5''	4°19'89''	5.26	101.8	2.08	21.28	76.64	2.80	3.04	92.60
	R1C	15°16'29.2''	4°19'94.7''	8.05	46.77	4.08	48.02	47.90	4.79	6.32	242.74
R2	R2A	15°19'38.0''	4°21'08.0''	7.19	191.6	0.60	12.78	86.62	2.10	3.08	98.60
	R2B	15°19'37.0''	4°21'11.2''	12.64	32.85	2.64	68.16	29.2	3.62	2.80	76.49
	R2C	15°19'37.3''	4°21'08.1''	7.95	195.9	0.27	9.07	90.6	7.20	3.20	133.60
	R2D	15°19'37.1''	4°21'06.8''	11.38	50.87	0.74	52.52	46.74	2.50	3.60	163.23
R3	R3A	15°22'49.6''	4°23'23.4''	1.73	225.30	1.50	6.69	91.81	1.72	4.20	89.75
	R3B	15°22'49.2''	4°23'23.9''	13.35	79.53	0.80	40.76	58.44	2.37	1.78	67.40

778 R1, R2, R3: Makelele, Kalamu, Nsanga Rivers, respectively. MO: total organic matter, TC:
779 total carbon, TN: total nitrogen, TP: total phosphorus

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Table 2. Metal content of surface sediment samples from River Makelele (R1), Kalamu (R2) and Nsanga (R3) analyzed by ICP-MS^a

Sampling sites	Sample number	Concentration (mg.kg ⁻¹)													
		Sc	Ti	Cr	Co	Ni	Cu	Zn	As	Mo	Ag	Cd	Sn	Sb	Pb
Makelele	R1A	0.71	63.93	12.57	0.96	3.94	31.68	177.15	1.03	0.32	0.10	0.76	1.89	0.20	38.03
	R1B	0.37	41.67	8.43	0.71	2.01	18.19	128.10	0.49	0.08	0.07	0.23	0.49	0.22	37.80
	R1C	1.30	98.89	28.51	3.93	9.80	71.91	549.64	1.64	0.22	0.31	1.26	1.61	0.32	132.29
Kalamu	R2A	0.22	49.67	6.67	1.27	2.95	23.52	304.68	0.83	0.00	0.69	1.13	0.97	0.60	64.49
	R2B	0.26	54.31	10.14	1.30	4.04	39.79	333.54	0.65	0.06	0.21	0.86	0.60	0.77	71.20
	R2C	0.12	30.55	4.77	0.68	2.27	33.04	177.62	0.44	n.a	0.07	0.41	0.57	0.69	65.83
	R2A	0.21	50.67	8.45	1.24	4.33	37.55	286.76	0.55	0.13	0.23	0.78	0.88	0.66	64.57
Nsanga	R3A	0.12	26.36	7.51	0.53	11.18	213.03	130.17	0.29	0.17	0.32	0.48	1.47	0.49	24.59
	R3B	0.18	53.38	14.01	1.41	16.94	325.14	396.72	0.88	0.54	0.54	1.54	1.98	1.47	165.30
Rec ^b .max				37.30			35.70	123.00	5.90			0.60			35.00
LKSD 4				21	11	32	30	189		2	0.2	1.9		1.5	93

^a Total variation coefficients for triplicate measurements are smaller than 5 % for ICP-MS analysis. The recovery values from the ICP-MS triplicate measurements for reference material (LKSD 4) was above 97.5 % for all elements.

^b Canadian Sediment Quality Guidelines for the Protection of Aquatic Life recommendation. In bold represent the concentration of the heavy metals above the recommended concentration according to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life recommendation (CCME EPC-98E 1999).

n.a – analysis not performed.

800 Table 3. *Igeo* and EF values for Cu, Zn and Pb in surface sediments.

Sampling sites	Sample number	<i>Igeo</i>			EF		
		Cu	Zn	Pb	Cu	Zn	Pb
Makelele	R1A	-1.16	3.67	2.62	3.12	88.43	42.78
	R1B	-0.40	3.80	2.76	4.35	79.69	38.88
	R1C	-0.67	2.89	2.65	7.87	92.49	78.35
Kalamu	R2A	-0.48	3.58	2.62	5.08	84.80	43.64
	R2B	2.02	2.44	1.23	51.15	68.38	29.52
	R2C	2.63	4.05	3.98	50.68	135.26	128.81
Nsanga	R2D	-0.73	2.88	1.86	1.28	15.70	7.70
	R3A	-1.53	2.42	1.85	1.40	21.62	14.58
	R3B	0.45	4.52	3.66	1.58	26.44	14.54

<i>Igeo</i> ≤ 0	Class 0 - practically unpolluted	EF < 1	no enrichment
0 < <i>Igeo</i> < 1	Class 1 - unpolluted to moderately polluted	EF < 3	minor enrichment
1 < <i>Igeo</i> < 2	Class 2 - moderately polluted	EF 3 - 5	moderate enrichment
2 < <i>Igeo</i> < 3	Class 3 - moderately to heavily polluted	EF 5 - 10	moderately severe enrichment
3 < <i>Igeo</i> < 4	Class 4 - heavily polluted	EF 10 - 25	severe enrichment
4 < <i>Igeo</i> < 5	Class 5 - heavily to extremely polluted	EF 25 - 50	very severe enrichment
5 > <i>Igeo</i>	Class 6 - extremely polluted	EF > 50	extremely severe enrichment

Table 4a. Concentration (in $\mu\text{g kg}^{-1}$ dry weight) of polychlorinated biphenyl (PCBs), and polycyclic aromatic hydrocarbons (PAHs) in sediment samples from River Makelele (R1), Kalamu (R2) and Nsanga (R3).

	Makelele				Kalamu			Nsanga		
	PCBs (µg kg ⁻¹)									
	LOQ	R1A	R1B	R1C	R2A	R2B	R2C	R2D	R3A	R3B
28 ^a	0.05	0.65	0.54	2.64	0.74	1.50	0.34	1.50	<0.05	0.69
52	0.05	0.73	0.51	2.85	0.56	1.15	0.29	1.21	<0.05	0.97
101	0.10	0.84	0.77	4.48	0.80	1.40	0.73	1.75	<0.10	0.97
105	0.05	0.22	0.27	2.02	0.36	0.48	0.22	0.52	<0.05	0.40
118	0.10	0.63	0.65	4.27	0.58	1.25	0.57	1.56	<0.10	1.11
128	0.05	0.15	0.22	1.68	0.32	0.43	0.33	0.67	<0.05	0.24
138 ^a	0.05	0.76	1.27	7.91	1.65	2.84	2.32	3.83	0.42	1.47
149	0.10	0.63	0.80	5.85	1.44	2.01	2.15	3.18	0.36	1.15
153	0.05	1.17	1.46	10.89	1.94	3.79	3.77	5.39	0.70	2.09
156	0.05	<0.05	<0.05	0.92	0.15	0.32	0.17	0.41	<0.05	0.06
170	0.05	0.23	0.38	3.10	0.86	1.40	1.49	2.02	0.53	0.53
180	0.05	0.37	0.83	6.33	1.68	2.95	3.25	4.12	1.45	1.05
Total PCBs (Σ7 x 4.3)		22.14	25.92	169.29	34.18	63.98	48.46	83.24	11.05	35.90
TEL ^b (Σ7 PCBs)	34.1									
PEL ^b (Σ7 PCBs)	277									
	PAHs (µg kg ⁻¹)									
Naphthalène	0.5	14.61	14.82	103.60	35.90	46.52	98.01	93.95	<0.50	50.45
Acenaphthylene	0.5	1.43	1.65	7.94	3.23	4.03	3.16	5.07	1.15	6.58
Acénaphthène	0.5	1.50	1.20	9.03	3.17	3.44	2.19	3.91	<0.50	14.45
Fluorène	0.5	6.00	5.22	46.41	10.94	20.04	6.67	17.55	<0.50	43.61
Phénanthrène	0.5	27.90	20.72	170.41	45.10	72.95	47.68	84.15	6.51	159.82
Anthracène	0.5	2.82	2.49	25.10	5.66	8.88	5.54	10.45	<0.50	16.85
Fluoranthène	1	20.33	12.83	108.55	29.75	51.11	31.04	48.17	3.56	105.45
Pyrène	1	24.11	19.64	168.99	34.33	59.11	33.69	51.22	4.97	154.30
Benzo (a) Anthracène	1	6.67	5.37	42.40	11.81	19.99	12.18	18.30	<1.00	46.64
Chrysène	1	21.07	10.21	78.71	22.32	35.29	21.50	37.19	2.55	69.87
Benzo(b)Fluoranthène	1	11.75	9.68	71.17	21.91	32.29	21.03	34.47	1.72	82.27
Benzo (k) Fluoranthène	1	3.44	3.42	24.13	6.92	10.27	7.30	12.25	<1.00	30.28
Benzo (a) Pyrène	1	5.86	5.70	39.87	12.66	18.22	11.47	20.07	<1.00	50.03
Dibenz (a,h) Anthracène ^{a*}	1	<1.00	<1.00	9.42	3.15	4.22	3.32	4.66	<1.00	12.58
Benzo (g,h,i) Perylène*	1	6.85	9.54	62.67	17.95	25.96	13.97	31.18	2.10	58.45
Indeno (1,2,3c,d) pyrene ^{a*}	1	4.74	6.22	43.54	13.47	19.90	11.00	22.69	<1.00	49.50
Σ 16 PAH congeners		159.08	128.71	1011.94	278.27	432.22	329.75	495.28	22.56	951.13
TEL ^c (Σ13 PAHs)	610									
PEL ^c (Σ13 PAHs)	22800									

^aChromatographic separation on a ZB-XLB column. All remaining compounds on a ZB-5ms column.

^bThreshold 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. (CCME, 2002).

^cMacDonald et al 2000b. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems.

*Not included in the sum of ($\sum 13$ PAHs) TEL and PEL values

825 Table 4b. Concentration (in $\mu\text{g kg}^{-1}$ dry weight) of organochlorine pesticides (OCPs) and
826 BDEs in sediment samples from river Makelele (R1), Kalamu (R2) and Nsanga (R3)

	Makelele				Kalamu				Nsanga		Rec ^a
	OCPs (µg kg ⁻¹)										
	LOQ	R1A	R1B	R1C	R2A	R2B	R2C	R2D	R3A	R3B	
hexachlorobenzène	0.05	<0.05	0.40	1.44	<0.05	0.09	<0.05	0.23	0.10	<0.05	
alpha-HCH	0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	
beta-HCH	0.05	0.10	<0.05	0.14	<0.05	<0.05	0.12	<0.05	<0.05	<0.05	
gamma-HCH	0.10	0.26	0.17	0.44	<0.10	0.12	0.43	<0.10	<0.10	<0.10	
delta-HCH	0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	
chlorpyrifos-methyl ^c	1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	
chlorpyrifos-ethyl ^c	0.50	1.95	2.30	16.98	1.86	3.68	1.55	1.82	<0.50	3.36	
gamma-chlordane	0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	
alpha-chlordane	0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	
dieldrin	0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	
endrin	0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	
heptachlor	0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	
aldrin ^c	0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	
heptachlor epoxid A	0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	
heptachlor epoxid B	0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	
endosulfan I	1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	
endosulfan II	1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	
endosulfan sulfate	0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	
endrin aldehyde	0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	
endrin ketone	0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	
methoxychlor	0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	
acetochlor ^c	1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	
oxy-chlordane ^c	0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	
trans-nonachlor	0.10	<0.10	<0.10	0.20	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	
mirex	0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	
cyhalothrin-λ (lambda)	1.00	2.67	1.71	12.42	2.29	3.33	<1.00	<1.00	<1.00	<1.00	
cypermethrin a	5.00	13.84	<5.00	31.12	10.85	8.17	<5.00	<5.00	<5.00	34.95	
cypermethrin b	7.00	16.61	<7.00	20.80	<7.00	<7.00	<7.00	<7.00	<7.00	<7.00	
deltamethrin	7.00	43.83	27.31	227.48	42.68	97.33	43.83	32.17	12.49	69.14	
DDTs (µg kg ⁻¹)											
p,p'-DDE	0.10	146.75	9.57	63.71	9.54	15.92	11.03	20.99	0.66	9.97	
o,p'-DDE	0.10	7.51	0.26	1.72	0.23	0.40	0.33	0.46	<0.10	0.18	
p,p'-DDD	0.10	21.57	5.10	39.40	5.84	10.15	4.95	12.79	0.21	4.86	
o,p'-DDD ^c	0.10	22.03	1.47	9.18	1.56	2.59	1.81	3.62	<0.10	1.33	
p,p'-DDT	0.10	29.17	4.79	17.14	6.49	2.70	3.73	3.41	0.27	3.09	
o,p'-DDT ^c	0.10	43.58	0.56	1.47	1.05	0.55	0.78	0.81	0.09	0.82	
Σ6 pesticides		270.61	21.75	132.62	24.71	32.31	22.63	42.08	1.23	20.25	
TEL ^b (Σ6DDTs)	6.15										
PEL ^b (Σ6DDTs)	20.03										
PBDE (µg kg ⁻¹)											
BDE28	0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	44
BDE47	0.10	1.80	0.55	4.24	1.21	1.93	0.83	2.27	1.32	8.66	39
BDE100	0.10	0.54	0.18	1.17	0.40	0.54	0.28	0.75	0.51	2.95	0.4
BDE99	0.10	2.23	0.75	5.87	1.27	2.16	0.97	2.55	1.79	12.88	0.4
BDE154	0.15	0.29	<0.15	0.69	<0.15	0.42	<0.15	0.36	0.28	1.48	440
BDE153	0.15	<0.15	<0.15	0.92	<0.15	0.50	<0.15	0.55	<0.15	1.98	440
Σ6 PBDEs		4.86	1.48	12.90	2.88	5.55	2.09	6.48	3.90	27.95	

827 The values in bold represent the concentration of the PBDEs above the recommended concentration according to the
828 Canadian Federal Environmental quality guidelines Polybrominated Diphenyl Ethers (PBDEs). (Canadian Environmental
829 Protection Act, 1999.

830 Rec^a. Federal Environmental quality guidelines Polybrominated Diphenyl Ethers (PBDEs) in sediments.
831 <<https://www.ec.gc.ca/ese-ees/>>

832 ^bThreshold effect levels (TELs)/Probable effect levels (PELs) (dry weights). Canadian sediment quality guidelines for the
833 protection of aquatic life. Canadian Council of Ministers of the Environment. (CCME, 2002).

834 ^cChromatographic separation on a ZB-XLB column. All remaining compounds on a ZB-5ms column.

835 Table 5. The values of Fluo/ (Fluo + Pyr), IDP/ (IDP + BghiP), BaA/ (BaA + Chry), and
 836 LMW/HMW ratios.

	Makelele	Kalamu	Nsanga
Fluo/ (Fluo + Pyr)	0.39-0.46	0.46-0.48	0.41-0.42
IDP/ (IDP + BghiP)	0.39-0.41	0.42-0.44	*NA-0.46
BaA/ (BaA + Chry)	0.24-0.35	0.33-0.36	NA-0.40
**LMW/HMW	0.52-0.56	0.56-0.98	0.44-0.51

837
 838 *Not available due to the concentration of individual PAH compound being below the
 839 Limit of quantification.
 840 **LMW/HMW: Ratio of low molecular weight (LMW) PAHs (i.e. Naphthalene (Naph),
 841 Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Fl), Phenanthrene (Phen), Anthracene (Anthr)
 842 to high molecular weight (HMW) PAHs (i.e. fluoranthene (Fluo), pyrene (Pyr), benzo[a]anthracene
 843 (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene
 844 (BaP), indeno[1,2,3-cd]pyrene (IDP), dibenz[a,h]anthracene (DahA) ,and benzo[g,h,i]perylene
 845 (BghiP).

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Table 6. Spearman's rank-order correlation of selected parameters^a analyzed in the surface sediments

	Zn	Cd	Pb	TOM	Grain size	TC	TN	TP	PCBs	PAHs	DDTs	PBDEs
Cu	0.517	0.533	0.500	0.00	0.0833	-0.350	-0.0667	-0.250	-0.050	0.100	-0.333	0.183
Zn		0.917	0.900	-0.283	0.117	-0.467	0.183	0.367	-0.167	-0.300	0.267	-0.183
Cd			0.733	-0.167	0.250	-0.667	-0.117	0.117	-0.350	-0.400	0.200	-0.200
Pb				-0.467	0.150	-0.183	0.467	0.467	0.0167	-0.200	0.233	-0.267
TOM					-0.633	0.117	-0.517	-0.117	0.533	0.733	0.367	0.767
Grain size						-0.367	0.0333	-0.0167	-0.633	-0.617	-0.350	-0.667
TC							0.300	0.183	0.733	0.500	0.0667	-0.0333
TN								0.567	0.3	0.050	0.050	-0.0667
TP									0.4	0.233	0.733	0.0333
PCBs										0.883	0.450	0.517
PAHs											0.367	0.783
DDTs												0.283

^aParameters include toxic metals, median grain size, total organic matter, TC, TN, TP, PCBs, PAHs, DDTs and PBDEs [$n = 9$, statistically significant coefficients ($p < 0.05$) are in bold.

876 Figure caption

877 Figure 1. Location map of the study area. A: Location Map of Congo DR in Africa. B: Map of
878 Congo DR. C: Location map of studied Rivers, R1: Makelele, R2: Kalamu, R3: Nsanga at
879 Kinshasa, Congo DR.

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881
882 Figure 2. Score plot for principal component analysis (PCA) applied to sediment measurement
883 across sampling sites: (a) PCA of PCBs congeners, (b) PCA of pesticides congeners, (c) PCA
884 of PBDEs congeners and (d) PCA of PAHs congeners

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887 Fig. 1.

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Fig. 2.