

Assessment of physico-chemical properties and metal contents of water and sediments of Bodo Creek, Niger Delta, Nigeria

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Some physico-chemical properties and the concentrations of the metals Fe, Mn, Ni, Cd, Cr, Co, Cu, Pb, and Zn in water and sediments were examined from September 2011 to January 2012 in Bodo Creek, where oil spills have been recurrent. Temperature, pH, total dissolved solid, conductivity, salinity, dissolved oxygen, biological oxygen demand (BOD), chemical oxygen demand (COD), total hardness, sulfate, nitrate, and phosphate were determined in surface water. Particle size, total organic matter (TOM), and pH were also determined in the sediments. The parameters were within permissible limits except the mean values of BOD, COD, total hardness, and sulfate that exceeded levels permissible for domestic use. The sediments consisted mainly of sand, with TOM ranging from 0.2% to 5.5%. With the exception of cadmium that was below detection limit, metal levels (mg kg^{-1}) in the sediments were 12 (Mn), 1070 (Fe), 10 (Cu), 10 (Zn), 5.3 (Cr), 1.1 (Pb), 1.0 (Ni), and 0.5 (Co) while in water they were 24, 98, 21, 6.9, 4.0, 0.6, 0.18, and 0.16, respectively. The latter were higher than World Health Organization recommended permissible levels for both surface and drinking water.

Keywords: trace metals; oil spill; water permissible levels; sediment particle size; contamination

Introduction

Human activities can alter the geochemical cycles of metals resulting in increased contamination. Although metals enter water bodies from many natural and anthropogenic sources, an important one is oil spills, which occur almost daily in the Niger Delta, Nigeria's hub of oil and gas production. An average of 273 oil spills with a volume of 115,000 barrels has occurred annually in the delta (UNDP 2006; UNEP 2011). Bodo is a network of brackish water creeks on the upper reaches of the Andoni–Bonny river system in the lower Niger Delta basin affected by incessant crude oil spills from abandoned pipelines, criminal damage (sabotage), and lack of maintenance of oil facilities (Legborsi 2007).

On 28th August 2008, a fault in the Trans-Niger pipeline resulted in a significant oil spill into Bodo Creek. The oil poured into the swamp and creek for weeks (finally stopped on 7 November 2008), covering the area with a thick slick of oil that killed aquatic organisms. A second major spill was reported on 2nd February 2009 (Amnesty International 2009).

Bodo Creek is a strong livelihood supporting base for the people of Bodo community and their neighbors. It is a major source of drinking and bathing water, especially for

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fisherfolks of Ogoni who are in close contact with the water. The creek is also used for fishing, transportation, cassava fermentation, recreation, waste disposal, small-scale aquaculture, and sand dredging. In a recent report, UNEP (2011) stated that the drinking water sources in Ogoni community may have been affected by pollution from oil spills, and drinking water sampled from 28 wells in 10 communities were oil-contaminated.

Some trace metals with relatively high toxicity and potential for bioaccumulation are high priority pollutants. Cd, Cr, Co, Pb, Mn, and Ni recognized by the United State Environmental Protection Agency as hazardous trace elements were investigated during this study, along with Fe, Zn, and Cu. These metals tend to accumulate in sediments, which may act as short- or long-term sinks in aquatic systems and sources of further contamination. Accumulation of metals is controlled by granular composition of the sediments and the physico-chemical properties of the water. Sediment grain size and organic matter content are two critical factors influencing their distribution and their capacity for pollution (Liaghati, Preda, and Cox 2003; Selvaraj et al. 2010). Grain size determines the surface area, the settling velocity, and the deposition rate of suspended solids in the water column, as well as the degree of chemical partitioning between sediment and water (Lin, Chen, and Su 2003; Aprile and Bouvy 2008).

Since the major oil spills of 2008 and 2009, minor oil spills have continued to occur in Bodo Creek and there is urgent need to assess their effect on the metal concentrations and physico-chemical properties of the sediment and water. Knowledge about the changing concentrations and the distribution of metals between various compartments helps to provide evidence of the health quality of a wetland system and is needed for conceiving good environmental management programs for the Niger Delta.

Materials and methods

Study area

Bodo Creek is a brackish water that adjoins the Bodo community in Ogoni land. Onwugbuta-Enyi, Zabbey, and Erundu (2008) have described the creek's structure and hydrology. It is characterized by tidal flats, influenced by a semi-diurnal tidal regime. The water level and salinity increase and decrease depending on the lunar cycle (RPI 1985). The area experiences heavy rainfalls from April to October and sporadic rainfalls from November to March.

Three sampling stations were georeferenced through global positioning system. These were upstream, downstream, and midstream from locations that have had some history of oil pollution or are close to oil production facilities (Figure 1). Station 1 is located on an expansive tidal flat (7°16.804"E; 4°35.601"N) having roots of black mangrove without stems or leaves and completely coated in oil. Station 2 (7°16.071"E; 4°36.263"N) is located on an open tidal flat with stunted red mangrove as well as aged and unproductive dwarf coconut trees at the edges of the supra-littoral shores. Shore and water surface were slightly coated with oil. Station 3 is located close to an oil pipeline in a forested mangrove area with an inflow of fresh water (7°16.074"E; 4°37.240"N). The area is close to agricultural land and homesteads.

Sample collections

Samples were collected from September 2011 to January 2012. At each site, four sediment sub-samples were collected using a plastic trowel at a depth of 2 to 30 cm from four

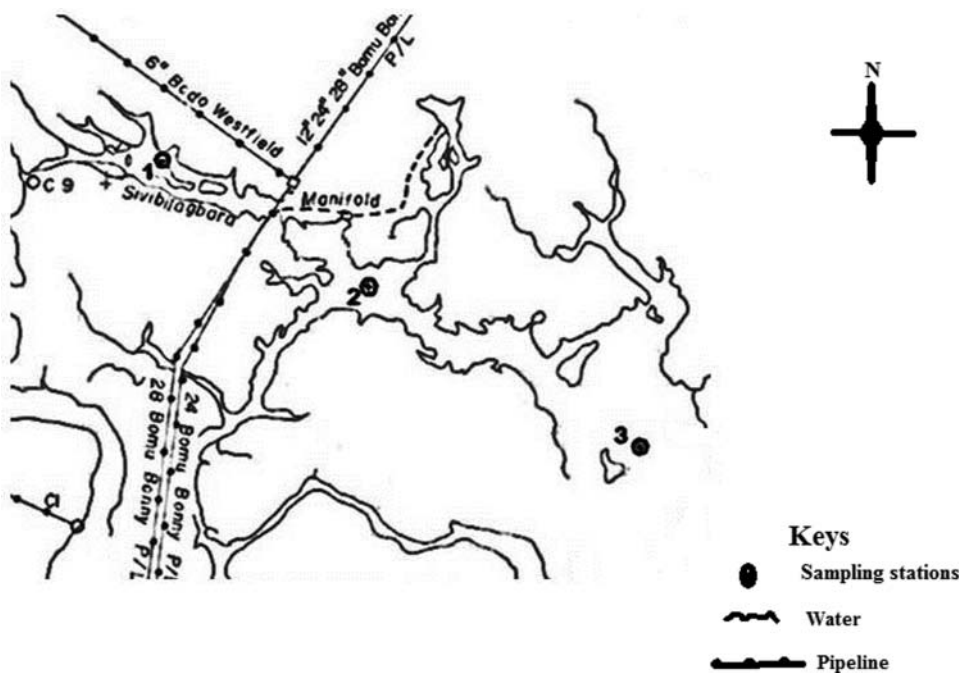


Figure 1. Map of Bodo Creek showing the sampling stations.

randomly selected nodes. These sub-samples were homogenized to form a representative sample. The composite samples were transferred to aluminum sampling packs and sealed. Care was taken not to disturb the fine surface algal flock that was scraped off during the sampling process. Water samples were collected against the flow of current using pre-cleaned 500 mL polyethylene bottles. All samples were preserved, placed in a cool box, transported to the laboratory and stored at 5 °C prior to further analysis.

Physico-chemical analysis

Temperature, pH, total dissolved solid (TDS), conductivity, salinity, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), total hardness, SO_4^{2-} , NO_3^- , and PO_4^{3-} of surface water were determined following standard methods (APHA 1998). Particle size analysis was carried out using a laser granulometer (LS 230 with P.I.D. S., Coulter, CA, USA) after filtering through a 2 mm stainless steel wire sieve (Buckinghamshire, UK). Total organic matter (TOM) in sediment was determined by measuring weight loss after burning in a preheated muffle furnace at 450 °C for 4 h (Van Reeuwijk 2002). Sediment pH was measured (model HI 2211, Hanna, Woonsocket, USA) in a suspension of 10 g of sediment in 25 mL deionized water after shaking for 2 h using a pH meter.

Metal analysis

Aliquots of 0.25 g of air dried sediment samples were weighed into a Teflon inset of a microwave digestion vessel and 2 mL concentrated (90%) nitric acid (Sigma-Aldrich, Dorset, UK) were added. The metals were extracted using a microwave accelerated

reaction system (MARS Xpress, CEM Corporation, Matthews, North Carolina) at 1500 W power (100%), ramped to 175 °C in 5.5 min, held for 4.5 min, and allowed to cool down for 1 h. The cool digest solution was filtered through the Whatman 42 filter paper and made up to 100 mL in a volumetric flask by adding deionized water.

For the water samples, 2 mL concentrated (90%) nitric acid (Sigma-Aldrich) was added to 0.2 mL water and the volume was made up to 10 mL with deionized water (X 5 dilution). Metal concentrations were analyzed by inductively coupled plasma mass spectrometry (ICP MS: model X7, Thermo Electron, Winsford-Cheshire, UK).

All chemicals and reagents used were of analytical grade and of highest purity possible. Analytical blanks were prepared with each batch of the digestion set and analyzed (one blank for every set of 12 samples) in the same way as the samples. The analytical methodologies were confirmed using certified reference materials for sandy clay (CRM 049-050, Sigma-Aldrich RTC, Salisbury, UK).

Statistical analysis

Statistical analyses were done using Minitab version 16 package and Microsoft Excel (MS Excel). Analysis of variance (ANOVA) was performed to compare the means and the statistical significance was considered for $p < 0.05$.

Results and discussions

Physico-chemical parameters

The spatial variations in physico-chemical parameters of the water are presented in [Table 1](#). Water temperature varied from 26.7 °C to 27.8 °C, which is within the range typical for the Niger Delta region. The exact temperature depends on the time of day and of the sunlight absorbed by the water. Spatial variations of pH values were identical among the stations and varied from 8.8 to 8.9, with station 3 having the least value.

Dissolved oxygen mean values ranged from 4.7 to 5.5 mg L⁻¹. Spatial variations in BOD were between 13–19 mg L⁻¹, COD 24 to 44 mg L⁻¹, salinity 2580 to 16,200 mg L⁻¹, TDS 3070 to 188,000 mg L⁻¹, conductivity 195–287 μS cm⁻¹, total hardness 151–453 mg L⁻¹, and sulfate 115–654 mg L⁻¹. Lower values were obtained in station 3 when compared with the two other stations ([Table 1](#)). Inflow of fresh water tends to reduce the salinity and conductivity in station 3 but nitrate (0.9 mg L⁻¹) values were highest for this station. Except for temperature, phosphate, and pH, physico-chemical parameters of station 3 were significantly different from the two other stations.

The mean values of salinity, temperature, and pH showed a gradual increase from September 2011 until January 2012, coinciding with the onset of the dry season. Decreases in DO and total hardness were observed during this period. The other parameters did not show any particular trend. The mean values of BOD, COD, total hardness, and sulfate exceeded the Department of Petroleum Resources (DPR) (2002) accepted maximum permissible levels for domestic use in Nigeria.

The sediments of Bodo Creek exhibit fluctuating pH values that ranged from 5.7 to 8.0, that is, from acidic to alkaline. Sediments from station 3 had pH values of 7.0–8.0 while stations 1 and 2 had pH values of 7.4–8.0 and 5.7–6.7, respectively.

The sediments of Bodo were dominated by sand particles of fine and medium size, which ranged 27%–63% and 12%–40%, respectively. The clay–silt fractions in the sediments ranged from 0.08% to 8.9%. TOM ranged from 0.18% to 5.5%. Particle size

Table 1. Variations in physico-chemical parameters of Bodo Creek in comparison with national standards in Nigeria.

Parameters	Station 1	Station 2	Station 3	AMCS	DPR
Temp (°C)	26.7 ± 0.4 ^a (26.4–29.7)	27.8 ± 1.3 ^a (26.7–29.6)	27.7 ± 1.0 ^a (26.7–29.2)	27.8	30
pH	8.8 ± 0.2 ^a (8.5–9.1)	8.9 ± 0.1 ^a (8.7–9.0)	8.8 ± 0.1 ^a (8.7–8.9)	8.8	6–9
DO (mg L ⁻¹)	5.4 ± 0.8 ^a (4.5–6.4)	5.5 ± 0.4 ^a (5.1–6.1)	4.7 ± 0.3 ^b (4.2–5.0)	5.2	20
BOD (mg L ⁻¹)	15 ± 6 ^a (10–24)	19 ± 4 ^a (12–23)	13 ± 2 ^b (9–15)	15	10
COD (mg L ⁻¹)	44 ± 3 ^a (40–48)	43 ± 2 ^a (40–45)	24 ± 3 ^b (21–29)	37	30
Salinity (mg L ⁻¹)	15,900 ± 3650 ^a (12,500–19,900)	16,200 ± 2500 ^a (13,300–19,400)	2580 ± 1670 ^b (1250–5420)	11,500	–
TDS (mg L ⁻¹)	18,300 ± 900 ^a (17,300–19,400)	18,800 ± 500 ^a (18,800–18,900)	3070 ± 940 ^b (2003–4290)	13,400	2000
Conductivity (μS cm ⁻¹)	2870 ± 234 ^a (2600–3200)	2730 ± 116 ^a (2590–2870)	195 ± 74 ^b (127–278)	1930	–
Total hardness (mg L ⁻¹)	453 ± 186 ^a (280–700)	369 ± 95 ^a (240–489)	151 ± 79 ^b (40–245)	324	100
PO ₄ ³⁻ (mg L ⁻¹)	0.01 ± 0.0 ^a (0.003–0.02)	0.01 ± 0.0 ^a (0.01–0.0)	0.01 ± 0.0 ^a (0.01–0.0)	0.01	5.0
NO ₃ ⁻ (mg L ⁻¹)	0.2 ± 0.1 ^a (0.01–0.3)	0.2 ± 0.1 ^a (0.08–0.3)	0.9 ± 0.1 ^b (0.8–0.9)	0.45	20
SO ₄ ²⁻ (mg L ⁻¹)	654 ± 108 ^a (537–762)	636 ± 40 ^a (580–690)	115 ± 105 ^b (10–276)	468	50–200

Notes: ($n = 24$). Values are mean \pm SD and range values in parentheses. Values in each row with the same superscript are not significantly different at $p < 0.05$. AMCS – average means concentration of the sampling stations. DPR – Department of Petroleum Resources (2002) limits for substances discharge into water for domestic use in Nigeria.

plays an important role in nutrient accumulation in the sediments because fine-grained particles often have greater surface to volume ratio and more organic matter (Aprile and Bouvy 2008; Wang, Liu, and Tang 2004).

Distribution of metals

Metals are released to the water column through sediment resuspension, adsorption–desorption, reduction–oxidation reactions, and the action of degrading organisms (Barakat et al. 2012). The content of Fe in the water ranged from 20 to 180 mg kg⁻¹, while Mn, Pb, Cr, Zn, Co, Ni, Cu, and Cd ranged from 8.8 to 36 (Mn), 0.07 to 1.22 (Pb), 2.0 to 5.8 (Cr), 1.4 to 18 (Zn), 0.04 to 0.42 (Co), 0.07 to 0.31 (Ni), 4.7 to 53 (Cu), and < 0.1 mg kg⁻¹ (Cd) (Figure 2(a)–2(c)). These values were compared with World Health Organization (WHO) levels for Cu (2 mg kg⁻¹), Cd (0.003 mg kg⁻¹), Cr (0.05 mg kg⁻¹), Pb (0.01 mg kg⁻¹), and Ni (0.07 mg kg⁻¹). Except for cadmium, the study results indicated that the metal contents appeared higher than international quality criteria for public

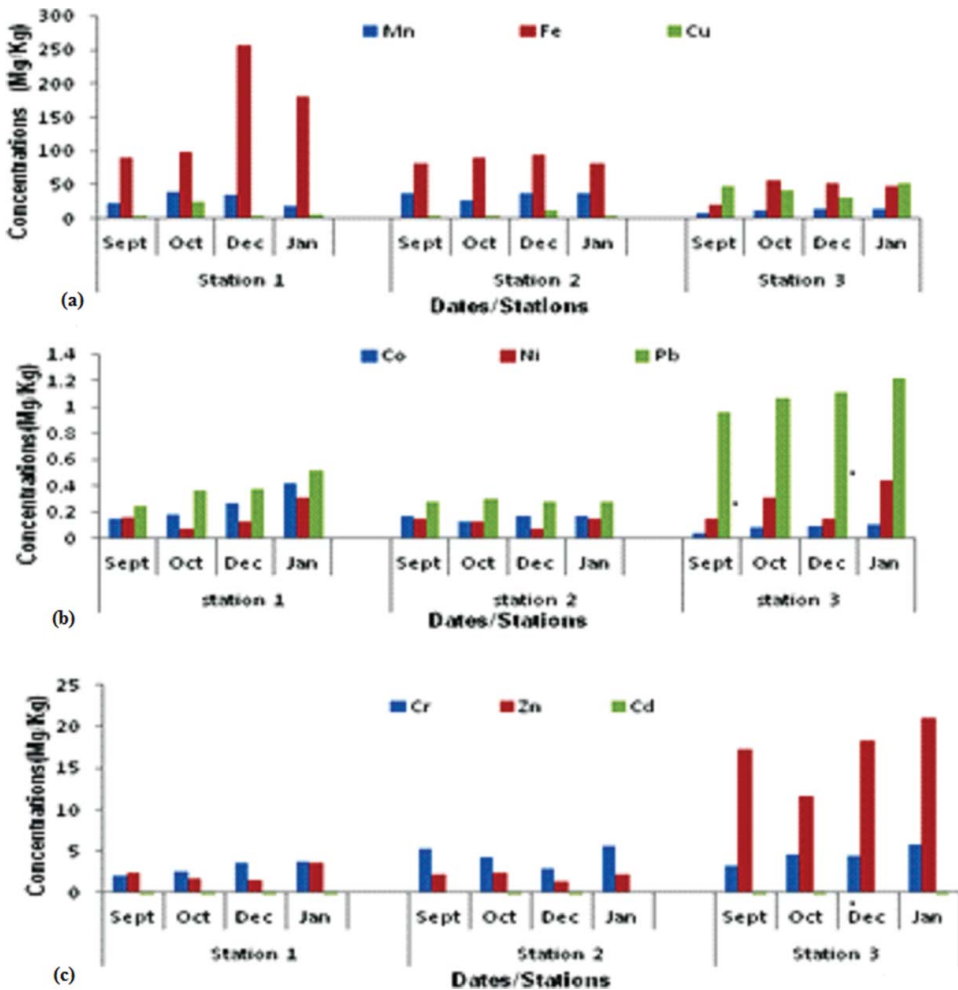


Figure 2. (a)–(c) Distribution of metal concentrations (mg kg⁻¹) in water from Bodo Creek.

surface water or drinking water (WHO 2011; FEPA 2003). WHO did not established guidelines for Fe, Mn, and Zn because they are not of health concern at levels found in drinking water.

Except for Mn and Cr which were highest at station 2, concentrations of Pb, Zn, Ni, and Cu were highest at station 3, and Fe, Cd, and Co at station 1. ANOVA showed no significant variations ($p < 0.05$) among the different sampling dates except for Fe and Mn. Cu and Zn values at station 3 were significantly different. The metal values of Bodo Creek reported here were higher than those reported for Ikot Ada Udo with a history of oil spills in the Niger Delta (Udo 2008).

Cu, Zn, and Pb are closely associated with crude oil and municipal wastes disposal (Chindah, Braide, and Sibeudu 2004). These metals tend to increase in less saline and highly turbid media (Selvaraj et al. 2010; Wright and Welbourn 2002). This could explain the high concentrations of these metals observed at station 3, which is near the oil pipeline, and the homesteads.

Table 2. Metal concentrations (mg kg⁻¹) in sediment from Bodo Creek in comparison with standards.

Metals	Station 1	Station 2	Station 3	AMCS	DPR/FEPA*	Shale value ^a
Mn	8.9 ± 4 ^a (4–17)	14 ± 8 ^a (5–32)	12 ± 6 ^a (5–30)	12	–	850
Fe	813 ± 320 ^a (369–1480)	1380 ± 870 ^a (488–3600)	1020 ± 730 ^a (432–2800)	1070	20	47,200
Co	0.6 ± 0.3 ^a (0.2–1.3)	0.9 ± 0.3 ^a (0.4–1.4)	0.2 ± 0.1 ^b (0.1–0.4)	0.5	20	19
Ni	1.2 ± 0.5 ^a (0.5–2.2)	1.4 ± 0.4 ^a (0.6–2.3)	0.6 ± 0.2 ^b (0.4–1.0)	1.0	0.8	68
Cu	9.6 ± 4.2 ^a (4.2–16)	8.8 ± 2.9 ^a (4.5–14)	12 ± 4.5 ^a (4.8–23)	10	35 /20	45
Zn	4.8 ± 1.5 ^a (2.7–7.5)	5.3 ± 0.8 ^a (4.0–7.8)	22 ± 11 ^b (4.5–38)	10	50–300	95
Cd	0.008 ± 0.1 ^a (ND–0.2)	–0.04 ± 0.2 ^a (–0.9–0.1)	0.054 ± 0.2 ^b (–0.009–1.0)	–0.009	0.03–0.3	0.3
Pb	1.0 ± 0.2 ^a (0.7–1.2)	0.9 ± 0.21 ^a (0.09–1.3)	1.4 ± 0.48 ^b (0.80–2.3)	1.1	2–20	20
Cr	4.9 ± 2.6 ^a (2.1–10.1)	5.3 ± 2.0 ^a (2.6–9.2)	5.6 ± 3.9 ^a (1.9–13.6)	5.3	0.5	90

Notes: ($n = 24$). Values are mean \pm SD and range values in parentheses. Values in each row with the same superscript are not significantly different at $p < 0.05$. ND = Not detected. AMCS – average means concentration of the sampling stations. *DPR – Department of Petroleum Resources 2002 or FEPA – Federal Environmental Protection Agency 2003 – national limits in Nigeria. ^a Shale values from Turekian and Wedepohl (1961).

The metal concentrations in the sediments from Bodo Creek are summarized in Table 2. The order of abundance of elements in sediment is Fe > Mn > Zn > Cu > Cr > Pb > Ni > Co > Cd. Iron is the fourth most abundant element in the earth's crust and is considered as a main factor determining the adsorption capacity (Wright and Welbourn 2002). Fe is not a hazardous element but its concentration (1070 mg kg⁻¹) exceeded the limit (20 mg kg⁻¹) established by the Rivers State Ministry of Environment and Natural Resources (RSMENR 2002) and the national standard (DPR 2002). The highest concentration of Fe was observed at station 2, which was significantly different ($p < 0.05$) from the values for other stations. These values were higher than those reported for Ngada River and Cross River (Ayotunde, Offem, and Ada 2012; Akan et al. 2010). The Mn concentrations found here are higher than those (0.5–4.0 mg kg⁻¹) in River Orogodo sediment in the Niger Delta (Issa et al. 2011). The Cu concentrations of 8.8–12 mg kg⁻¹ in Bodo Creek sediments were higher than those observed by Chindah et al. (2009) and Osuji and Onojake (2004) in the Niger Delta.

Similar trends were observed for Ni and Co, their concentrations being highest at station 2 and lowest at station 3. They did not show much variation when compared with other rivers in the Niger Delta (Ayotunde, Offem, and Ada 2012; Chindah et al. 2009). For Zn, higher concentrations were recorded at station 3 (22 mg kg⁻¹), and lowest at station 2 (4.8 mg kg⁻¹).

Low levels of Pb recorded in this study (0.9–1.4 mg kg⁻¹) are consistent with previous results in Niger Delta (Adeleye, Shelle, and Akinnigbagbe 2011; Chindah et al. 2009). Similarly, low levels of Cd are in agreement with previous findings for the Niger

Delta (Otitoju and Otitoju 2013; Vincent-Akpu and Mmom 2012; Ideriah, David-Omeiema, and Ogbonna 2012; Issa et al. 2011; Adeleye, Shelle, and Akinnigbagbe 2011). Concentrations of Cr varied from 4.9 to 5.6 mg kg⁻¹, which is higher than 0.08–0.31 mg kg⁻¹ reported for sediments from the Abonnema shoreline (Ideriah, David-Omeiema, and Ogbonna 2012).

The average metal load of Bodo Creek is quite low when compared with shale values (Turekian and Wedepohl 1961) and Sediment Quality Standards of other regions (USEPA 2008; CCME 2002; WDOE 1995). The reason for the low values have been affirmed to the high energy of current and the volume of water that ensures proper flushing of the system (Chindah, Braide and Sibeudu 2004). Onwugbuta-Enyi, Zabbey, and Erondu (2008) described Bodo Creek as a “mixing sponge” for the waters from the Andoni and Bonny rivers. The hydrodynamic and chemical complexity of a particular river, which is peculiar to the behavior of each metal, makes it difficult to compare concentrations from one water body to another. Nevertheless, the values in this study were higher or similar to those reported previously for the Niger Delta (Issa et al. 2011; Inengite, Oforka, and Osuji 2010; Osuji and Onojake 2004).

Conclusions

The spatial variations observed in metal contents were due to differences in physico-chemical parameters, silt and clay contents of different sites. Metal levels in sediment were low when compared with the shale values (Turekian and Wedepohl 1961) and Sediment Quality Standards of other regions (USEPA 2008; CCME 2002; WDOE 1995). This implies that the concentrations of the metals analyzed were not high enough to suggest serious contamination in the sediment. However, the higher concentration of metals in Bodo water suggests that it is not fit for domestic use. This implies that there is need for policy makers to initiate processes of restoration of this water body to meet internationally acceptable standard for domestic use.

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Disclosure statement

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