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Bitumen seepage: Impact and interaction on heavy metal concentrations in surface water

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Abstract

The association and interaction among metals in bitumen polluted water may affect the availability of the metals even at toxic levels to the surrounding environment and biota that are dependent on such water. The study was carried out at Ode-Irele in Ondo State bitumen belt, Southwest of Nigeria, where there are bitumen seepages, and Ebute-Irele where there are no records of seepages served as control. Composite samples of surface water were collected to a depth of 30cm midstream on the sites. Heavy metals – Manganese, Iron, copper, zinc, lead, chromium, cadmium, nickel, vanadium, arsenic, calcium, magnesium, potassium, and sodium were determined using standard methods. Data on metals' concentrations were analyzed using descriptive statistics and t-test at $p < 0.05$. The associations that exist among metals of surface water were analysed using regressive correlation to determine which metal increased or decreased with rise and fall in the level of other metals. Values obtained were compared with Federal Environmental Protection (FEPA) and World Health Organisation (WHO) Guidelines. Results of the study revealed that nickel, calcium, magnesium, and sodium were higher in seepage site than that of control, but, nickel was significantly higher in surface water of seepage site, 0.40 ± 0.00mgL-1 than that of control, 0.30 ± 0.00mgL-1. Manganese, iron, copper, zinc, chromium, cadmium, nickel, vanadium, and arsenic, as well as calcium were higher than guideline levels. Nickel, iron, manganese, vanadium, calcium and sodium which are elemental components of bitumen could pose serious environmental problems. There were significant positive associations between iron and copper, manganese and vanadium, iron and sodium, calcium and magnesium, as well as between magnesium and sodium. The finding also revealed significant negative association between lead and zinc. The heavy metals in surface water that were higher in seepage site and higher than guideline values in Ondo State bitumen belt and especially those that are elemental components of bitumen could have toxic effects on the environment, and so they should be closely monitored during the bitumen development phase.

Key words: Bitumen, Concentration, Heavy metal, Toxic, Water

Introduction

Bitumen otherwise known as asphalt as defined by Rasoulzadeh *et al.* (2011) is a highly viscous liquid or semisolid material, which is mainly produced from crude oil refinery process, and is also present in some natural deposits. Asphalt composition can be divided into four generic groups: saturates, aromatics, resins, and asphaltenes (Rasoulzadeh *et al.*, 2011). The molecules present in bitumen include among other things heteromolecules of sulphur, oxygen, nitrogen and metals. Others include combinations of alkanes, cycloalkanes, and aromatics (Read and Whiteoak, 2003). Asphalt institute and Eurobitume (2015) gave the elemental analysis of bitumen from various sources to contain carbon as 80.2-84.3% by weight, hydrogen (9.8-10.8%W), nitrogen (0.2-1.2%W), sulphur, 0.9-6.6%W), oxygen (0.4-1.0%W), nickel (10-139ppm), vanadium (7-1590ppm), iron (5-147ppm), Manganese (0.1-3.7), calcium (1-335ppm), magnesium, 1-134ppm), sodium (6-159ppm).

How bitumen functions has to do with how molecules interact with each other as well as with other materials such as aggregate surfaces and water. The amount of heteromolecules of sulphur, nitrogen, oxygen and metals in some bitumen molecules makes them slightly polar. In bitumen chemistry, if molecules contain hetero-atoms, they are better able to form molecular associations, and this has great influence on the physical properties as well as performance of bitumen (Goodrich *et al.*, 1986). Notwithstanding, bitumen is very much insoluble in water because of its inert property (kriech, 1990; Brandt and de Groot, 2001).

Paving and roofing materials made from bitumen materials are subject to water runoff from rainfall. Also, bituminous products are often used in lining drinking water reservoirs and pipelines for the supply of drinking water. In addition, to prevent liquid industrial waste products from leaching into the soil, retention ponds are often coated with asphalt, as bitumen is also used to line hazardous waste sites so as to prevent rainwater from leaching the wastes into groundwater (APA, 2011). The contaminations of highway runoff water and roadside soils by heavy metals have been reported (Warren and Birch, 1987; Strecker *et al.*, 1990; Pagotto *et al.*, 2000; Lau *et al.*, 2009). But, further research has revealed the contamination to have come from vehicles that used the roads rather than from bitumen pavements (Cooper et al., 1996). Heavy metals including both essential and non-essential elements have ecotoxicological effect to living organism (Storelli *et al.*, 2015). Pollution of water by heavy metals is a serious global problem due to the toxicity and the ability to accumulate in the water and the subsequent consumers (Fabio *et al.*, 2016). Heavy metal toxicity is one of the major current environmental health problems and is potentially dangerous because of bio-accumulation through the food chain (Aycicek *et al.*, 2008) and this can cause hazardous effects animal and human health (Aschner, 2002). Concentrations of heavy metals in the aquatic ecosystems are generally monitored by analyzing their accumulation in water, sediments, and associated biota (Camusso, Vigano, & Balestrini, 1995). Several studies on the bituminous deposit of Ondo state have been carried out (Lameed and Ogunsusi, 2002a; Lameed and Ogunsusi, 2002b; Adebiyi and Asubiojo, 2008; Olajire *et al.*, 2007, 2008; Olabemiwo *et al.*, 2011; Fagbote and Olanipekun, 2013; Victor-Oji *et al.*, 2017; Ogunsusi and Adeleke, 2019). However, most of the studies have focused on the characteristic constituents, hydrocarbon content and metal toxicity of the mineral. Nonetheless, there is dearth of information on the quality of surface water bodies in the bitumen belt of Ondo State, Nigeria, particularly with regards to interaction of heavy metals with one another. This study therefore aimed at evaluating the impact of bitumen seepage on the heavy metal concentration of surface water in the bitumen belt of ode-Irele, Ondo state, Nigeria, and how the metals associate with one another in order to influence their availability. It was hypothesised that there is no significant difference in metal concentrations in surface waters between seepage and control sites and that; increases or decreases in metal concentrations are not significantly associated with one another.

Materials and Methods

Study site

The study was carried out at Ode-Irele in Ondo State, Southwest of Nigeria (Fig 1). Ode-Irele is located in the southern fringe of the state between Latitudes 06^0 16^1N to 06^0 40^1 N and Longitudes 004^0 47^1 E to 005^0 10^1 E.

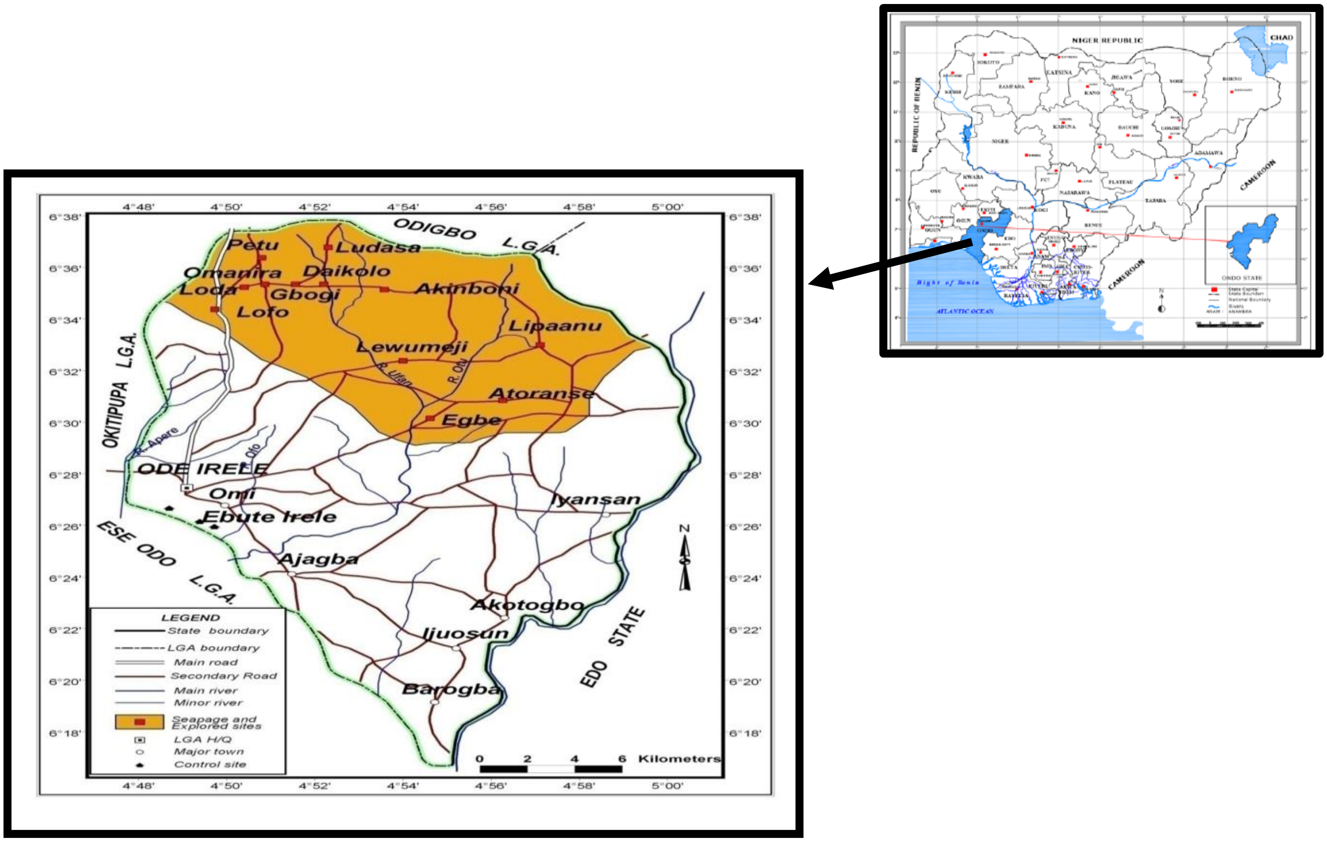

Fig 1: Bitumen exploration belt of Irele local Government Area, Ondo State, Nigeria**. Source.** Ogunsusi and Adeleke (2017)

Sampling Techniques

Composite water samples were collected to a depth of 30 cm midstream at seepage sites in Loda (S1), Ludasa (S2), Petu (S3), and Omanira (S4). Composite samples of water were also collected at four locations (C1, C2, C3 and C4) in Ebute-Irele which served as the control site, about 12 km away from the seepage sites. The water samples were collected in plastic bottles and were taken to the Department of Agronomy, University of Ibadan, Nigeria within 12 hours where the samples were then subjected to analysis of metal concentrations. The sample containers (plastic bottles) were pre-rinsed at least three times with the sample water. Metals - Fe, Mn, Cu, Pb, Cd, Cr, Ni, V, Zn and As, as well as Ca, Mg, K, and Na were determined using atomic absorption spectrometer as described by Perkin-Elmer, 1968.

Data analysis

Data on metals' concentrations from the seepage and control sites were analyzed using descriptive statistics and t-test at $p < 0.05$. The associations that exist among metals of surface water were analysed using regressive correlation to determine which metal increased or decreased with rise and fall in the level of other metals. Values of parameters obtained were compared between seepage and control sites, and with recommended Federal Environmental Protection Agency (FEPA, 1991; 2003), World Health Organization (WHO, 2004; 2010), and FEQGs (2016) guidelines. The standard guidelines are useful in assessing the risk of surface water pollution as indicated by Song *et al.* (2013). The risk assessment is also useful for proper management of water (Adhikary *et al.*, 2010).

Results

Heavy Metals Concentrations in Surface Water

Result of heavy metals presence in surface water of bitumen seepage and control sites in Table 1 showed that the heavy metals were not significantly different between seepage and control sites. Nonetheless, Ni, Ca, Mg, and Na were higher in seepage site than that of control. However, Ni was found to be significantly higher in surface water of seepage site 0.40 ± 0.00mgL-1 than that of control 0.30 ± 0.00mgL-1.

Trace Heavy Metals Concentrations and their Permissible Limits

Manganese level across all locations sampled ranged between 9.80 and 16.20mgL-1 (Table 2). The range of Mn values was higher than WHO (2010) guideline of 0.40mgL-1 and FEPA (2003) guideline of 0.03mgL-1. Iron level ranged between 1.80 and 2.20mgL-1, and was higher than WHO (2010) guideline of 0.3mgL-1 and FEPA (2003) guideline of 0.03mgL-1. Copper level ranged between 0.60 and 0.70mgL-1. This range of Cu level was lower than WHO (2010) limitation guideline of 2.0mgL-1, but, higher than FEPA (2003) limitation guideline of 0.3mgL-1. Zinc level varied between 1.50 and 1.70mgL-1. This range of values falls below WHO (2010) guideline of 3.0mgL-1, but higher than FEPA (2003) guideline of 0.012mgL-1. Lead level ranged between 0.005 and 0.05mgL-1, and were far below WHO (2010) guideline of 0.01mgL-1 and FEPA (2003) guideline of 0.06mgL-1. This is in tandem with the work of Israel *et al*, 2008 in which low concentrations of lead was also observed from the treated effluents which were dumped for physicochemical properties, metallic and non-metallic ions analysis.

The range of values for chromium was between 0.02 and 0.07mgL-1. The lower limit was lower than WHO (2010) and FEPA (1991) guideline of 0.05mgL-1, while the upper range was higher. Cadmium varies between 0.02 and 0.03mgL-1, and was higher than WHO (2010) guideline of 0.003mgL-1, but lower than FEPA (2003) guideline of 0.4mgL-1. The range of nickel varied between 0.004 and 0.40mgL-1. The lower range was lower compared to WHO (2010) guideline of 0.1mgL-1 and FEPA (1991) 0.1 – 0.2mgL-1, but the upper range was higher. Vanadium ranged between 0.03 and 0.4mgL-1. The lower range was lower than FEQGs guideline of 0.12mgL-1, but the upper range was higher. Arsenic level ranged between 0.01 and 0.02mgL-1, but were still within WHO (2010) and FEPA (1991) guideline of 0.01mgL-1.

Associations among Trace Heavy Metals

Linear associations that exist among heavy metals of water in the bitumen are presented in Table 3. The result shows the following positive associations:

The level of Fe in water positively correlated with the levels of each of copper, Cu, Manganese, Mn, Lead, Pb, Chromium, Cr, Nickel, Ni, Vanadium, V, and Zinc, Zn, as well as Ca, Mg, K, and Na. The association between Fe and each of Cu and Na was, however, found to be significant ($P<0.05$), as the level of the two heavy metals rises and falls together with Fe. Copper level was also found to be positively correlated with the levels of each of Fe, Mn, Pb, Cr, Ni, V and Zn, as well as Na. As the levels of each of the heavy metals increased, so did that of Cu. Manganese level also rises and falls with respective increasing and decreasing levels of Fe, Cu, Pb, Cr, Ni, V and as well as Zn, Ca, Mg, K, and Na. The positive association between Mn and V was found to be significant, ($P<0.05$). Nickel positively correlated with Fe, Cu, Mn, Pb, Cr, V, As and Zn, as well as Na. Vanadium correlated positively with each of Fe, Cu, Mn, Pb, Cr, Ni, As, Zn, Ca, Mg, K and NA, but the association with Mn was significant. The level of Pb was positively influenced by Mn, Fe, Cu, Ni, V, Ca, and Na levels in water. Levels of Fe, Cu, Mn, Cd, Ni, V, As and Zn also positively affect the level of Cr in water. The level of Cr and each of the heavy metals rise and fall with increases and decreases in chromium level. Cadmium level was positively influenced by Cr, As, Zn, Ca, Mg, and K levels in water. The levels of the heavy metals rise and fall together. Arsenic and each of Cr, Ni, V, As, Zn, Mg, and K levels also were found to rise and fall together in water. Also, there was positive association between Zn and each of Fe, Cu, Mn, Cr, Cd, Ni, V, As, Ca, Mg, and K. calcium positively correlated with each of Mg and K. magnesium also correlated positively with Ca, K and Na, while K positively correlated with Ca, Mg and Na.

The result further reveals the following negative associations:

Arsenic had negative correlation with each of Fe, Cu, Mn and Pb. As the level of As rises the level of each of the heavy metals falls, the level of As falls and vice versa.

able 1: Trace Heavy Metals in Surface Water

Metal	Mean mgL^{-1}		t-value	df	P	SD		FEPA (1991)	FEPA (2003)	WHO (2004)	WHO (2010)	FEQGs (2016)
	Seepage Site	Control Site				Seepage	Control					
Mn	12.00	12.00	0.26	6	0.81	0.0030	0.0010		0.03mgL-1		0.40mgL-1	
Fe	2.10	2.10	0.38	6	0.71	0.0000	0.0000		0.03mgL-1		0.30mgL-1	
Cu	0.65	0.60	1.00	6	0.36	0.0006	0.0008		0.03mgL-1		2.00mgL-1	
Zn	1.50	1.70	0.83	6	0.44	0.0001	0.0004		0.012mgL^{-1}		3.00mgL-1	
Pb	0.05	0.07	0.30	6	0.77	0.0000	0.0000		0.06mg/		0.01mgL-1	
Cr	0.05	0.07	2.18	6	0.10	0.0000	0.0000	0.05mgL-1			0.05mgL-1	
Cd	0.03	0.03	0.66	6	0.54	0.0000	0.0000		0.04mgL^{-1}		0.003mgL-1	
Ni	0.40*	0.30*	2.45*	6*	0.05*	0.0000*	0.0000*	0.1– 0.2mgL^{-1}			0.07mgL-1	
V	0.30	0.30	0.47	6	0.66	0.0002	0.0001					0.12mgL-1
As	0.01	0.01	0.00	6	1.00	0.0000	0.0000	0.01mgL-1			0.01mgL-1	
Ca	141.30	137.50	0.75	6	0.48	0.0090	0.0141			150mgL-1		
Mg	57.80	53.00	1.96	6	0.10	0.0039	0.0029			150mgL-1		
K	3.00	4.00	1.73	6	0.13	0.0008	0.0008			200mgL-1		
Na	13.30	4.00	1.00	6	0.36	0.0185	0.0008			200mgL^{-1}		

NB: marked t-value is significant at $P < 0.05000$

Table 2: Available Trace Heavy Metals in Surface Water

Location	Elements (mgL-1)									
	Mn	Fe	Cu	Zn	Pb	Cr	Cd	Ni	V	As
S1	12.20	2.20	0.60	1.50	0.06	0.06	0.03	0.4	0.30	0.01
S2	9.90	1.80	0.70	1.50	0.04	0.05	0.02	0.4	0.40	0.01
S3	16.20	2.20	0.60	1.60	0.005	0.02	0.02	0.4	0.03	0.02
S4	9.80	2.00	0.70	1.50	0.04	0.06	0.03	0.4	0.40	0.01
Mean	12.00	2.10	0.65	1.50	0.04	0.05	0.03	0.3	0.3	0.01
C1	11.20	2.00	0.60	2.20	0.04	0.06	0.03	0.3	0.3	0.02
C2	12.00	1.90	0.50	1.60	0.03	0.07	0.3	0.2	0.4	0.01
C3	13.30	2.20	0.70	1.80	0.05	0.08	0.02	0.4	0.3	0.01
C4	9.90	2.30	0.60	1.20	0.04	0.07	0.03	0.3	0.3	0.01
Mean	12.00	2.10	0.60	1.50	0.04	0.05	0.03	0.3	0.3	0.01
FEPA(1991)						0.05		0.1 - 0.2	-	0.01
FEPA(2003)	0.03	0.03	0.30	0.0123	0.06		0.04		-	
WHO(2010)	0.40	0.3	2.00	3.00	0.01	0.05	0.003	0.01	-	0.01

Copper level had negative association with each of Cd, As, Ca, Mg, and K. As the level of Cu increases in water, those of Cd and As decreases, and vice versa. The level of Pb also rises with decreasing levels of each of Cr Zn, Mg, and K. in water. The level of Cr increases with decrease in each of Ca, Mg, and K and vice versa. Cadmium also had negative associations with each of Fe, Cu, Mn, Pb, Ni, V, and Na. The association between Cd and Pb was, however, found to be significant ($p<0.05$). Negative correlation also existed between As and each of Ca and Na. Calcium level decreases with increases in the levels of Na

.

Table 3. Influence of the Presence of Trace Heavy Metals in Surface Water of Ondo State Bitumen Belt: Impacts and Interaction

	Fe	Cu	Mn	Pb	Cr	Cd	Ni	V	As	Zn	Ca	Mg	K	Na
Fe	1.0	0.8*	0.8	0.6	0.0	-0.7	0.2	0.4	-0.4	0.3	0.2	0.1	0.1	0.8*
Cu	0.8*	1.0	0.6	0.5	0.2	-0.6	0.4	0.2	-0.2	0.3	-0.3	-0.4	-0.4	0.7
Mn	0.8	0.6	1.0	0.6	0.4	-0.7	0.6	0.9*	-0.1	0.3	0.2	0.1	0.0	0.8
Pb	0.6	0.5	0.6	1.0	-0.3	-1.0*	0.3	0.4	-0.8	-0.5	0.1	-0.3	-0.2	0.5
Cr	0.0	0.2	0.4	-0.3	1.0	0.1	0.8	0.6	0.8	0.6	-0.6	-0.2	-0.3	0.3
Cd	-0.7	-0.6	-0.7	-1.0*	0.1	1.0	-0.4	-0.4	0.7	0.4	0.1	0.4	0.3	-0.6
Ni	0.2	0.4	0.6	0.3	0.8	-0.4	1.0	0.8	0.3	0.2	-0.6	-0.4	-0.4	0.5
V	0.4	0.2	0.9*	0.4	0.6	-0.4	0.8	1.0	0.2	0.2	0.1	0.3	0.2	0.6
As	-0.4	-0.2	-0.1	-0.8	0.8	0.7	0.3	0.2	1.0	0.7	-0.3	0.2	0.0	-0.1
Zn	0.3	0.3	0.2	-0.5	0.6	0.4	0.2	0.2	0.7	1.0	0.0	0.3	0.1	0.3
Ca	0.2	-0.3	0.2	0.1	-0.6	0.1	-0.6	0.1	-0.3	0.0	1.0	0.9*	0.7	-0.0
Mg	0.1	-0.4	0.1	-0.3	-0.2	0.4	-0.4	0.3	0.2	0.3	0.9*	1.0	0.9*	0.1
K	0.1	-0.4	0.0	-0.2	-0.3	0.3	-0.4	0.2	0.0	0.1	0.7	0.9*	1.0	0.3
Na	0.8*	0.7	0.8	0.5	0.3	-0.6	0.5	0.6	-0.1	0.3	-0.0	0.1	0.3	1.0

NB: marked correlations are significant at $P < 0.05000$

Macro Heavy Metals Concentrations and their Permissible Limits

The concentrations of macro heavy metals and their permissible limits are as presented in Table 4. The result showed that calcium level ranged between 132 and 152 mgL-1 in seepage site. The lower range was lower than WHO (2004) guideline of 150 mgL-1, but, the upper range was higher than the guideline. Magnesium ranged between 55 and 62mgL-1, and the values were lower than WHO (2004) guideline of 150mgL-1. The range of K stood between 2 and 4mgL-1 which were lower than WHO (2004) guideline of 200mgL-1. Sodium ranged between 4 and 41mgL-1 in bitumen seepage site, all of which were lower than WHO (2004) guideline of 200mgL-1.

Table 4: Available Macro Heavy Metals in Surface Water

Location	Elements (mgL-1)			
	Ca	Mg	K	Na
S1	132.00	54.00	2.00	4.00
S2	145.00	60.00	3.00	4.00
S3	136.00	55.00	3.00	4.00
S4	152.00	62.00	4.00	41.00
Mean	141.00	58.00	3.00	13.00
C 1	125.00	55.00	3.00	4.00
C 2	145.00	51.00	5.00	5.00
C3	121.00	50.00	4.00	3.00
C 4	149.00	56.00	4.00	4.00
Mean	135.00	53.00	4.00	4.00
WHO (2004)	150mgL-1	150mgL-1	200mgL-1	200mgL-1

Discussion

The mean values of heavy metals in surface water of bitumen seepage and control sites which are not significantly different from one another is a pointer to the fact that the metals may not pose serious environmental problem. This implies that the levels of the heavy metals in bitumen are not enough to bring about accumulated release of the metals in the water. Notwithstanding, Ni, Ca, Mg, and Na were higher in seepage site than that of control. The elemental analysis of bitumen has shown the preponderance of metals such as Ni, V, Fe, Mn, Ca, and Na in bitumen sample (Asphalt institute and Eurobitume, 2015). Therefore, these metals that were higher in seepage site might have been leached from bitumen, and may so be of potential environmental threat if they accumulate in surface water. This is, however not in agreement with the finding of similar study carried out by Itodo *et al.* (2018) which showed that heavy metals (Ca, Mg, Na and K) were higher in control site than the study site. But, the finding of Akinbile and Ogedengbe (2009) showed that the levels of some heavy metals (such as Mn, Ca, Fe, Cu, and Mg) were toxic and injurious to human, animals and aquatic lives.

The level of Mn that was higher than those of WHO (2010) and FEPA (2003) guidelines, points to the possible toxic level of the metal in the study area. Where mean concentration of Mn in drinking water was very high, there has been reported concentration correlation with cancer incidence and mortality (Zhang *et al.*, 2014). Manganese has also been reported to be widely distributed and one of the most abundant elements in the earth's crust. Mn is an essential trace element with many biological functions but toxic at higher doses [Rikson *et al.*, 2005]. Manganese is even a component of bitumen (Asphalt institute and Eurobitume, 2015). Therefore, the toxic level of Mn in the study area could have emanated from bitumen seepage. Iron has been found to be higher than WHO (2010) and FEPA (2003) guidelines, and this may pose a potential environmental threat. As one of the elemental components of bitumen, this toxic level might have come up as a result of transportation of the metal form bitumen seepage source to the nearby surface water. Findings of Mandour (2012) have revealed that Fe is even readily found in soil and water, and that liver cirrhosis was related to drinking water contaminated mainly with iron.

Copper level ranged between 0.60 and 0.70mgL-1. This range of Cu level was lower than WHO (2010) limitation guideline of 2.0mgL-1, but, higher than FEPA (2003) limitation guideline of 0.3mgL-1. The upper range of Cu is likely to pose a potential environmental threat since it is higher than FEPA (2003) guideline. Although human can adapt to excessive exposure to Cu from water by decreasing the absorbed fraction as exposure increases (Turnlund *et al.*, 1989; Uauy *et al.*, 1998), yet Cu absorption may be interfered with by some metals. Worst still is that consuming Cu in excess of 5–6 mgL-1 results in nausea, vomiting, and diarrhea (WHO, 2003). Since Zn level was higher than FEPA (2003) guideline, it can then be said that the metal is likely to be of potential environmental threat. Owing to the poor mobility of Zn in anaerobic environments, severe Zn contamination is likely to occur in surface water primarily near point source of its release (Barceloux and Barceloux, 1997). According to their finding also, Zn compounds can produce irritation and corrosion of the gastrointestinal tract, along with acute renal tubular necrosis and interstitial nephritis.

The range of lead which was lower than WHO (2010) and FEPA (2003) guidelines may not be a serious environmental threat. This is in tandem with the work of Israel *et al.* (2008) in which low concentrations of lead was also observed from the treated effluents which were dumped for physicochemical properties, metallic and non-metallic ions analysis. Notwithstanding, hyper accumulation of the metal in surface water should be prevented as much as possible, because, findings of Martin and Griswold (2009) have indicated chronic exposure of lead can result into many human ailments among which are mental retardation, and brain damage, kidney damage.

The upper limit of Cr that was higher than WHO (2010) and FEPA (1991) guidelines may possibly pose a potential environmental threat. This is owing to the fact that Cr is highly soluble in water, highly mobile and is easily reduced. The metal is known to affect the respiratory tract, liver, kidney, gastrointestinal and immune systems as well as the blood. It also causes dermatitis and ulceration of the skin (Saha *et al.*, 2011). Since cadmium level was higher than WHO (2010) guideline, the metal may therefore pose a potential environmental threat. This high level may be attributed to the solubility of the metal and its compound in water. Jaishankar *et al.*

(2014) in their finding reported high solubility of cadmium in water when compared with other metals. This tends to enhance the bioaccumulation of the metal, hence its bioavailability. According to them Long-term exposure to cadmium can result in morphopathological changes in the kidneys. Nickel is naturally occurring in surface water. But, the upper range that was higher than WHO (2010) and FEPA (1991) guidelines might have come from bitumen since the metal is one of the elemental composition of bitumen (Asphalt institute and Eurobitume, 2015), and was even significantly higher in seepage site than that of control site. Therefore, the metal may be of potential environmental threat if it accumulates in surface water.

The upper range of vanadium that was higher than FEQGs (2016) guideline may be a threat to human as well as animal health. A variety of health problems have been reported in subjects that has taken high doses of vanadium even as food supplements (EFSA, 2004) not to talk of exposure to an unknown but high lethal source of the metal. The upper range of arsenic which was higher than WHO (2010) and FEPA (1991) guidelines may pose a potential environmental problem to humans and animals that depend on it. IARC (2004) has proved a strong body of evidence linking arsenic intake with a variety of health problems, especially the long-term exposure to arsenic in drinking water. Even Lower levels of arsenic exposure can cause a number of human health problems such as nausea and vomiting, reduced production of erythrocytes and leukocytes, etc., (Smith *et al.,* 2000).

The lower range of Ca may not pose any environmental threat and be beneficial to human and animal consumption because Ca contributes to hardness of water which is one of its natural characteristics that enhances its palatability and consumer acceptability. Mortality rates and heart diseases are lower in areas with hard water (Tiwari *et al.*, 2015). But, the upper range which was higher than WHO (2004) guideline makes it toxic. Ca could have been leached from bitumen, because the metal is one of the elemental components of bitumen (Asphalt institute and Eurobitume, 2015). Magnesium is also known to contribute to total hardness in water, but, its levels were lower than WHO (2004) guideline. This makes it not to be of potential environmental threat, even though it is one of the elemental components of bitumen (Asphalt institute and Eurobitume, 2015). Potassium is one of four cations – Ca2+, Mg2+, Na+ and K+ that account for total cationic concentrations of natural water, and it is usually the least abundant of the four cations (Talling, 2010). Low concentration of K can limit the distribution of aquatic organisms. No wonder for this study too that K had the least level and was also lower than the guideline of WHO (2004). Therefore, low level of K may be of potential threat to the environment, particularly aquatic organisms that depends on it as source of salt. Sodium level in the study area may not pose potential environmental threat because of its low level compared to WHO (2004) guideline. This has been proved by van Dam *et al.* (2014) that replacing Ca and Mg with Na ion did not cause toxicity as it even increased reproduction in aquatic organism, as Mg was higher in toxicity than Na.

Conclusion

Findings on metal concentration of surface water samples in the bitumen belt of Ondo State, Nigeria clearly indicated that Ni, Ca, Mg, and Na were higher in seepage site than that of control, as Ni was statistically higher in seepage than control site.

Mn, Fe, Cu, Zn, Cr, Cd, Ni, V, and As, as well as Ca were higher than WHO (2004; 2010) and FEPA (1991; 2003) guidelines. The levels of these metals should, therefore, be closely monitored to avoid hyper accumulation in surface water during the actual development of bitumen.

The metals with which each of Fe, Mn, Ni, V, and Ca had positive correlation and especially those ones that were significant should be closely guided during bitumen development phase. This owed to the fact that the metals apart from being higher than guidelines are also elemental components of bitumen which could speed up accumulation of the metals in surface water and raise their toxicity levels.

Nickel, that was statistically higher in seepage site that that of control should be closely monitored because of its attendant environmental effects.

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