

ASSESSMENT OF LABILE METALS IN EFFLUENTS FROM LUBRICATING OIL COMPANY IN OSOGBO OSUN STATE, NIGERIA

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Abstract

Effluent and sediment samples were collected on seasonal basis, comprising of three months (August to October, 2014) in the wet season and three months (December 2014 to February 2015) in the dry season from five points around a lubricating oil company in Osogbo - Nigeria. The sequential extraction method was used to respectively fractionate the sediment and effluent samples, then analyzed by Atomic Absorption Spectrophotometry (AAS) to determine concentrations of five heavy metals: Mn, Ni Co, Cd and Pb. Results showed that in wet season, higher concentration of Mn was found in exchangeable fraction, Ni and Pb were more pronounced in carbonate bound fraction, Cd in Fe-Mn oxide fraction, while Co was more in residual fraction. In dry season, Pb was more concentrated in exchangeable fraction, Co in residual fraction, Mn in Fe-Mn oxide fraction, Cd in organic matter bound, while Ni was more concentrated in the carbonate fraction. In both seasons for sediment samples, Cd concentrations were found above the set limit by WHO. The speciation study of the effluent showed that, Mn, Co and Ni concentration were found more in Organic substances fraction in both seasons, Pb was more concentrated in free metal ion fraction in wet season while it was high in organic fraction in the dry season. Concentrations of all metals in the effluent samples in both seasons were above the maximum permissible limit for effluent. The high mobility factors of heavy metals in the sediment indicated that the metals were labile and bioavailable thereby making the soil and the living organisms vulnerable to possibility of high heavy metal bioaccumulation.

Key Words: Heavy Metals, Speciation, Effluents, Sediment

Introduction

In the history of man, the use of metals has a great benefits and as well its unexpected consequences (Amore *et al.*, 2005). Metals get into the environment from variety of sources, including those naturally occurring biogeochemical cycle (Juan *et al.*, 2010; Tessier *et al.*, 1979) and also from anthropogenic sources,

namely from domestic, industrial effluents, urban, storm water, run-off and atmospheric sources (Forstner and Wittman, 1981).

Although determination of total metal concentrations have been applied widely but is not enough method to know the mobility and bioavailability of heavy metals in the effluent and sediment and

their potential impact on the environment because it depend on the chemical form of heavy metals (Amos *et al.*, 2014, Alvarez *et al.*, 2002). Speciation of heavy metals in effluent and associated sediments gives better understanding of the extent of mobility and bioavailability of different metal fractions and its application for agricultural purposes.

Total metal evaluation alone cannot really show the metal that is bioavailable because it may be poor indicators of uptake by plants. Hence, to evaluate and quantify different chemical forms of metals in samples such as sediments and effluent, employing appropriate method during extraction procedure are more essential than before. Among numerous sequential extraction procedures (SEPs) that have been developed for sediment samples, the 5-step SEP by Tessier *et al.* (Tessier *et al.*, 1979), short SEP by Maize (Maize *et al.*, 1997), the 6-step Kersten-Förstner procedure (Kersten and Förstner, 1986) are the three most standard methods for speciation of metals. Also for water speciation the 3-step SEP by Tokalioglu *et al.* (2000) is the most standard method for speciation metals of an environmental material.

The speciation of heavy metals shows strong influences on the mobility, bioavailability and toxicity of heavy metals in both contaminated sediment and waste water (Ure and Davidson 2002; Hass and Fine 2010; Qingsong *et al.*, 2013).

For sediment samples, Tessier *et al.*, (1979) classifies forms of heavy metal into separate fractions:

Exchangeable: The exchangeable form of heavy metals is mobile and it is used to quantify the short term availability of heavy metals for plants uptake

(Brummer, 1986, Amos *et al.*, 2014). It occurs in ion exchange complexes. Metal bound to carbonate can also be easily released at lowered soil reaction available to plant (Gawdzik and Gawdzik, 2012, Amos *et al.*, 2014).

The important factor governing metal speciation is the hydrogen ion activity (pH). pH affect both solubility of metal hydroxide mineral and adsorption-desorption process. Under high pH condition in water, metal hydroxide minerals have very low solubility because its activity is proportional to pH (Amos *et al.*, 2014).

Metal adsorbed to oxides: Oxide of aluminium, manganese and iron provides sites for chemical adsorption of metals (Amos *et al.*, 2014). Adsorption that occurs when metals are attached to surfaces of particulate matter is also strongly dependent on pH (Bourg, 1988; Brummer, 1986; Amos, 2014). Adsorption also vary with concentration of complexing agent also increase pH of the adsorption (Amos, 2014; Bourg, 1998) and precipitation of heavy metals with oxide, hydroxide, but carbonates decreasing the mobility of the metal (Jenne, 1986; Amos *et al.*, 2014). Metal that bounded to oxide are very stable but dangerous because when it undergo reduction-oxidation condition in the soil they can be made available overtime time.

Metal bounded to organic matter: According to Brummer, metal bound to organic matter fraction are very stable in the soil and not available for plant (Brummer, 1986). Complexation of heavy metal with dissolved organic matter can cause it mobility which increases the extent of leaching of metal

in the soil (Molenaar and Beltrami 1998; Schaecke *et al.*, 2002; Amos *et al.*, 2014).

Bio-availability of heavy metal can reduce because of the decrease in organic matter decomposition overtime (Mcbride, 1995; Schmidt 1997). According to Silveira *et al.*, the more electronegative the metal ion, the strong it bounded with organic matter (Silveria *et al.*, 2003)

Metal in the residual fraction: The residual fraction of heavy metals is considered the inactive fraction as regard chemical processes in the soil. They are found in between the mineral layer and on edge clay layer (Amos *et al.*, 2014; Calvet *et al.*, 1989)

Materials and Methods

Sample Collection and Pre-treatment

The effluent and sediment samples were collected in 1 L treated polyethylene bottles from five different sites along the discharge path of the lubricating oil company in Osogbo in wet (August, September, October) and dry season (December, January, Febuary) respectively. The geographical locations of these sites were determined using GPS-Magellian GPS 3010. The map of the study area (Fig. 1) depicts the sampling sites in Osogbo Osun State, Nigeria.

Tables 1 present the geographical locations of the sampling site. The study area lies within longitudes 4°31'0.41" to 4°31'07.1" and latitudes 7°47'13.1" to 7°47'13.7" while the land elevation is within 37.66m to 78.12m above sea level.

Table 1: Geographical Locations of the Sampling Sites in Osogbo

Sampling site	Elevation (m)	GPS Values	
		Latitude (N)	Longitude (E)
Point 1	66.96	7°47'13.7"	4°31'06.9"
Point 2	50.22	7°47'13.1"	4°31'07.1"
Point 3	36.27	7°47'13.1"	4°31'06.5"
Point 4	78.12	7°47'13.3"	4°31'04.8"
Point 5	55.80	7°47'13.5"	4°31'0.41"
Control point	37.66	7°47'13.2"	4°31'02.7"

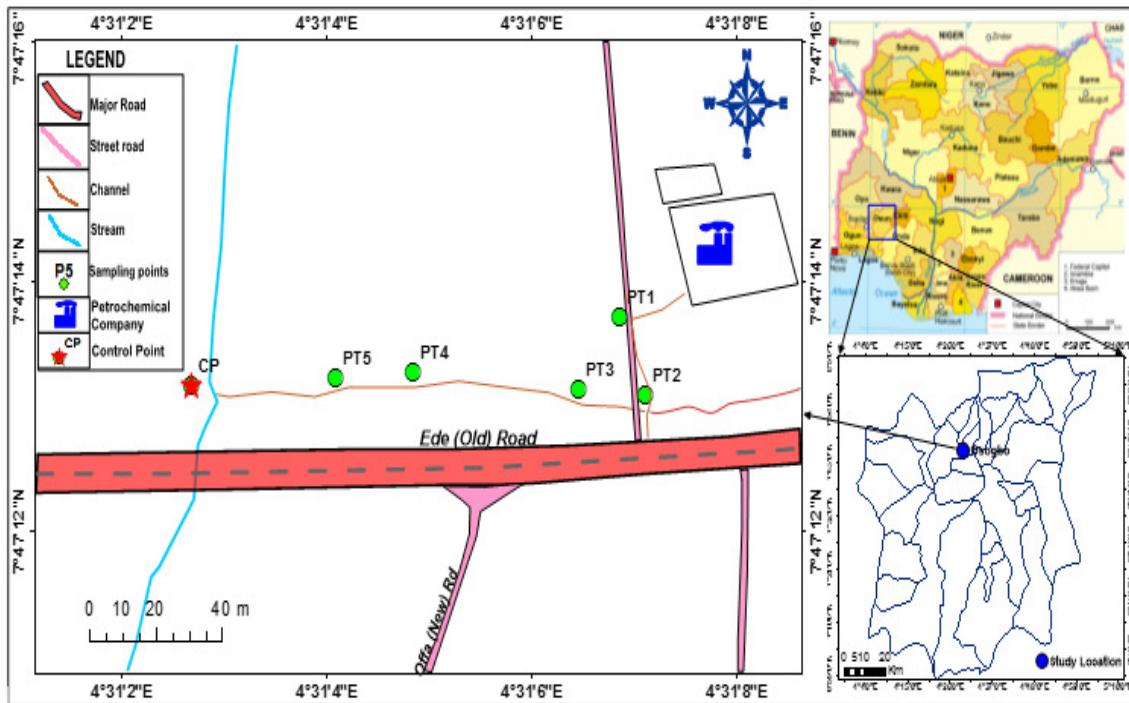


Fig. 1: The locations of the sampling sites in Osogbo

Determination of Total Metal Concentration in Sediment Samples

One gram of sediment sample was digested with 30mL aqua regia (HCl: HNO₃; 3:1) on a hot plate equipped with a thermostated at a temperature between 150 °C and 180 °C. The contents of the Teflon beaker were replenished with more aqua regia to avoid total evaporation. After approximately two hours of digestion, 5 mL HF was added to the Teflon beaker and the temperature of the hot plate was decreased to induce simmering. The sample was then digested for a further 30 minutes. The Teflon beaker containing the sample was allowed to cool to room temperature before it was quantitatively transferred into a 25 mL volumetric flask and filled to capacity with twice distilled water. A blank determination was conducted using the procedure described above, without the sample. Concentrations of Mn, Ni,

Co, Cd and Pb were determined by Atomic Absorption Spectrophotometry at the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria.

Sequential Extraction of Metals from Sediment Samples

A sequential extraction procedure (Tessier *et al.*, 1979) was used to extract and partition Mn, Ni Co, Cd and Pb into exchangeable, bound-to-carbonate, bound to Fe-Mn oxides, bound to organic matter and residual fraction species.

Exchangeable (F1): A 1.0 g sample was extracted from the sediment sample with 20mL 1M MgCl₂ by continuous agitation for one hour at room temperature.

Carbonate-bound (F2): The residue from F1 was treated at room temperature with 20 mL 1M CH₃COONa adjusted to pH=5 with CH₃COOH, and continuous agitation were maintained for five hours.

Fe-Mn oxide bound (F3): The residue from F2 was extracted with 40mL 0.04M NH₂OH.HCl in 25% (v/v) CH₃COOH with occasional agitation for five hours.

Bound to organic matter (F4): The F3 residue was added to 7.5 mL of 0.02M HNO₃ and 12.5 mL of 30% H₂O₂ adjusted to pH = 2 with HNO₃. The mixture was heated to 85 °C for two hours with occasional agitation. A second aliquot containing 7.5 mL of 30% H₂O₂ was added and further heated for three hours at 85 °C with intermittent agitation. After cooling, 12.5 mL of 3.2M CH₃COONH₄ in 20% (v/v) HNO₃ was added to prevent the adsorption of the extracted metals into oxidized sediments. The mixture was then diluted to 40mL, followed by 30 minutes of continuous agitation.

Residual (F5): The residue from F4 was digested by 15mL of concentrated HNO₃ and then refluxed for one hour, filtered and washed with 10mL of hot 3M HNO₃.

Resin and Column Preparation

The Amberlite XAD-16 resin was ground to enlarge the surface area for maximum adsorption and sieved with 60-80 mesh before being washed successively with methanol, water, 1M HNO₃ in acetone, water, 1M NaOH and water. A sample of 400mg of Amberlite XAD-16 resin was slurry-packed into a glass column (10 mm i.d (internal diameter) x 100 mm length) fitted with glass wool. Prior to use, the column was preconditioned with 5 – 10 mL portions of blank solution (distilled water). Concentrations of Mn, Ni, Co, Cd and Pb were determined by Atomic Absorption Spectrophotometry.

Speciation Analysis for Effluent Samples

Following the determination of heavy metals in effluent samples after sorption on Amberlite XAD-16 resin, the speciation of effluent samples was separated into three fractions (Tokalioglu *et al.*, 2000): metals in suspended particles, metals bound to organic substances and free metal ions.

Metals in suspended particles: Effluent samples were filtered through a 0.45 µm Millipore membrane filter (47 mm in diameter). The membrane filters loaded with suspended particles were dissolved in concentrated HNO₃, centrifuged, evaporated to near dryness and then collected in 2 mL samples with 2M HNO₃.

Metals bound to humic substances: The effluent samples were filtered through a 0.45 µm filter, and the obtained filtrates were passed through adsorbent column packed with Amberlite XAD-16 resin at a flow rate of 2 - 2.5 mL min⁻¹. The effluent was reserved in order to determine the free metal ion contents. The metals bound to humic substances were then eluted with 1M HCl in acetone.

Free metal ions: A 2 mL sodium tetra borate reagent was added to the effluent. The solution was passed through the column filled with Amberlite XAD-16 resin. The trace metals adsorbed on the resin were eluted with 1M HCl in acetone, and the residue was dissolved in 0.7 mL of 2M HNO₃.

Mobility Factor (MF) Determination

The relationship adopted by (Salbu *et al.*, 1998; Narwal and Singh, 1998) was used to determine the mobility factor of the metals. This relationship is:

$$MF = \frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5} \times 100 \dots\dots\dots (1)$$

Where: F₁ = Exchangeable metal content fraction, F₂ = Metal content bound to carbonate fraction, F₃ = Metal content bound to Fe-Mn oxide fraction, F₄ = Metal content bound to organic matter fraction, F₅ = Residual metal content fraction.

Risk Assessment Code (RAC)

Risk assessment code (RAC) was first adopted by Singh *et al.*, 1997. RAC is to assess the availability of metals in the sediment. This relationship is:

$$\% F1 + \% F2 \dots\dots\dots (2)$$

Where: F1 = Percentage exchangeable metal content fraction, F2 = Percentage metal bound to carbonate fraction.

The mobility and stability of elements which relatively define their toxicity strongly depend on binding forms in different phases. According to RAC classification, less than 1% of total metal in exchangeable/carbonate phase has no adverse impact on aquatic environment. Low risk defined in range between 1% and 10% while medium risk is 11-30% and 31-50% indicates high risk. Higher percentage than 50% of the total metal has very high risk and can poses dangerous impact by entering into food chain.

Results and Discussion

The results of the speciation analysis on sediments for some heavy metals are provided in Fig. 2 and Fig. 3 for wet and dry season respectively. As you move down along the path (point 1 to point 5) of discharge, accumulation of the metals (Pb, Ni and Co) in exchangeable and carbonate increases which makes the near- by river the sink of the effluent (Fig. 1) and its aquatic organism at risk. The results indicate an occurrence of the highest Mn percentage in exchangeable fraction in wet season and Fe-Mn oxide fraction in dry season. Adeyeye *et al.* (2016) also reported that a Mn quantity is

high in the exchangeable fraction in the runoff sediment collected from osogbo. This is an indication that Mn availability in the sediment being investigated is likely to be lithogenic in origin in wet season. The least concentration of Mn appeared in the organic matter and residual fraction. The concentrations of Mn analyzed in both seasons were found below permissible limits of 1000 µg/g set by WHO (2003). For Ni, the speciation result shows that it had highest accumulation in carbonate fraction in both wet and dry season which could make Ni to be available in the sediment at the slighted change in pH (Amos *et al.*, 2014). The concentrations of Ni analyzed in both wet and dry season were below the recommended permissible limit of 50 µg/g by WHO. Speciation pattern of Cd shows that in wet season, the lowest concentration of Cd in the fraction was obtained in the residual fraction but in dry season it was low in Fe-Mn oxide. However, the highest concentration was obtained in Fe-Mn oxide in wet season and high in the organic matter fraction in dry season. High concentration of Cd in non-residual fraction indicates that it may be easily transferred into the food chain with time (Pardo and Guadalix, 1996).

The concentrations of Cd analyzed in both seasons were found above permissible limits of (3 µg/g) set by WHO for sediment. These metals will bioaccumulate and stored faster than excreted (Abdel-shafy and Abdel-basir, 1991; Antunes *et al.*, 2003; Davies *et al.*, 2006). Cadmium exposure during human pregnancy, leads to reduced birth weights and premature birth (Henson and Chedrese, 2004). Long-term exposure leads to a buildup in the kidneys and possible kidney disease, lung damage, and fragile bones (ATSDR, 2008). In the sediment, Co predominated in this order; residual fraction > Fe-Mn oxide > organic matter. Carbonate fraction in wet season

shows high immobility of Co (Amos *et al.*, 2014), but in dry season carbonate fraction had the highest concentration. However, the concentrations of Co analyzed in both wet and dry season were below the recommended permissible limit of 50 (µg/g) by WHO in sediment. The accumulation of Pb in both seasons was high in the carbonate fraction and this can be made available to the environment at the slightest change in pH of the sediment (Amos *et al.*, 2014). The concentration of Pb analyzed in both seasons were below the set permissible limit of 100 µg/g by WHO (2003) in sediment.

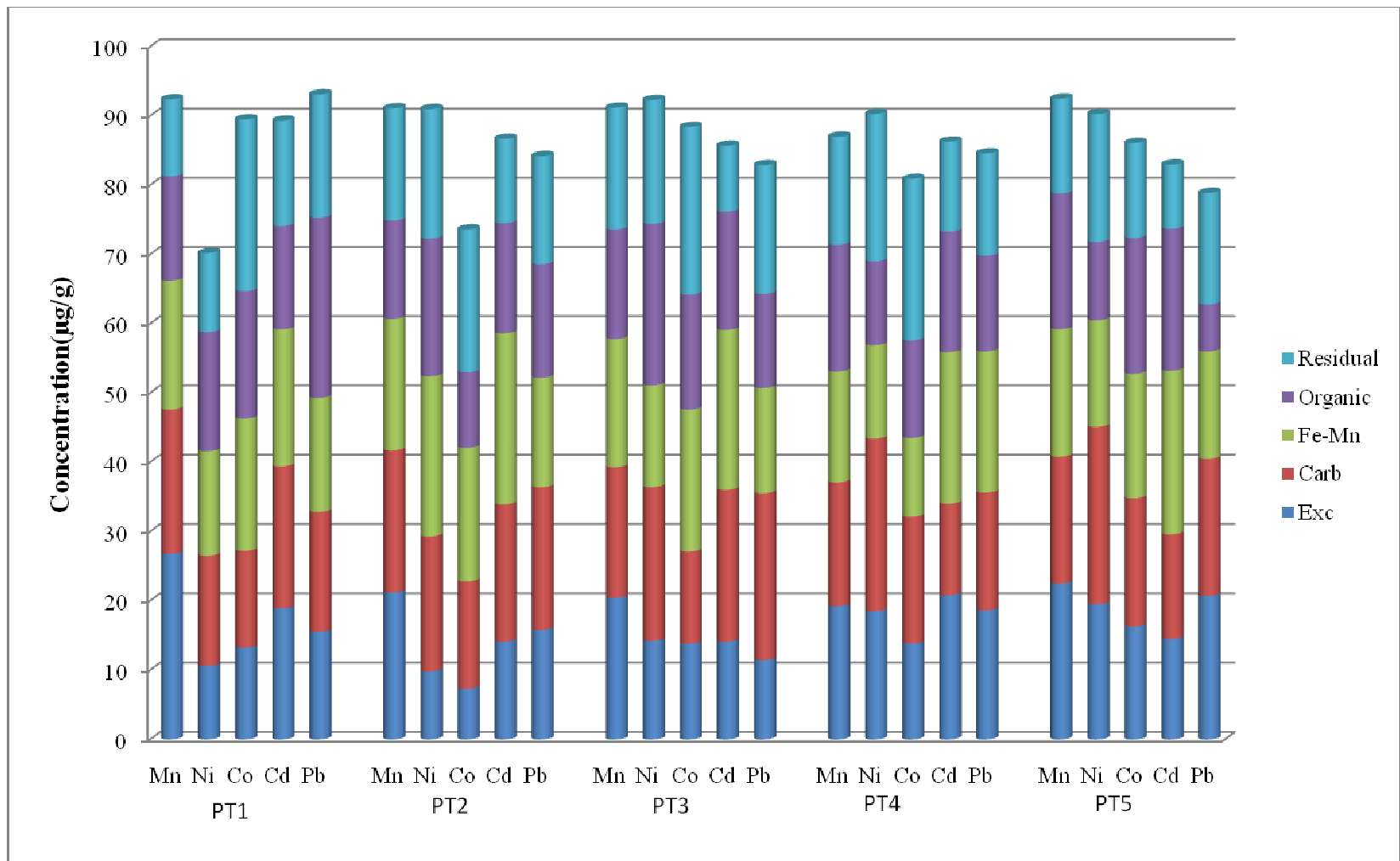


Fig. 2: Summary of total mean levels of heavy metals ($\mu\text{g/g}$) in each fractions sediment samples in wet season

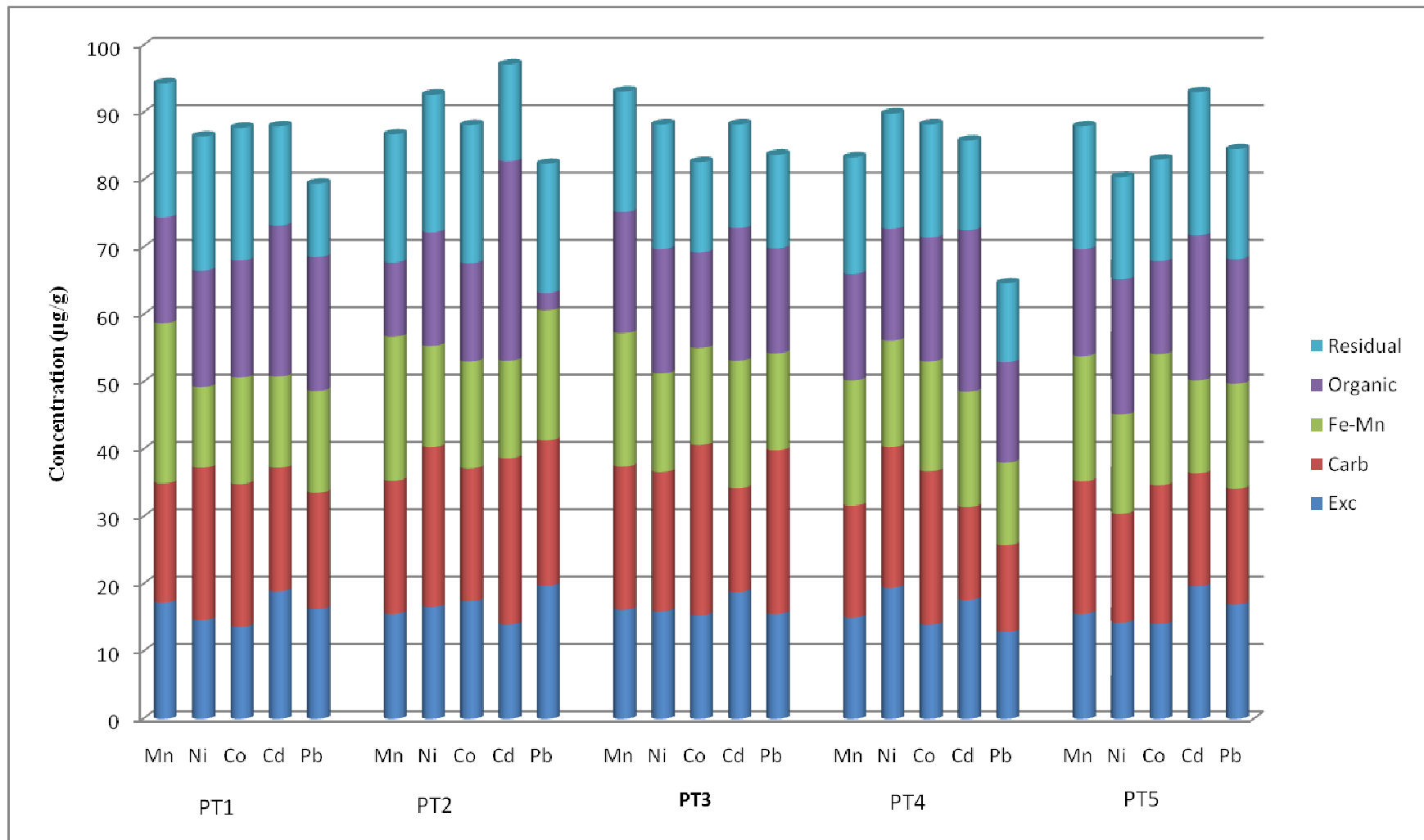


Fig. 3: Summary of total mean levels of heavy metals (µg/g) in each fractions sediment samples in dry season

The overall mean of the mobility factor MF for the heavy metals studied (Table 2) were in the order: Co (33.85%) < Cd (37.78%) < Ni (40.99%) < Pb (43.70%) < Mn (45.42%) for wet season and Mn (39.41%) < Cd (39.62%) < Ni (41.52%) < Co (42.24%) < Pb (43.92%) for dry season. In wet and dry seasons, the mobility factor showed that the levels of Ni and Pb were high confirming values obtained in their chemical speciation study. All these metals can be said to be highly environmentally labile and bioavailable (Xian, 1987; Salbu *et al.*, 1998). However, all the humans, plants, animals

around this area are quite vulnerable to the heavy metals exposure.

Risk Assessment Code (RAC)

The calculated values (Table 2) according to equation 2 by Singh *et al.*, (1997), shows that risk assessment code (RAC) obtained in both wet and dry seasons for all the sampling points revealed that all the metals analyzed for the effluent sediment samples falls to the categories of high risk and very high risk. The RAC value obtained for Ni, Pb and Cd were significantly high which is a concern for the environment and human health.

Table 2: Calculated Risk Assessment Code and Mobility Factor (mf %) of the sediment samples

Metal	Wet Season					Dry Season				
	Mn	Ni	Co	Cd	Pb	Mn	Ni	Co	Cd	Pb
PT1	51.52	37.78	30.28	44.15	35.36	37.36	43.08	39.72	42.62	42.30
PT2	46.72	32.24	30.99	39.16	43.23	40.76	43.57	42.18	39.88	50.24
PT3	43.10	38.43	30.61	41.98	43.32	40.26	41.56	47.57	38.95	47.62
PT4	42.65	48.06	39.56	39.40	42.12	37.99	44.92	41.64	36.66	39.88
PT5	44.12	45.82	40.40	35.68	51.31	40.18	37.87	41.75	39.28	40.37
MF%	45.42	40.99	37.78	33.85	43.70	39.41	41.52	39.62	42.24	43.92

The water speciation data for Mn, Ni, Cd, Co and Pb in wet and dry season as presented in Fig. 4 and Fig. 5 respectively. Mn was found predominantly in the organic fraction in both seasons. Adeyeye *et al.* (2016) also indicated the predominance of Mn in the organic fraction. It may likely due to the presence of the metal in the effluent being discharged and Mn due to anthropogenic and lithogenic origin in the environment. The concentrations of Mn analyzed were found above permissible limits by NSDWQ, 2007; WHO, 2007 and FEPA, 1999 for wastewater discharged in to surface water. For Ni, both wet and dry seasons,

showed that Ni had the highest concentration in organic fraction. This finding is supported by Adeyeye *et al.* (2016). The concentrations of Ni in the effluent were above the maximum permissible limit set by (NSDWQ, WHO and FEPA). From the fig. 4 and 5, Co had higher concentration in suspended particle fractions in wet season and in dry season, Cobalt is found in greater quantities in organic fraction. The values of Co were above the maximum recommended limit set by WHO in both seasons (WHO, 2007). Speciation analysis of Cd in both wet and dry seasons shows that Cd were found in higher concentration in the suspended

particle fraction. The concentration of Cd in both season were above the set limit of 0.05 mg/L by FEPA. Lead (Pb) in wet season were found in higher concentration in free metal ion, indicating that the effluent was contaminated with Pb and that it may be readily available for plant uptake and found its way into human system. In dry season, Pb concentration was very high in organic substances. The concentration of Pb

analyzed were found above the permissible limits by (NSDWQ, WHO and FEPA) for wastewater discharged into the surface water. Exposure to high Pb levels can severely damage the brain and kidneys and cause death. High levels of exposure to lead may cause miscarriage in pregnant women. In men, high level exposure can damage the organs responsible for sperm production (OSHA, 2004).

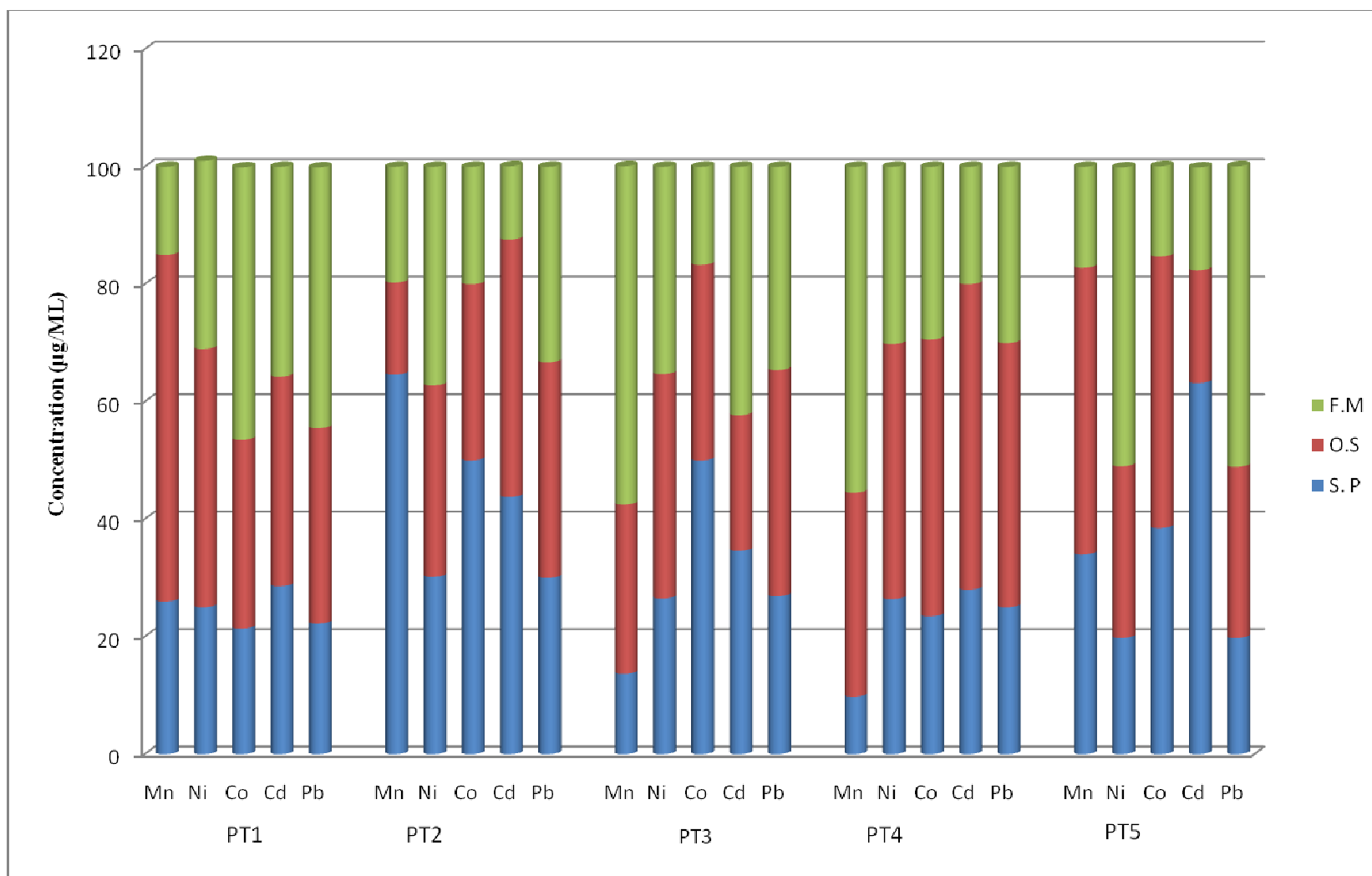


Fig. 4: Total metal concentration ($\mu\text{g/ml}$) in various chemical fractions in the effluent samples in wet season
 S.P = Suspended Particle; O.S = Organic Substance; F.M = Free Metal ion

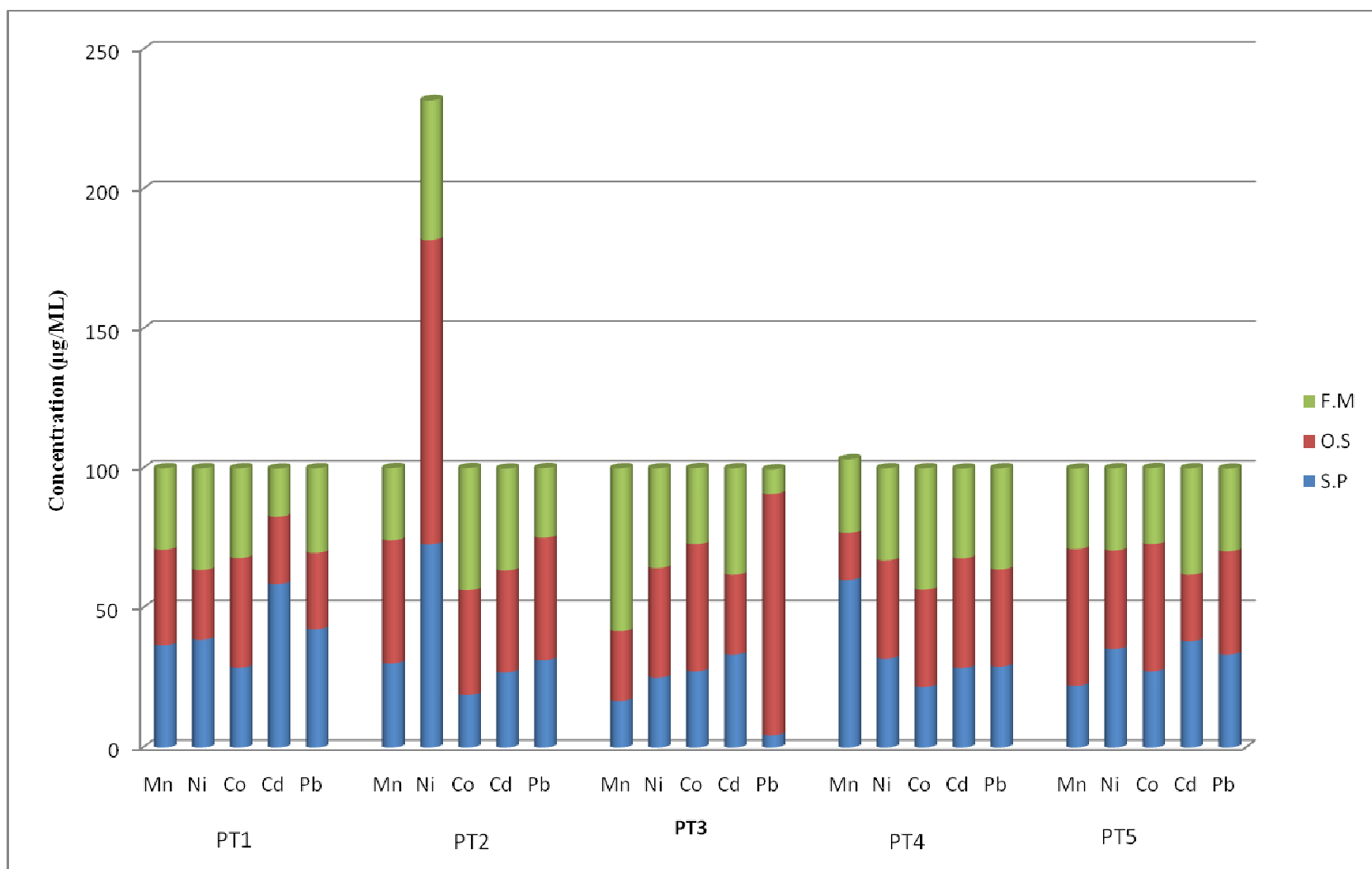


Fig. 5: Total metal concentration (µg/ml) in various chemical fractions in the effluent samples in dry season
 S.P = Suspended Particle; O.S = Organic Substance; F.M = Free Metal ion

Conclusion

Figures 2, 3, 4 and 5 presents chemical fractionation of both effluent and sediment. For the effluent sediment samples in wet season, it was polluted with Mn, Ni, and Pb while in dry season it was polluted with Ni, Co and Pb (Ni and Pb are elements of health concern) since significant amount of these metals were found in high concentration in the exchangeable and bounded to carbonate fractions which are the labile, bioavailable and toxic chemical fraction. The heavy metals concentrations in the sediment were below the set maximum permissible limit by WHO, 2003 standard except for Cd in both seasons. Exposure to high levels of cadmium can cause renal dysfunction, obstructive lung disease which has been linked to lung cancer. It can also cause skin irritation and ulceration. In Japan, the *Itai-itai* sickness associated with bone damage as a result of the regular consumption of rice contaminated with Cadmium was reported (Bulinski *et al.*, 1993). The distribution of the studied metals in the various chemical fractions, results of mobility factors and risk assessment code confirmed their mobility, bioavailability and their potential to cause pollution. The effluent water samples were polluted with Pb in wet season. It was very obvious from results obtained that the effluent from the lubricant industry were loaded with Ni and Pb a major environmentally concern metal. Ni as one of the catalysts of hydrogenation and lead as one of the component of anti knock agent. The concentrations of heavy metals in the effluent water in both wet and dry seasons were found above the standard maximum permissible set by WHO, 2007. Therefore, a better method of waste

management would be needed to avoid/curtail the menace of heavy metal pollution into the nearby aquatic environment.

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