University of Tehran Press

Pollution

Print ISSN: 2383-451X
Online ISSN: 2383-4501

https://jpoll.ut.ac.ir/

Chemical Speciation, Bioavailability and Risk Assessments of Potentially Toxic Metals in Rainwaters as Indicators of Air Pollution

Abiodun Odunlami Adegunwa[1] | Festus Mayowa Adebiyi[2,3] | Olabode Idowu Asubiojo[2] | Odunayo Timothy Ore[2✉*]

1. Department of Pure and Applied Chemistry, Osun State University, Osogbo, Nigeria
2. Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria
3. Management and Toxicology Unit, Department of Biological Sciences, Elizade University, Ilara-Mokin, Nigeria

Article Info

Article type:
Research Article

Article history:
Received: 15.082022
Revised: 10.10.2022
Accepted: 01.11.2022

Keywords:
Rainwater;
Bioavailability;
Heavy metals;
Speciation;
Risk assessment

ABSTRACT

Heavy metals contamination of rainwater is a function of the adsorbed metals present in the particulates of the atmosphere in which the rain was formed from and rainwater chemistry is an alternative way of monitoring urban air pollution for predominant metal species. Three distinct sampling sites (residential, industrial and commercial) were investigated in the south western part of Nigeria for one year. After acid digestion, quantification was done using a double-beam Atomic Absorption Spectrophotometer (AAS). The obtained results showed that heavy metals were predominantly present as free metal ion in the commercial and industrial areas but Mn and As mainly occurred in the suspended fraction. Residential area presented major fractions as bound to organic complexes except Cu and Cd which were principally available as suspended fraction. The health risks associated with the intake of the studied rainwaters indicated susceptibility to possible carcinogens upon consumption due to total RI > 10-4. Ecological risk assessment equally shown a very high level of ecological risks related with the metals due to RI > 600. Sequel upon this, there is need for better sensitization of the citizenry to the sources and control of these pollutants.

Cite this article: Odunlami Adegunwa, A., Mayowa Adebiyi, F., Idowu Asubiojo, O., & Timothy Ore, O. (2023). *Chemical Speciation, Bioavailability and Risk Assessments of Potentially Toxic Metals in Rainwaters as Indicators of Air Pollution.* Pollution, 9(1): 316-331.
http//doi.org/10.22059/poll.2022.347219.1573

DOI: http//doi.org/10.22059/poll.2022.347219.1573

INTRODUCTION

The emissions of gaseous elements and particulates into the atmosphere has been a global phenomenon as pollutants can be transported over great distances from their discharge source before being deposited as dry or wet precipitation (Yang *et al.*, 2013). The growing population and the negative footprint of unplanned urbanization and industrialization to support the rising populace has damaging impact on the natural environment due to the emission of different gaseous particles with deleterious effect into the atmosphere (Ahmed *et al.*, 2015; Adegunwa *et al.*, 2019; Fazeli *et al.*, 2019). As a result of this, ambient air pollution has been labelled to be one of the most serious ecological problems in societies at all levels of economic advances

*Corresponding Author Email: *oreodunayo@yahoo.com*

(USEPA, 2015). Though, atmospheric pollution can be from natural and man-made sources. Reports have it that many of these toxic substances emanated from unceasing industrial and commercial activities with direct emissions into the ambient air without information from air regulatory bodies of their environmental potential risks (Keefe, 2013). Particulates matter most especially $PM_{2.5}$ which easily enter human lungs by inhalation through the respiratory system have been reported to contain heavy metals that have been listed as priority pollutants because of their persistent nature, bioaccumulation and toxicity at relatively low concentration (Islam *et al.*, 2015a; Ahmed *et al.*, 2015). Recent trends of research have linked some acute adverse health effects to the prevalence of some toxic species of heavy metals (Tripathi *et al.,* 2010).

Wet precipitation has been an effective alternative route through which gaseous, particulates and other aerosols are washed down and get deposited (Robert, 2002; Efe 2005; Efe 2006; Igwo-Ezikpe and Awodele, 2010; Chughtai *et al.*, 2014; Adegunwa *et al.*, 2019). Precipitation of lower raincloud in the atmosphere dissolve particulate matter which adsorbed the heavy metals and washed it down when rain falls on the earth surface (Obaidy and Joshi, 2006). This settle either directly on surface waters or on soils before being transported to surface water bodies where they accumulate causing detrimental effects on the receptor (Emerole *et al.*, 2015). The concentrations of heavy metals content of rainwater are a direct hinge of the environmental pollution level in the atmosphere of the area under investigation. (Seto and Hara, 2006; Strayer *et al.*, 2007). In other words, rain is a vital means of regulating the levels of atmospheric pollutants (Robert, 2002). This process allows rainwater to be effectively used as environmental indicators of ambient air pollution (Kulshrestha *et al.,*1995; Asthana and Asthana, 2003; Yoboue *et al.*, 2005).

The chemistry of an element in an environmental matrix may not be fully understood without exploring the wide range of chemical form in which they exist under probable condition/medium. Metal speciation give a way of characterization for possible transformation between the various available chemical form which suggest their environmental behaviors viz; distribution, mobility, bioavailability and toxicity nature (Templeton *et al.*, 2000; Ore and Adeola, 2021). Metals can exist in different phase as free metal ions, particulates bound and metals bound to mineral matrix such as humic and fulvic substances and particulates in liquid medium (Mohiuddin *et al.*, 2012).

The area of environmental monitoring and assessment has witnessed studies of the total concentration of total heavy metals in different environment matrix with little attention given to speciation analysis of heavy metals (Umoren *et al.*, 2019). Information of the distribution of species of heavy metals in the environment is important for adequate evaluation of their toxicological impacts in order to characterize metal behavior in any environmental matrix (Adebiyi *et al.,* 2020).

There has been no scientific research undertaken to monitor concentrations of the different species form of heavy metals in the study area. Therefore, the objectives of this study are to determine the levels of heavy metals in their specie form using rainwater as the environmental indicator of aerial pollution of the investigated region. The health and ecological risk associated with the exposure to the heavy metals in the rainwater was also evaluated.

MATERIALS AND METHODS

Description of the study area

Ibadan (7°24ˊ39ˊˊ N and 3°54ˊ21ˊˊ E) is about 128 km away from inland Northeast of Lagos and 530 km Southwest of Abuja, Nigeria. It is a resident to about 5,580,894 million people (NPC, 2006) with land mass covering a total area of 3,080 square kilometers. The city ranges in elevation from 150 m in the valley area to 275 m above sea level. The city harbors many industrial estates with the selected study areas chosen as Oluyole industrial estate, University of Ibadan, and Iwo-road (Figure 1). Eight (8) equidistance points at each area were used for rainwater sample collection. Each of the investigated study areas has some unique anthropogenic features; such as industrial, residential, and commercial activities.

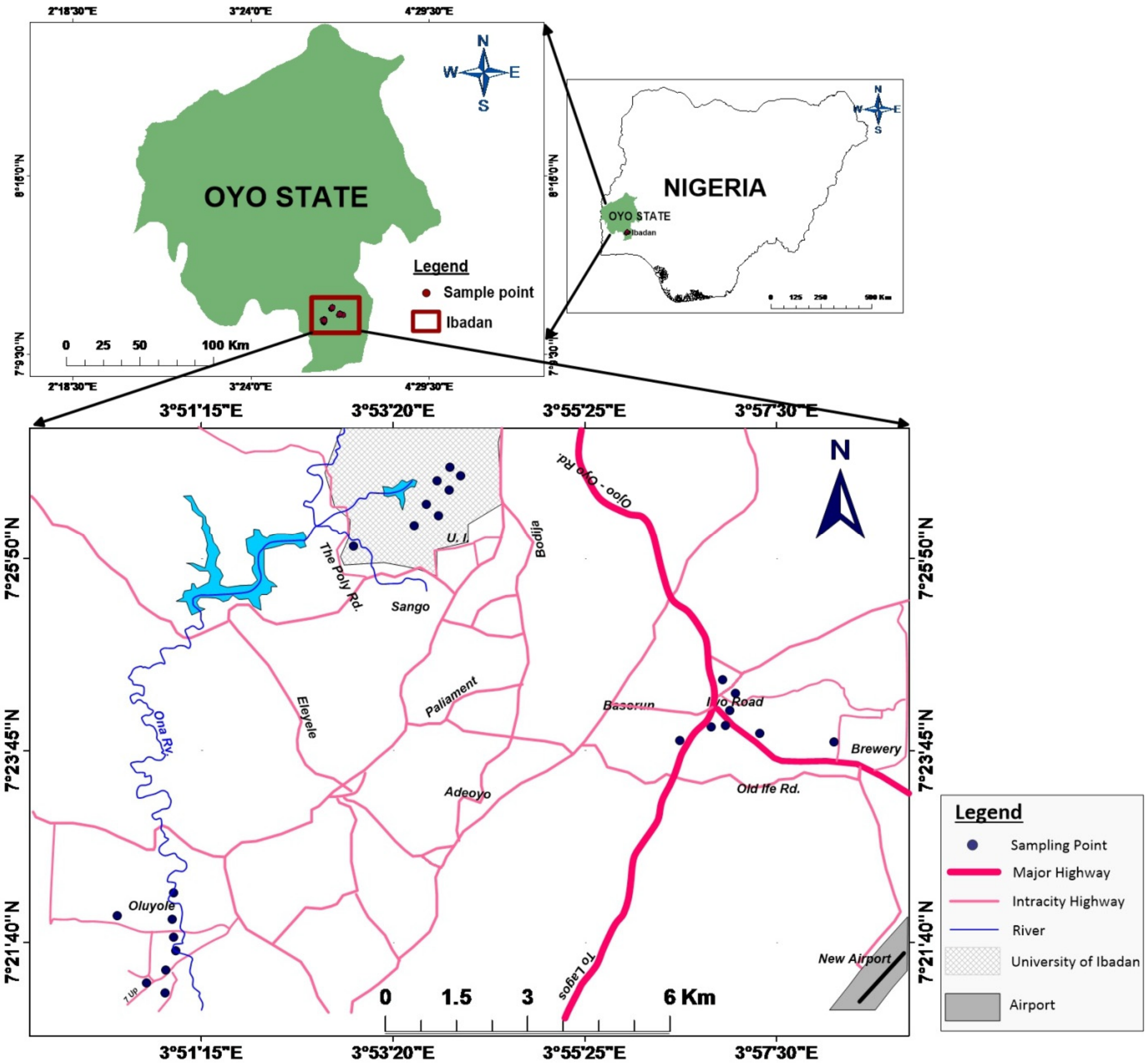

Fig. 1. Map of the study area in Ibadan, Oyo State, Nigeria.

Sample collection, storage, and pre-treatment

Open air sampling of rainwater was done from twenty-four different points at various geographical locations measured with a Geographical Position System (GPS) device. The rainwater samples were taken from an open air of each sampling sites in a clean polypropylene container placed 1.5 m above the ground level on a support at only the start of rain events to ensure that only wet depositions are collected and that there is no splashing of suspended soil particles alongside the targeted rainwater. The collected rainwater samples were taken to the laboratory in the ice box. The samples were kept in 1% HNO_3 at 4 ^oC until the time of analysis.

Resin and column preparation

Amberlite XAD-16 of 20-40 mesh with a pore size of about 10 nm and surface area of 825 m^2/g obtained from Aldrich South Africa was crushed to expand the sorption surface and sieved to 60-80 mesh using a 212 nm sieve size. The resin was separately washed with methanol, water, 1 mol/L HNO_3 in acetone, water, 1 mol/L NaOH, and water. 800 mg of Amberlite XAD-16 resin suspended in water was then packed in slurry form into a glass burette column fitted with a glass mesh.

Speciation of the rainwater metal ions

In this investigation, the method of Tokalioglu *et al.* (2000) was adopted with slight modifications. The rainwater samples were filtered through a 0.45 μm membrane filter, the residue was dissolved in 10 mL concentrated HNO_3, centrifuged, evaporated to near dryness and then collected in a volume of 10 mL of 2 mol/L HNO_3 to analyze for metals bound to suspended particles. The filtrate was passed through an adsorbent column packed with Amberlite XAD-16 resin at a flow rate of 2-2.5 mL/min. The metal adsorbed by the resin was eluted with 1 mol/L HCl in acetone at a flow rate of 1 mL/min and later evaporate to near dryness and dissolved in 0.7 mL of 2 mol/L nitric acid to analyze for metals bound to organic substances. 0.95 g of sodium tetraborate reagent was added to the filtrate from the Amberlite XAD-16 and made to pass through another column set up also packed with Amberlite XAD-16 resin. The metals sobbed on the resin was eluted again with 1 mol/L HCl in acetone at a flow rate of 1 mL/min and then evaporate to near dryness with dissolution in 0.7 mL of 2 M nitric acid for free metal ions analysis.

Data Treatment

For the interpretation of the geochemical data the following statistical methods were used: Descriptive statistics were performed in addition to contamination factor, pollution load index, modified degree of contamination, and potential ecological risk assessments to investigate the pollution status of the investigated areas (Abrahim and Parker 2008; Duodu *et al.* 2016; Oyewole and Adebiyi, 2017; Adebiyi and Ore, 2021; Adebiyi *et al.,* 2022). The groups of ecological risk index endorsed by Hakanson (1980) is presented in Table 1. Human health risk assessments such as chronic daily intake, carcinogenic and non-carcinogenic risk indices were carried out to determine the health risks associated with oral exposure to the rainwater (USEPA 2015; Saha *et al.* 2016; Adebiyi *et al.,* 2021).

RESULTS AND DISCUSSION

Chemical Speciation and Distribution of Heavy Metals in the Rainwater samples

The results of the speciation analysis of all the elements considered in this study from residential, industrial, and commercial areas are presented in Tables 2, 3, and 4 respectively, showing the mean levels of metals in their various species. The sequential chemical partitioning technique was adopted in order to quantify the association of metal concentrations with various sedimentary phases (Nasrabadi *et al.,* 2010). It is evident from these results that the metals are bound to different fractions at varying strengths which gives a clear indication of their binding power and in turn proffer assessment of the risk associated with the presence of these metals in the environment.

The sequences of the overall mean Pb concentrations in decreasing order were: organic bound > free ion > suspended in the residential area, free ion > suspended > organic bound in the

Table 1. Indices of corresponding degrees of potential ecological risk (Hakanson, 1980)

Er value	Grades of ecological risk of single metal	RI value	Grades of potential ecological risk of the environment
Er < 40	Low risk	RI < 150	Low risk
40 ≤ Er < 80	Moderate risk	150 ≤ RI < 300	Moderate risk
80 ≤ Er < 160	Considerable risk	300 ≤ RI < 600	Considerable risk
160 ≤ Er < 320	High risk	RI > 600	Very high risk
Er > 320	Very high risk		

Table 2. Elemental Speciation Concentrations (mg/L) of Rainwater Samples in Residential area

Metals	Specification	Onset	Peak	Late	Mean
Pb	Bound to suspended particles	0.103±0.1	0.115±0.12	0.080±0.02	0.099±0.08
	Bound to organic substances	0.174±0.1	0.103±0.10	0.170±0.05	0.149±0.08
	Free metal ion	0.114±0.1	0.150±0.15	0.100±0.011	0.121±0.08
	Total	0.391±0.3	0.368±0.37	0.35±0.081	0.369±0.24
Cu	Bound to suspended particles	0.065±0.01	0.014±0.05	0.004±0.001	0.027±0.02
	Bound to organic substances	0.048±0.03	0.068±0.01	0.016±0.001	0.044±0.01
	Free metal ion	0.049±0.01	0.073±0.03	0.039±0.004	0.053±0.01
	Total	0.162±0.05	0.155±0.09	0.059±0.006	0.125±0.04
Cd	Bound to suspended particles	0.111±0.01	0.052±0.020	0.107±0.02	0.09±0.01
	Bound to organic substances	0.051±0.02	0.120±0.010	0.061±0.01	0.077±0.01
	Free metal ion	0.095±0.05	0.068±0.010	0.022±0.01	0.061±0.02
	Total	0.257±0.08	0.240±0.040	0.190±0.04	0.228±0.04
Fe	Bound to suspended particles	0.038±0.006	0.003±0.015	0.021±0.010	0.020±0.01
	Bound to organic substances	0.061±0.015	0.058±0.02	0.004±0.002	0.041±0.01
	Free metal ion	0.075±0.030	0.022±0.01	0.015±0.010	0.037±0.01
	Total	0.174±0.051	0.083±0.045	0.04±0.022	0.098±0.03
Mn	Bound to suspended particles	0.223±0.12	0.079±0.02	0.049±0.02	0.117±0.05
	Bound to organic substance	0.190±0.07	0.244±0.14	0.134±0.01	0.189±0.07
	Free metal ion	0.143±0.05	0.185±0.10	0.080±0.05	0.136±0.06
	Total	0.556±0.24	0.508±0.26	0.263±0.08	0.442±0.18
Zn	Bound to suspended particles	1.859±0.50	0.500±1.00	0.846±0.21	1.068±0.57
	Bound to organic substance	2.890±1.30	1.350±1.20	0.571±0.10	1.603±0.86
	Free metal ion	1.694±1.50	2.810±0.75	0.284±0.18	1.596±0.81
	Total	6.443±3.30	4.66±2.95	1.701±0.49	4.267±2.24
As	Bound to suspended particles	0.014±0.01	0.006±0.001	0.002±0.001	0.007±0.004
	Bound to organic substance	0.014±0.05	0.027±0.005	0.010±0.001	0.017±0.018
	Free metal ion	0.009±0.01	0.011±0.040	0.003±0.002	0.007±0.017
	Total	0.037±0.07	0.044±0.046	0.015±0.004	0.031±0.039

industrial area and free ion > organic bound > suspended in the commercial area. This showed that the free and the organic bound species are in high proportion in the analyzed rainwaters. Free species are known to be highly soluble in water and could permeate biological membranes owing to their high oxidizing potential. This metal species has implications in the pathogenesis of many diseases such as gastrointestinal cancer (Cuong and Obhard 2006).

Copper equally showed a dominant chemical species as a free metal ion in all the studied area. The sequences of the overall mean concentrations in decreasing order were: free > organic bound > suspended in the residential area and Free > suspended > organic bound in the industrial and commercial areas. Free metal ions are labile; it is readily available for uptake by living organisms. According to the free ion activity model (FIAM), reports have it that the toxicity of metals on aquatic organisms is related to the free metal ion activity (Zheng *et al.* 2008). The high concentrations of Cu existing as free ion would be dangerous due to its toxicity and deleterious side effects in man and aquatic organisms. The presence of Cu dominantly in the free metal ion form is consistent with the report of Zhu *et al.* (2015).

Cadmium was present mainly as bound to suspended particles at the early and late rainy

Table 3. Elemental Speciation Concentrations (mg/L) of Rainwater Samples in Industrial area

Metals	Specification	Onset	Peak	Late	Mean
Pb	Bound to suspended particles	0.103±0.1	0.115±0.12	0.080±0.02	0.099±0.08
	Bound to organic substances	0.174±0.1	0.103±0.10	0.170±0.05	0.149±0.08
	Free metal ion	0.114±0.1	0.150±0.15	0.100±0.011	0.121±0.08
	Total	0.391±0.3	0.368±0.37	0.35±0.081	0.369±0.24
Cu	Bound to suspended particles	0.065±0.01	0.014±0.05	0.004±0.001	0.027±0.02
	Bound to organic substances	0.048±0.03	0.068±0.01	0.016±0.001	0.044±0.01
	Free metal ion	0.049±0.01	0.073±0.03	0.039±0.004	0.053±0.01
	Total	0.162±0.05	0.155±0.09	0.059±0.006	0.125±0.04
Cd	Bound to suspended particles	0.111±0.01	0.052±0.020	0.107±0.02	0.09±0.01
	Bound to organic substances	0.051±0.02	0.120±0.010	0.061±0.01	0.077±0.01
	Free metal ion	0.095±0.05	0.068±0.010	0.022±0.01	0.061±0.02
	Total	0.257±0.08	0.240±0.040	0.190±0.04	0.228±0.04
Fe	Bound to suspended particles	0.038±0.006	0.003±0.015	0.021±0.010	0.020±0.01
	Bound to organic substances	0.061±0.015	0.058±0.02	0.004±0.002	0.041±0.01
	Free metal ion	0.075±0.030	0.022±0.01	0.015±0.010	0.037±0.01
	Total	0.174±0.051	0.083±0.045	0.04±0.022	0.098±0.03
Mn	Bound to suspended particles	0.223±0.12	0.079±0.02	0.049±0.02	0.117±0.05
	Bound to organic substance	0.190±0.07	0.244±0.14	0.134±0.01	0.189±0.07
	Free metal ion	0.143±0.05	0.185±0.10	0.080±0.05	0.136±0.06
	Total	0.556±0.24	0.508±0.26	0.263±0.08	0.442±0.18
Zn	Bound to suspended particles	1.859±0.50	0.500±1.00	0.846±0.21	1.068±0.57
	Bound to organic substance	2.890±1.30	1.350±1.20	0.571±0.10	1.603±0.86
	Free metal ion	1.694±1.50	2.810±0.75	0.284±0.18	1.596±0.81
	Total	6.443±3.30	4.66±2.95	1.701±0.49	4.267±2.24
As	Bound to suspended particles	0.014±0.01	0.006±0.001	0.002±0.001	0.007±0.004
	Bound to organic substance	0.014±0.05	0.027±0.005	0.010±0.001	0.017±0.018
	Free metal ion	0.009±0.01	0.011±0.040	0.003±0.002	0.007±0.017
	Total	0.037±0.07	0.044±0.046	0.015±0.004	0.031±0.039

periods in the residential area. Metals associated with suspended fractions, usually form part of the crystalline structure of minerals and are often relatively stable and inert, they are not easily released into the mobile and bioavailable phases (López-Gonzáles *et al.* 2006; Wong *et al.* 2007). Metals in this fraction pose relatively no/little effect on the environment as they are not readily available for absorption. This suggests that Cd in this area is primarily derived from anthropogenic inputs rather than the geochemical background (MacFarlane and Burchett, 2000). On the other hand, the existence of Cd majorly as a free ion in the industrial and commercial area is a major cause of concern as the metal could be readily available for uptake by exposed organism. This might be regarded as a pollution indicator due to the possible detrimental effects of the metal species and cadmium in particular (Yuan *et al.* 2004). Cadmium is toxic to fish and other aquatic organisms and can cause adverse health effects such as renal disease and cancer to humans (Ogunfowokan *et al.* 2009).

The chemical partitioning of Zn is similar to that of Pb. Zinc, which is one of the most abundant metals in the studied rainwater is hosted largely as the free ion of which the industrial area has the highest mean concentrations. The proportions of Zn bound to organic substances

Table 4. Elemental Speciation Concentrations (mg/L) of Rainwater Samples in Commercial area

Metals	Specification	Onset	Peak	Late	Mean
Pb	Bound to suspended particles	0.108±0.03	0.006±0.001	0.011±0.01	0.041±0.013
	Bound to organic substances	0.162±0.01	0.121±0.040	0.052±0.03	0.111±0.026
	Free metal ion	0.187±0.05	0.140±0.030	0.114±0.08	0.147±0.16
	Total	0.457±0.09	0.267±0.071	0.177±0.12	0.299±0.199
Cu	Bound to suspended particles	0.060±0.02	0.151±0.12	0.008±0.001	0.073±0.047
	Bound to organic substances	0.019±0.01	0.055±0.06	0.010±0.001	0.028±0.023
	Free metal ion	0.147±0.05	0.152±0.02	0.128±0.004	0.142±0.024
	Total	0.226±0.08	0.358±0.20	0.146±0.006	0.243±0.094
Cd	Bound to suspended particles	0.031±0.01	0.015±0.01	0.002±0.001	0.016±0.007
	Bound to organic substances	0.069±0.01	0.033±0.01	0.008±0.005	0.036±0.008
	Free metal ion	0.098±0.03	0.007±0.01	0.012±0.001	0.039±0.013
	Total	0.198±0.05	0.055±0.03	0.022±0.007	0.091±0.028
Fe	Bound to suspended particles	0.067±0.01	0.108±0.03	0.039±0.01	0.071±0.016
	Bound to organic substances	0.052±0.01	0.065±0.01	0.027±0.01	0.048±0.01
	Free metal ion	0.073±0.02	0.215±0.11	0.059±0.02	0.115±0.05
	Total	0.192±0.04	0.388±0.15	0.125±0.04	0.234±0.025
Mn	Bound to suspended particles	0.227±0.12	0.144±0.10	0.105±0.03	0.158±0.08
	Bound to organic substances	0.210±0.03	0.083±0.02	0.110±0.01	0.134±0.02
	Free metal ion	0.167±0.01	0.208±0.01	0.084±0.01	0.153±0.01
	Total	0.604±0.16	0.435±0.13	0.299±0.05	0.445±0.036
Zn	Bound to suspended particles	2.672±0.18	1.800±0.01	0.792±0.13	1.754±0.10
	Bound to organic substances	2.843±1.10	1.244±0.04	2.100±0.41	2.062±0.51
	Free metal ion	2.538±0.12	2.072±0.10	2.530±0.10	2.380±0.10
	Total	8.053±1.40	5.116±0.15	5.422±0.64	6.196±0.71
As	Bound to suspended particles	0.009±0.001	0.003±0.001	0.001±0.001	0.004±0.001
	Bound to organic substances	0.010±0.005	0.001±0.001	0.000±0.001	0.003±0.002
	Free metal ion	0.001±0.001	0.005±0.002	0.006±0.002	0.004±0.001
	Total	0.02±0.007	0.009±0.004	0.007±0.004	0.011±0.004

were relatively low to other species in the sampled rainwater of all the areas studied. The sequences of the overall mean concentrations in decreasing order were: Organic bound > Free > Suspended in the residential area and Free > organic bound > suspended in the commercial area while the industrial area showed free ion > suspended > organic bound. Similar results reported in Malaysia by Nemati *et al.* (2011) also have it that metals like Zn exist more as free metal ion. These studies suggest that Zn is mainly found as a free ion which is labile and bioavailable because of its stronger affinity for the non-residual fraction. The free metal fraction is the most labile/exchangeable metal specie and constitutes the most dangerous phases for the environment. Though, chemical transformation/transition may occur depending upon the surrounding physical and geochemical conditions (Ryan *et al.* 2002; Wong *et al.* 2007).

Rainwater from residential area had Fe strongly associated with fractions bound to organic substance. On the contrary to the residential area, industrial and commercial areas presented high mean concentrations of Fe as free ion. The high concentration of Fe in the industrial and commercial areas may be due to the use of sludge or municipal compost, pesticides, fertilizers, and emissions from municipal wastes incinerators, car exhausts, residues from metalliferous mines, and smelting industries (Jain *et al.* 2004). The sequences of the overall mean concentrations in decreasing order were: organic bound > free ion > suspended particles in the residential area and Free > suspended > organic bound in the industrial and commercial area. These indicated that there are high concentrations of the free species which are known to be highly soluble in water and could permeate biological membrane owing to their high oxidizing potential. The higher concentration of metals in this fraction could be regarded as a pollution indicator as reported by Yuan *et al.* (2004).

Manganese was found in the rainwater from commercial area mainly in the fraction bound to suspended particles. The sequences of the overall mean concentrations in decreasing order were: organic bound > free > suspended in the residential area and, suspended > free ion > organic bound in the industrial and commercial area. However, a change in pH of the rainwater could affect the reduction of Mn to dissociate from Mn-organic complexes and change the speciation to free Mn species which is a more toxic specie due to its availability.

Comparatively high mean concentrations of As were recorded at the residential area as metal bound to organic substances. This confirms the high affinity of As to organic matter and its tendency to easily form complexes with the organic matter due to the high stability of the organic-As complex (Li *et al.* 2001; Morillo *et al.* 2004; Ramirez *et al.* 2005). The sequences of the overall mean concentrations in decreasing order were: suspended = free ion > organic bound in the commercial area, free > suspended > organic bound in the industrial area, and organic bound > free ion = suspended in the residential area. Accumulation of As in specie form of free ion over time could result in serious damage to the physiological function of its receptor (Agoramoorthy and Pandiyan, 2015).

Human Health Risk Assessment

The health risk indices of the investigated metals associated with the drinking of the rainwater by both adults and children in the residential, industrial, and commercial areas are presented in Tables 5, 6, and 7 respectively. The chronic daily intake (CDI) values for Pb, Cu, Cd, Fe, Mn, Zn and As for both adult and children in the residential areas who consumed the rainwater was found to be less than 1. The same trend was observed for the industrial and commercial areas as well. The CDI values follow the trend: Zn > Mn > Pb > Cd > Cu > Fe > As in the residential areas. The CDI values follow the trend: Zn > Cu > Mn > Pb > Cd > Fe > As in the industrial areas. The CDI values follow the trend: Zn > Mn > Pb > Cu > Fe > Cd > As in the commercial areas. All the investigated metals (Cu, Fe, Mn, and Zn) other than Pb, Cd and As were found to be within or less than their respective oral reference dose (R*f*D) limits as described by the United States Environmental Protection Agency (USEPA, 2015). The high levels of As is consistent with the

Table 5. Health Risk Indices of the analyzed metals in the rain water samples of the Residential area

Parameter	Onset (mg/L)	Peak (mg/L)	Late (mg/L)	Mean (mg/L)	CDI^a	CDI^c	RfD	HI^a	HI^c	RI^a	RI^c
Pb	0.391	0.368	0.350	0.369	0.010562	0.023104	0.004	3.45E-07	7.55E-07	1.17E-06	2.56E-06
Cu	0.162	0.155	0.059	0.125	0.003581	0.007833	0.04	1.17E-08	2.55E-08		
Cd	0.257	0.240	0.190	0.229	0.006543	0.014313	0.001	8.55E-07	1.87E-06	1.28E-03	2.40E-07
Fe	0.174	0.083	0.040	0.099	0.002829	0.006188	0.3	1.23E-09	2.69E-09		
Mn	0.556	0.508	0.263	0.442	0.012638	0.027646	0.14	1.18E-08	2.58E-08		
Zn	6.443	4.660	1.701	4.268	0.121943	0.26675	0.3	5.31E-08	1.16E-07		
As	0.037	0.044	0.015	0.032	0.000914	0.002	0.0003	3.98E-07	8.71E-07	1.79E-05	4.68E-10
TOTAL								1.67E-06	3.66E-06	1.30E-03	2.80E-06

❖ CDI = Chronic daily intake, RfD = oral reference dose, HI = Non-carcinogenic risk index, RI = Carcinogenic risk index, a = adults, c = children

Table 6. Health Risk Indices of the analyzed metals in the rain water samples of the Industrial area

Parameter	Onset (mg/L)	Peak (mg/L)	Late (mg/L)	Mean (mg/L)	CDI^a	CDI^c	RfD	HI^a	HI^c	RI^a	RI^c
Pb	0.437	0.665	0.452	0.518	0.0148	0.032375	0.004	4.83E-07	1.05E-06	1.64E-06	3.59E-06
Cu	0.406	0.518	1.345	0.756	0.02161	0.047271	0.04	7.06E-08	1.54E-07		
Cd	0.16	0.292	0.263	0.238	0.00681	0.014896	0.001	8.90E-07	1.94E-06	1.33E-03	2.92E-03
Fe	0.117	0.231	0.142	0.163	0.004667	0.010208	0.3	2.03E-09	4.44E-09		
Mn	0.788	1.043	0.422	0.751	0.021457	0.046938	0.14	2.00E-08	4.38E-08		
Zn	8.282	7.894	3.032	6.402	0.182933	0.400167	0.3	7.97E-08	1.74E-07		
As	0.015	0.045	0.026	0.028	0.000819	0.001792	0.0003	3.56E-07	7.80E-07	1.60E-05	3.51E-05
TOTAL								1.90E-06	4.16E-06	1.35E-03	2.95E-03

❖ CDI = Chronic daily intake, RfD = oral reference dose, HI = Non-carcinogenic risk index, RI = Carcinogenic risk index, a = adults, c = children

Table 7. Health Risk Indices of the analyzed metals in the rain water samples of the Commercial area

Parameter	Onset (mg/L)	Peak (mg/L)	Late (mg/L)	Mean (mg/L)	CDI^a	CDI^c	RfD	HI^a	HI^c	RI^a	RI^c
Pb	0.457	0.267	0.177	0.300	0.008581	0.018771	0.004	2.80E-07	6.13E-07	9.53E-07	2.08E-06
Cu	0.226	0.358	0.146	0.243	0.006952	0.015208	0.04	2.27E-08	4.97E-08		
Cd	0.198	0.055	0.022	0.091	0.002619	0.005729	0.001	3.42E-07	7.48E-07	5.13E-04	1.12E-03
Fe	0.192	0.388	0.125	0.235	0.006714	0.014688	0.3	2.92E-09	6.39E-09		
Mn	0.604	0.435	0.299	0.446	0.012743	0.027875	0.14	1.18E-08	2.60E-08		
Zn	8.053	5.116	5.422	6.197	0.177057	0.387313	0.3	7.71E-08	1.68E-07		
As	0.02	0.009	0.007	0.012	0.000343	0.00075	0.0003	1.49E-07	3.26E-07	6.72E-06	1.47E-05
TOTAL								8.86E-07	1.94E-06	5.21E-04	1.14E-03

❖ CDI = Chronic daily intake, RfD = oral reference dose, HI = Non-carcinogenic risk index, RI = Carcinogenic risk index, a = adults, c = children reported high As levels in groundwater of Kurdistan, Iran (Nasrabadi and Bidabadi, 2013) and Haraz River, Iran (Nasrabadi *et al.,* 2015).

The non-carcinogenic risk index (HI) associated with the consumption of rainwater by both adults and children in the study areas was found to be of the trend: Industrial > Residential > Commercial. The HI values of each investigated metal associated with the drinking of the rainwater by both adults and children were generally lower than 1. This suggests that the adults and children in the residential, industrial, and commercial areas would not suffer significant non-carcinogenic health risks upon consumption of the rainwater.

The carcinogenic health risk index (RI) associated with the oral exposure route of Pb, Cd and As by drinking the rainwater follows the same trend as observed for the non-carcinogenic risk index. The RI values for the metals with a carcinogenic potential for the adults in the residential, industrial, and commercial areas were higher than the acceptable lifetime carcinogenic risk of 10^{-5} set by USEPA. Other than the children in the residential areas with a RI value of 2.80E-06, the RI values observed for the metals in the rainwater upon consumption by the children were also higher than the acceptable lifetime carcinogenic risk in the industrial and commercial areas respectively. This implies that the children in the residential areas, the adults in the residential, industrial and commercial areas alongside the children in the industrial and commercial areas, are susceptible to possible carcinogens emanating from the consumption of the rainwater.

Ecological Risk Assessment

The ecological risk indices containing the contamination factor, the pollution load index, the modified degree of contamination, the potential ecological risk factor, and the potential ecological risk index associated with the metals present in the rainwater in the residential, industrial and commercial areas are presented in Tables 8, 9 and 10 respectively. Variations exist in the contamination factor of the analyzed metals in the respective study areas. In the residential areas, Cu and Zn showed low contamination, Fe and As showed considerable contamination while Pb, Cd, and Mn presented very high contamination. The industrial areas displayed low contamination by Cu, moderate contamination by Zn and As, considerable contamination by Fe, and very high contamination by Pb, Cd, and Mn. Also, the commercial areas showed low contamination by Cu, moderate contamination by Zn and very high contamination by Pb, Cd, Fe, and Mn.

Table 8. Ecological Risk Indices of the analyzed metals in the rain water samples of the Residential area

Parameter	Onset	Peak	Late	Mean	DWPL	CF	Tr	Er
Pb	0.391	0.368	0.350	0.369	0.05	7.393	5	36.966
Cu	0.162	0.155	0.059	0.125	1	0.125	5	0.626
Cd	0.257	0.240	0.190	0.229	0.005	45.800	30	1374
Fe	0.174	0.083	0.040	0.099	0.03	3.300	-	-
Mn	0.556	0.508	0.263	0.442	0.05	8.846	1	8.846
Zn	6.443	4.660	1.701	4.268	5	0.853	1	0.853
As	0.037	0.044	0.015	0.032	0.01	3.200	10	32
PLI						3.193		
mCd						9.931		
RI								1453.294

❖ DWPL= Drinking water permissible limit (CCME, 2007), CF = Contamination factor,

❖ mCd = Modified degree of contamination, PLI = Pollution load index, T_r = Toxicological response factor,

❖ E_r = Potential ecological risk factor, RI = Potential ecological risk index

Table 9. Ecological Risk Indices of the analyzed metals in the rain water samples of the Industrial area

Parameter	Onset	Peak	Late	Mean	DWPL	CF	Tr	Er
Pb	0.437	0.665	0.452	0.518	0.05	10.360	5	51.800
Cu	0.406	0.518	1.345	0.756	1	0.756	5	3.781
Cd	0.16	0.292	0.263	0.238	0.005	47.666	30	1430
Fe	0.117	0.231	0.142	0.163	0.03	5.444	-	0
Mn	0.788	1.043	0.422	0.751	0.05	15.020	1	15.020
Zn	8.282	7.894	3.032	6.402	5	1.280	1	1.280
As	0.015	0.045	0.026	0.028	0.01	2.866	10	28.666
PLI						5.264		
mCd						11.913		
RI								1530.549

- ❖ DWPL= Drinking water permissible limit (CCME, 2007), CF = Contamination factor,
- ❖ mCd = Modified degree of contamination, PLI = Pollution load index, T_r = Toxicological response factor,
- ❖ E_r = Potential ecological risk factor, RI = Potential ecological risk index

Table 10. Ecological Risk Indices of the analyzed metals in the rain water samples of the Commercial area

Parameter	Onset	Peak	Late	Mean	DWPL	CF	Tr	Er
Pb	0.457	0.267	0.177	0.300	0.05	6.006	5	30.033
Cu	0.226	0.358	0.146	0.243	1	0.243	5	1.216
Cd	0.198	0.055	0.022	0.091	0.005	18.333	30	550
Fe	0.192	0.388	0.125	0.235	0.03	7.833	-	0
Mn	0.604	0.435	0.299	0.446	0.05	8.920	1	8.920
Zn	8.053	5.116	5.422	6.197	5	1.239	1	1.239
As	0.02	0.009	0.007	0.012	0.01	1.200	10	12
PLI						3.105		
mCd						6.253		
RI								603.409

- ❖ DWPL= Drinking water permissible limit (CCME, 2007), CF = Contamination factor,
- ❖ mCd = Modified degree of contamination, PLI = Pollution load index, T_r = Toxicological response factor,
- ❖ E_r = Potential ecological risk factor, RI = Potential ecological risk index

With regards to the modified degree of contamination, the commercial areas exhibited a high degree of contamination by the investigated metals in the rainwater while the residential and industrial areas exhibited a very high degree of contamination by the investigated metals in the rainwater. The pollution load index indicated deterioration of the site quality of the residential, industrial, and commercial areas.

The potential ecological risk index (RI) is a reflection of the general situation of pollution brought about by the presence of individual metals. The RI indicated very high ecological risk by investigated metals in the residential, industrial areas, and commercial areas.

CONCLUSION

The use of rainwater as alternative for monitoring the urban air pollution to investigate the predominant metal species in rainwater for possible toxicological elucidation has explained the quality of ambient air of Ibadan city. It was discovered that most of the metals in the rainwaters existed as free ions and suspended bounds. The high concentrations of these metals existing as free ions have health implications due to their ready availability coupled with toxicity and deleterious side effect on humans. However, the sequence of metal species distribution reported in this study could shift at any slight change in water chemistry. The suspended bound metal species could become bioavailable when subjected to varying physicochemical variables like pH, temperature, and redox potential changes.

Also, the health risks associated with the intake of the studied rainwaters in the residential, industrial, and commercial areas indicate susceptibility to possible carcinogens. Ecological risk assessment equally indicates a very high level of ecological risks related with the metals in the rainwater. In view of the high levels of some toxic heavy metals in the atmospheric environment of Ibadan as demonstrated in this study, the need for better sensitization of the citizenry to the sources and control of these air pollutants is of necessity. Further comparative studies of aerial pollution via rainwater analysis and direct air sampling should be undertaken in other part of the country.

GRANT SUPPORT DETAILS

The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

REFERENCES

Abrahim, G. M. S. and Parker, P. J. (2008). Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand, *Environmental Monitoring and Assessment*, Vol.136, No.1-3, 227–238

Adebiyi, F. M., & Ore, O. T. (2021). EDXRF analysis and risks assessment of potentially toxic elements in sand fraction (tailing) of Nigerian oil sands. *Energy, Ecology and Environment*, *6*(3), 258-270.

Adebiyi, F. M., Olalekan, E. O., Ore, O. T., & Adegunwa, A. O. (2022). Speciation, source identification, and risk assessments of potentially toxic metals in oil-impacted soils around petroleum products retailing stations. *Petroleum Research*. https://doi.org/10.1016/j.ptlrs.2022.07.004

Adebiyi, F. M., Ore, O. T., Adegunwa, A. O., & Akhigbe, G. E. (2021). Source apportionment, health and ecological risk assessments of essential and toxic elements in kerosene-contaminated soils. *Environmental Forensics*, 1-11.

Adebiyi, F. M., Ore, O. T., Akhigbe, G. E. and Adegunwa, A. O. (2020). Metal fractionation in the soils around a refined petroleum products depot. *Environmental Forensics*. DOI: 10.1080/15275922.2020.1728432

Adegunwa, A. O., Adebiyi, F. M. and Asubiojo, O. I. (2019). Heavy Metal Analysis in Rainwaters as Indicator of Aerial Pollution. *Journal of Environmental Sciences*. Volume 01 Issue 03

Agoramoorthy, G. and Pandiyan, J. (2016). Toxic pollution threatens migratory shorebirds in India. *Environmental Science and Pollution Research* 23 (15), 15771–15772.

Ahmed, M. K., Baki, M. A., Islam, M. S., Kundu, G. K., Sarkar, S. K. and Hossain, M. M.(2015a). Human health risk assessment of heavy metals in tropical fish and shell fish collected from the river Buriganga, Bangladesh. *Environmental Science Pollution Research*., http:// dx.doi.org/10.1007/ s11356-015-4813-z.

Asthana, D. K. and Asthana, M. (2003). Environment: problems and solutions, S.chand and company limited, Ram Nagar, New Delhi, 15: 205-221

Chughtai, M., Mustafa, S. and Mumtaz, M. (2014). Study of Physicochemical Parameters of Rainwater: A CaseStudy of Karachi, Pakistan. *American Journal of Analytical Chemistry*, 5, 235-242. http://dx.doi.org/10.4236/ajac.2014.54029

Cuong, D. T. and Obbard, J. P. (2006). Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure, *Applied Journal of Geochemistry.* 21: 1335- 1346.

Duodu, G.O., Goonetilleke, A. and Ayoko, G. A. (2016). Comparison of pollution indices for the assessment of heavy metal in Brisbane River sediment. *Journal of Environmental Pollution*. 219, 1077-1091.

Efe, S. I. (2005). Urban effects on precipitation amount, distribution and rainwater quality in Warri metrololis, Ph. D. Thesis: Department of Geography and Regional Planning, Delsu –Abraka, pp. 10-103.

Efe, S. I. (2006). Quality of rainwater harvesting for rural communities of Delta State, Nigeria. *Journal of Environmental Science*, 26(3), 175-181. https://doi.org/10.1007/s10669-006-7829-8641

Emerole C. O., Emekaraoha M. and Emerole C. G. (2015). Quality of harvested rainwater in Owerri, Imo State, Nigeria. Journal of Applied Science 3: 1162-1166. *Environment Agency,*2010.www. environmentagency.gov.ok/static/document/research/SCH0049BPwb-e-e. 0/07/2011.

Fazeli, G., Karbassi, A., Khoramnejadian, S., & Nasrabadi, T. (2019). Evaluation of urban soil pollution: a combined approach of toxic metals and polycyclic aromatic hydrocarbons (PAHs). *International Journal of Environmental Research*, *13*(5), 801-811.

Hakanson, L. (1980). An Ecological Risk Index for Aquatic Pollution Control: A Sedimentological Approach, *Journal of Water Research*, 14, 975–1001, doi:10.1016/0043-1354(80)90143-8.

Igwo-Ezikpe M. N. and Awodele O. (2010). Investigation of some physico-chemical and microbiological parameters in rainwater collected from industrial areas of Lagos State, Nigeria. *Journal of Applied Science* 1: 26-38.

Islam, M. S., Ahmed, M. K., Habibullah-Al-Mamun, M. and Hoque, M. F. (2015a). Preliminary assessment of heavy metal contamination in surface sediments from a river in Bangladesh. Environ. Earth Sci. 73, 1837–1848.

Jain, C. K. (2004). Metal fractionation study on bed sediments of River Yamuna, India, *Journal of Water Resources*, 38: 569-578.

O'Keefe, B. (2013). Recent trends in air quality standards in Europe and Asia: what's next. In *HEI Annual Conference 2012*.

Kulshrestha, U. C., Kulshrestha, M. J., Sekar, R., Sastry, G. S. R. and Vairamani, M. (2003). Chemical Characteristics of Rainwater at an Urban Site of South-Central India. *Journal of Atmospheric Environment* 37: 3019–3026.

Kulshrestha, U. C., Sarkar, A. K., Srivastava, S. S. and Parashar, D. C. (1995a). Wet-only and bulk deposition studies at New Delhi (India). *Journal of Water, Air and Soil Pollution*, 85, 2137-2142

Li, X., Lin, X., Yiu, R., Wu, Y., Chu, H., Zeng, J. and Yang T. (2001). Optimization of Laccase-mediated Benzo[a]pyrene Oxidation an the Bioremedial Application in Aged Polycyclic Aromatic Hydrocarbons-contaminated soil, *Journal of Health Science*, 56(5):534-540

López-González., N., Borrego, J., Morales, J. A., Carro, O. and Lozano-Soria, O. (2006). Metal fractionation in toxic sediments of an estuary affected by acid mine drainage (southwestern Spain), *Journal of Estuarine Coastal Shelf Science*., 68: 297-304.

MacFarlane, G. B., Burchettt, M. D. (2000). Cellular distribution of Cu, Pb, and Zn in the Grey
Mangrove Avicemnia marina (Forsk.). Vierh Aquatic Botanic 68, 45–59.

Mohiuddin, K.M., Otomo, K., Ogawa, Y., Shikazono, N. (2012). Seasonal and spatial distribution of trace elements in the water and sediments of the Tsurumi river in Japan. *Environmental Monitoring Assessment* 184, 265–279.

Morillo, J., Usero, J. and Gracia, I. (2004) Chemosphere, *Environmental Bulletin* 55, 431 – 442.

Nasrabadi, T., & Bidabadi, N. S. (2013). Evaluating the spatial distribution of quantitative risk and hazard level of arsenic exposure in groundwater, case study of Qorveh County, Kurdistan Iran. *Iranian*

Journal of Environmental Health Science and Engineering, *10*(1), 1-8.
Nasrabadi, T., Abbasi Maedeh, P., Sirdari, Z. Z., Shirani Bidabadi, N., Solgi, S., & Tajik, M. (2015). Analyzing the quantitative risk and hazard of different waterborne arsenic exposures: case study of Haraz River, Iran. *Environmental earth sciences*, *74*(1), 521-532.
Nasrabadi, T., Nabi Bidhendi, G., Karbassi, A., & Mehrdadi, N. (2010). Evaluating the efficiency of sediment metal pollution indices in interpreting the pollution of Haraz River sediments, southern Caspian Sea basin. *Environmental monitoring and assessment*, *171*(1), 395-410.
National Population Census (NPC). (2006). Archive of the National Population census of Nigeria.
Nemati K, Abu Bakar N. K., Radzi Abas M, Sobhanzadeh E. (2011) Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia. *Journal of Hazardous Materials*, 192(1): 402-410.
Obaidy AHMJA and Joshi H. (2006). Chemical composition of rainwater in a tropical urban area of Northern India. *Journal of Atmospheric Environment*. 2006; 40:6886–6891.
Ogunfowokan, A. O., Oyekunle, J. A. O., Durosinmi, L. M., Akinjokun, A. I. and Gabriel, O. D. (2009). Speciation study of lead and manganese in roadside dusts from major roads in Ile-Ife, South Western Nigeria, *Journal of Chemical Ecology*. 25, 405– 415
Ore, O. T., & Adeola, A. O. (2021). Toxic metals in oil sands: review of human health implications, environmental impact, and potential remediation using membrane-based approach. *Energy, Ecology and Environment*, *6*(2), 81-91.
Oyewole, F. G. and Adebiyi, F. M. (2017). Total and speciation analyses of heavy metals in the sand fraction of Nigerian oil sands for human and ecological risk assessment. *Human and Ecological Risk Assessment: An International Journal.* 23 (8): 2046-2068.
Ramirez, M., Serena, M., Frache, R. and Correa, J. (2005). Metal speciation and environmental impact on sandy beaches due to El Salvador copper mine, Chile, *Marine Pollution Bulletin.*, 50: 62-72.
Robert, P.P. (2002). Meteorology at the Millennium. Academic Press. P 66
Ryan, P. C., Wall, A. J., Hillier, S. and Clark, L. (2002) Insights into sequential chemical extraction procedures from quantitative XRD: a study of trace metal partitioning in sediments related to frog malformities, *Journal of Environmental Geology*. 184: 337- 357.
Saha N, Mollah M, Alam M. and Rahman M. S. (2016). Seasonal investigation of heavy metals in marine fishes captured from the Bay of Bengal and the implications for human health risk assessment. *Journal of Food Control*. 70, 110–118.
Seto, S., Hara, H. (2006). Precipitation chemistry in western Japan: its relationships to meteorological patterns. *Journal of Atmospheric Environment*. 40, 1538–1549.
Strayer, H., Smith, R., Mizak, C., Poor, N. (2007). Influence of air mass origin on the wet deposition on nitrogen to Tampa Bay, Florida—an eight years study. *Journal of Atmospheric Environment.* 41, 4310–4322.
Templeton, D.M., Ariese, F., Cornelis, R., Danielsson, L.G., Muntau, H., Leeuwen, H.P. and Lobinski, R. (2000). *Journal of Pure and Applied Chemistry*, 72, 1453– 1470
Tokalioglu, S., Kartal, S. and Elci, L. (2000). Speciation and determination of heavy metals in lake waters by atomic absorption spectrometry after sorption on Amberlite XAD- 16 resin. *Journal of Analytical Sciences*, 16, 1169-1173
Tripathi, A., Tiwari, P.B., Mahima, and Singh, D. (2010). Assessment of air pollution tolerance index of some trees in Moradabad City, India. *Journal of Environmental Biology*, 30(4), 545-550
Umoren, A. S., Igwenagu, C. M., Ezeaku, P. I., Ezenne, G. I., Obalum, S. E. and Gyang, B. D.
(2019). Long-term effects of crude oil spillage on selected physicochemical properties including heavy metal contents of sandy tropical soil. Bulletin of Environmental Contamination and Toxicology 102: 468–476.
USEPA (United States Environmental Protection Agency). (2015). Regional Screening Level (RSL) Summary Table, November 2.
Wong, C. S. C., Wu, S. C., Duzgoren-Aydin, N. S., Aydin, A. and Wong, M. H. (2007). Trace metals contamination of sediments in an e-waste processing village in China, *Journal of Environment Pollution*, 145: 434-442.
Yang G., Wang Y., Zeng Y., Gao G. F. and Liang X. (2013) Rapid health transition in China, 1990–2010: findings from the Global Burden of Disease Study 2010. Lancet 381: 1987– 2015

Yobouè, V., Galy-Lacaux, C., Lacaux, J. P. and Siluè, S. (2005). Rainwater Chemistry and Wet Deposition over the Wet Savanna Ecosystem of Lamto (Cˆote d'Ivoire). *Journal of Pure and Applied Chemistry,* 52, 117-141

Yuan, C., Shi, J., He, B., Liu, J., Liang, L. and Jiang, G. (2004). Speciation of heavy metals in marine sediments from the east China Sea by ICP-MS with sequential extraction, *Journal of Environmental Science*, 30: 769-783.

Zheng, N. A., Wang, Q., Liang, Z., & Zheng, D. (2008). Characterization of heavy metal concentrations in the sediments of three freshwater rivers in Huludao City, Northeast China. *Environmental pollution*, *154*(1), 135-142

Zhu, Z. Z., Li, J., and Wang, Z. R. (2015). Concentrations and Speciation of Dissolved Heavy Metal in Rainwater in Guiyang, China. *Huan jing ke xue= Huanjing kexue*, *36*(6), 1952-1958.