

Fate and Potential Mobility of Arsenic (As) in the Soil of Mechanic

Workshops

Femi Francis Oloye^{1,5}, Isaac Ayodele Ololade¹, Oluyinka David Oluwole^{1,6}, Marcus Oluyemi Bello²,
Oluwabunmi Peace Oluyede³ & Oluwaranti Ololade⁴

¹ Department of Chemistry, Adekunle Ajasin University, Akungba Akoko, Nigeria

² Department of Microbiology, Adekunle Ajasin University, Akungba Akoko, Nigeria

³ Department of Environmental Biology and Fisheries, Adekunle Ajasin University, Akungba Akoko, Nigeria

⁴ Department of Chemistry, Federal University of Technology, Akure, Nigeria

⁵ Department of Chemistry, University of Aberdeen, United Kingdom

⁶ Department of Chemistry, Rhodes University, South Africa

Correspondence: Femi Francis Oloye, Department of Chemistry, Adekunle Ajasin University, Akungba Akoko, Nigeria. E-mail: pen2crown@gmail.com

Received: June 27, 2014 Accepted: July 8, 2014 Online Published: September 24, 2014

doi:10.5539/ep.v3n4p70

URL: <http://dx.doi.org/10.5539/ep.v3n4p70>

Abstract

In order to determine Arsenic (As) content in soils, from the vicinity of an automobile mechanic's workshop and to evaluate the contamination levels, different soil layers (0 – 15cm, 15 – 30cm and 30 – 45cm depth) were collected and analyzed for As content using atomic absorption spectrophotometer (AAS). Soil texture, conductivity, pH, total organic content and cation exchange capacity were also measured. Sequential extraction was carried out to determine geochemical phases of As. In the investigated soil samples, the mean total As concentrations were 2.45-2.53, 2.14-2.26 and 2.69-2.79 mg/kg for 0-15 cm, 15-30 cm and 30-45 cm depth respectively. Generally the affinity of As with the soil fraction increases in the order F3 < F6 < F1 < F2 < F5 < F4 < F7. The levels found in this study exceeded the background concentrations and safe limits for agricultural and residential purposes. The reported results indicate that the enrichment factors (EF) of As was 3.55-3.66, 4.04-4.26 and 3.49-3.62 mg/kg for top, middle and inner soils respectively; while the geoaccumulation index (*I_{geo}*) values of the metals in the soils studied indicate that they are uncontaminated to slightly contaminated with As. The results indicate that waste from auto-mechanic workshops represent a potential source of heavy metal pollution to the surrounding environment.

Keywords: Arsenic, contamination, pollution

1. Introduction

Arsenic (As) is widely known for its adverse effects on human health, and this element has been found in the groundwater of at least 70 countries and could pose a significant health threat to more than 140 million people (Chemistry world). People living near factories, farms, or waste sites -where As or pesticides were once used – can be exposed to As through touching, breathing, eye contact, drinking and eating of As contaminated foods. The US Environmental Protection Agency (EPA) and other agencies are currently reevaluating the current maximum contamination level (MCL) (50 µg/l) based on the health risks associated with drinking water containing As (Cai *et al.*, 2002). According to Lee and Lee (2011), the permissible levels for As in agricultural, residential and industrial soil are shown in Table 1 below.

Table 1. permitted As level in selected country

Country	As / mg/kg
Germany	50
Canada	30
Taiwan	60
US	50

As reacts with other elements to form organic and inorganic compounds. Inorganic As has been shown to be deadly. Unlike some toxic elements, As can cause negative outcomes as it directly effects systems in the human body (Chemistry world). The increased risk to human health from As is seen as a driver for increased research of As biogenerational cycling in the environment (Kim and Nriagu, 2000).

As can enter terrestrial and aquatic environments through both geogenic and anthropogenic activities. As pools naturally in surface soils, and such can arise from the net effects of geological, hydrological, soil forming biogeochemical processes and fossil fuels. Under typical soil forming conditions, the nature of As in the soil is controlled by the lithology of the parent rock materials, volcanic activity and precipitation (Cullen and Reimer, 1989). The primary anthropogenic contributions of As in soils arise from the combustion of municipal solid waste, application of arsenical pesticides, solid waste, sewage sludge, mining and smelting of Arsenic. The combustion of fossil fuels, industrial waste, wood preservation and metal refining also add to the overall cumulative effects of As contamination (Ning, 2002).

In many countries, the current standards for metal evaluation/contamination are based on the total concentrations of metals obtained using strong acid digestion solutions such as nitric acid or aqua regia (Gupta *et al.*, 1996; Ololade *et al.*, 2014). However, mobility of metals in soils, and their toxicity to the biosphere, is related to their association with various soil constituents rather than total concentrations (Sadiq, 1997) Important factors affecting As chemistry, and its mobility in soils, are soil solution chemistry (pH and redox conditions), solid composition, As bearing phases of adsorption and desorption, biological transformation, volatilization and cycling of As in soil (Baroni *et al.*, 2004). In addition, metal sulfide and sulfide concentrations, temperature, salinity, distribution and composition of biota appear to be significant factors determining the fate and transport of As (Cai *et al.*, 2002). Lastly, organic matter improves both the physical and chemical properties of soil and hence affects the toxicity and fate of As in different types of soils.

Arsenate is a salt of As which is the basis of most As contamination in groundwater. Adsorption of arsenate unto soil particles depends on various parameters, such as Al and Fe oxides, clay content, pH and the redox condition of the soil (Baroni *et al.*, 2004). Its availability on the other hands depends on source, chemical speciation and soil parameters (pH, EC, organic matter and colloid contents, soil texture and drainage condition (Eisler, 1994) .This is important as many soils have different physiochemical forms which are associated with soil constituents. It is the chemical forms of As associated with various soil phases, rather than their total concentrations that affects its mobility, bioavailability and toxicity to the biosphere (Cullen and Reimer, 1989).

Even though a lot of work had been reported on the chemical reactivity of As in soil, very little work has been carried out on As mobility in soil systems, and even less on determining the fate and mobility of As soils surrounding auto- mechanic workshops.

2. Material and Methods

2.1 Study Area

This investigation was carried out in auto-mechanic workshops in Ondo State, South-Western part of Nigeria (see Fig 1).

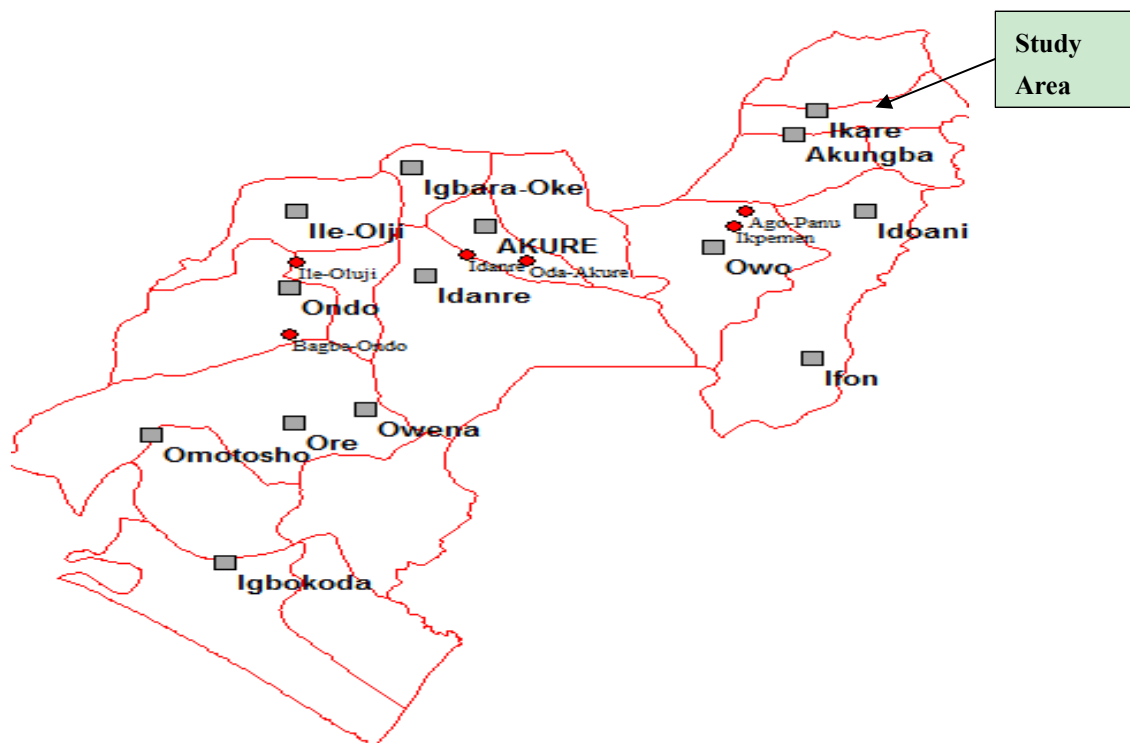


Figure 1. Map of Ondo state showing the area of study where the auto mechanic workshops are located

2.2 Sampling

The soil samples were obtained from three separate auto mechanic workshops in Akungba, Ifare and Akoko areas of Ondo State, Nigeria. At each of the workshops, there were three designated sites for sampling. At each site, samples were taken from different sampling depths: top soil surfaces (0 – 15 cm), middle soil (15 – 30 cm) and bottom soil (30 – 45 cm). Sampling was restricted to this depth because it provides the bulk of plant nutrients. During the sampling, the selected sampling sites were subdivided into grids of 20m x 20m, and samples were taken from the centre of each grid. To obtain composite samples of each site, a bulking method was employed to harmonize the samples. A coning and quartering method was applied repeatedly to reduce the sample volume for each site (Ololade *et al.*, 2014; Jackson, 1958). Each representative site sample was prepared by mixing one sample with the other replicates from different grids of the same site to overcome spatial variability. The soil samples were air – dried, ground, and sieved mechanically using a 2 mm sieve. The control (background) samples were obtained from a remote location within the industrial zone at the Adekunle Ajasin University Campus and from Akungba-Akoko which is far removed from the influence of any industrial activities.

2.3 Experimental

Soil physical and chemical properties were measured using standard operating procedures. Soil pH was measured in 1:2 (soil: 0.01 M CaCl₂) using a digital pH meter, and the particle size distribution was then determined by the hydrometer method (Bouyoucos, 1962). The temperature and relative humidity of the soil samples were taken in the field using appropriate instruments. Soil organic carbon and organic matter were determined using the Walkley-Black Method, and exchangeable acidity determination was done using a titration method, after extraction with 1N KCl. Exchangeable Ca, Mg, K, Na and effective cation exchange capacity (CEC) were also determined for pseudo total metal content analysis.

Quantification of total metallic content of digested soil samples and blanks was carried out with an atomic absorption spectrometer (AAS) (AA6300, Shimadzu, Japan), which was pre-calibrated using standard methods. To ensure that the atomic absorption spectrometer remained calibrated during the experiments, standards were analysed after every 10 runs. Soil samples were digested in accordance with the procedure used by Francis (2004). One gram of finely ground dried soil samples were mixed with 20 mL (1:1) HCl/HNO₃ acid mixture, and the contents were heated until dry. The residue was then extracted using a 2 M HCl solution and mixed with 50 mL of distilled water. The solution was then directly aspirated into an air-acetylene flame of AAS to obtain a

metal profile of the soils. To validate the digestion protocol of the soil samples, the quality assurance method of Uzairu *et al.*, 2009, was utilized through a spiking experiment, which involves spike recoveries using a multi-element standard solution (MESS). The amounts of spiked metals recovered, after digestion of the spiked samples, were used to calculate the percentage of metals recovered. Finally, a triplicate digestion and analysis of the soil samples and controls were carried out.

One of the latent problems with any sequential extraction is the lack of specificity of extractants toward particular elemental forms of association Shiowatana *et al.*, 2001. In order to overcome this problem, and to gain insight into fate and mobility of As in the tested soil samples, the approach described by Zein and Brummer, Wenzel *et al.*, and adopted by Ololade *et al.*, was adopted in accordance with Table 2; and levels of Arsenic in the fractions were analysed using the same AAS as described elsewhere (Ololade *et al.*, 2014).

All the chemicals (> 95 % purity) used in this work were purchased from Sigma – Aldrich (Steinheim, Germany). They were used without further purification.

Table 2. Sequential extraction scheme for As extractions

Fractions	Sample	Extractant	
1	Soil sample	1 mol.L ⁻¹ NH ₄ NO ₃	Mobile (water-soluble and exchangeable bonds and easily soluble metal- organic complexes)
2	Residual	+ 1 mol.L ⁻¹ NH ₄ OAc (pH 6.0)	Easily available bonds
3	Residual	+ 1 mol.L ⁻¹ NH ₂ -OH.HCL + 1 mol.L ⁻¹ NH ₄ OAc (pH 6.0)	Bonds with Mn oxides
4	Residual	+ 0.025 mol.L ⁻¹ NH ₄ -EDTA (pH 4.6)	Organic bonds
5	Residual	+ 0.02 mol.L ⁻¹ NH ₄ -Oxalate (pH 3.25)	Bonds with amorphous Fe oxides
6	Residual	+ 0.02 mol.L ⁻¹ NH ₄ -Oxalate + ascorbic acid (pH 3.25)	Bonds with crystalline Fe bonds
7	Residual	+ HF	Residual

3. Results and Discussion

3.1 Method Validation

The mean percentage recovery of As was used to spike the soil sample represented in Table 3. The mean percentage recovery from the spiked soil sample for As was 97.6, which is similar to the reported values in a similar matrix by Awofolu *et al.*, (2005). Therefore, the reproducibility of the methods and the precision and accuracy of the AAS machine was adjudged reliable since the acceptable recovery percentage was obtained and the standard error was less than 5%.

Table 3. Means % recoveries (± SD) of metal standard added to pre-digested soil sample

Metal	Spiked conc / mgL ⁻¹	% recovery
As	3.0	97.6 ± 2.9

Values are mean of triplicate analyses, SD is the standard deviation

3.2 Physico-Chemical Properties

The results for the soil physicochemical characterization are given in Table 4, the pH across the entire study area ranged in a narrow interval. Top soils across the study area suggested slightly acidic to neutral condition, while the middle and bottom layers suggest slightly acidic soil conditions. The relative humidity (RH) ranged from 56.5-61.4 %, which could be accounted for by the climatic variation of the study area. Sand is the major soil component in the size distribution (Cai *et al.*, 2002) and gives a decreasing order of sand > clay > silt in particle

size analysis. The percentages of total organic matter content (TOM) in all the samples were low (< 10 %). The TOM of the control area is much higher when compared to samples from the mechanic workshops; this difference in the TOM could be due to reaction of soil colloids with toxic metals from the waste of mechanic workshop which are indiscriminately dispersed within the shop and also the TOM concentrations in top soil > middle soil > bottom soil.

The cation exchange capacity (CEC) is highest in all the top soils, followed by the middle soils and the bottom soils; however, there is a variation in the soil samples where bottom soil has a higher CEC than the middle soil. In a similar manner to TOM, the soil CEC in the control is high when compared with that from the mechanic shops (Tlustors *et al.*, 2000). This reduction in CEC and TOM could be accounted for as a reflection of nutrient depletion by waste from the activities of the mechanic workshops.

The total concentration of As in the soil samples ranged from 2.45-2.53, 2.14-2.26 and 2.69-2.79 mg/kg for top, middle and bottom soils respectively. It will be observed that the bottom soils are in the highest range followed by top soil; this could be as a result of leaching of arsenic from top soil to the bottom soil, although the levels found indicated a low concentration when compare with those in Table 1. It is important to determine the amount present in different phases since As is toxic in any concentration, and total content is less important in determining As lability. However, the results apparently suggest a pollution plume in the study areas. Hence, a methodology to separate the metal-bearing phases was also employed, since it is impossible to consider the presence of metals and their compounds in the environment and their potential release to the ecosystem without considering its geochemical forms (Adamu *et al.*, 2013). In addition, distribution of a metallic contaminant amongst different phases profoundly affects its transport (Sager, 1992). It is the form in which As is associated with various phases rather than its total concentration that affects its mobility, bioavailability and toxicity. Thus, to assess the potential release of these As to localities in the vicinity, a sequential extraction protocol was employed, which could present characteristic bonding of the metals to the soils.

3.3 Results

Table 4. Chemical composition (Mean \pm S.D) of soil samples

Specifications	Soil Depth (cm)	Soil 1	Soil 2	Soil 3	Control
pH	0 – 15	7.10 \pm 0.21	6.90 \pm 0.11	6.51 \pm 0.22	6.71 \pm 0.11
	15 – 30	6.72 \pm 0.11	6.71 \pm 0.12	6.42 \pm 0.10	5.70 \pm 0.12
	30 – 45	5.61 \pm 0.22	6.60 \pm 0.21	6.22 \pm 0.21	5.71 \pm 0.10
Relative Humidity (%)		61.41	56.51	58.30	59.00
Organic Matter (%)	0 – 15	3.04 \pm 0.11	2.67 \pm 0.09	2.12 \pm 0.12	7.21 \pm 0.10
	15 – 30	2.82 \pm 0.20	1.27 \pm 0.10	0.28 \pm 0.06	5.27 \pm 0.07
	30 – 45	1.31 \pm 0.13	0.69 \pm 0.13	0.21 \pm 0.01	4.51 \pm 0.09
CEC (meq/100 g)	0 – 15	10.74 \pm 1.31	9.69 \pm 1.85	9.85 \pm 1.89	5.17 \pm 0.15
	15 – 30	6.83 \pm 1.03	7.08 \pm 1.15	5.21 \pm 0.77	4.29 \pm 0.11
	30 – 45	8.07 \pm 1.34	6.58 \pm 1.22	3.26 \pm 0.79	3.52 \pm 0.09
As (total, mg/kg)	0 – 15	2.51 \pm 0.22	2.45 \pm 0.24	2.53 \pm 0.22	0.69 \pm 0.25
	15 – 30	2.14 \pm 0.34	2.23 \pm 0.21	2.26 \pm 0.25	0.53 \pm 0.21
	30 – 45	2.69 \pm 0.19	2.72 \pm 0.17	2.79 \pm 0.19	0.77 \pm 0.13
Particle Size Distribution	Sand (%)	67 \pm 3	63 \pm 3	71 \pm 4	55 \pm 2
	Clay (%)	24 \pm 3	26 \pm 2	22 \pm 3	34 \pm 2
	Silt (%)	09 \pm 2	11 \pm 3	09 \pm 3	11 \pm 2
	T/C	SCL	SCL	SCL	SCL

S.D: Standard deviation; T/C: Textural Class; SCL : Sand clay loam

Chemical fractionation of As

Table 5 gives the experimental results obtained for the seven fractions in sequential extraction. For exchangeable

fractions, the fractions decreases in concentration down the soil profile, and the fractions in the control are low compared to the other samples. The fraction 2 represents easily available fractions and it decreased with soil depth. The sum of fraction 1 and 2 represent the bioavailability of As to plants (Shiowatana *et al.*, 2001). The mean concentrations of fraction 1 is in the range of 0.04-0.06 mg/kg. The mean concentrations of fraction 2 ranges between 0.09 – 0.18 mg/ kg, which is greater than the amount presents in the fraction 1 and control samples. This is an indication that the As deposited by the activities of mechanic workshops are in mobile phase. The percentage that bonds to manganese is lowest in all fractions, while the fractions bonds to organic matters shows higher concentrations, significantly more than that of the control samples. Since this fraction relates to the portion released under strong oxidizing conditions, then it constitutes a source of potentially available As in soil (Ure and Davidson, 1995). The As contents were more in amorphous Fe than crystalline Fe (Shane Dever Whiteacre, 2009). The range of As in the soil is greater than that found in the control. The greatest part of As was associated with residual fractions. These fractions in their inert phase correspond to the part of the As which cannot be mobilized. The inner soil contains the highest proportion residual fraction.

Generally the affinity of As with the soil fraction increases in order: $F_3 < F_6 < F_1 < F_2 < F_5 < F_4 < F_7$.

Table 5. Results of As binding fractions

Soils	Soil Depth (cm)	FRACTIONS						
		F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	F ₇
SOIL 1	0 – 15	0.06	0.09	-	1.13	0.10	0.03	1.75
	15 – 30	0.05	0.14	0.01	1.34	0.14	0.01	1.41
	30 – 45	0.04	0.18	0.02	1.46	0.20	0.02	1.81
Mean		0.05	0.14	0.01	1.31	0.14	0.02	1.66
S.D		0.01	0.05	0.01	0.17	0.05	0.01	0.22
SOIL 2	0 – 15	0.05	0.07	0.01	1.24	0.13	0.01	1.50
	15 – 30	0.04	0.15	0.01	2.07	0.16	0.02	1.12
	30 – 45	0.04	0.16	0.01	1.40	0.23	0.02	1.78
Mean		0.04	0.13	0.01	1.57	0.18	0.02	1.47
S.D		0.01	0.05	0.00	0.44	0.05	0.01	0.33
SOIL 3	0 – 15	0.07	0.09	0.01	0.73	0.16	0.01	1.57
	15 – 30	0.06	0.13	0.01	0.69	0.16	0.03	1.20
	30 – 45	0.04	0.15	0.02	0.80	0.19	0.02	1.83
Mean		0.06	0.12	0.01	0.74	0.17	0.02	1.53
S.D		0.02	0.03	0.06	0.06	0.02	0.01	0.32
CONTROL	0 – 15	0.02	0.02	-	0.12	0.03	-	0.34
	15 – 30	0.01	0.03	-	0.14	0.03	-	0.23
	30 – 45	-	0.03	0.01	0.16	0.05	<0.01	0.42
Mean		0.01	0.03	0.00	0.14	0.04	-	0.33
S.D		0.01	0.01	0.01	0.02	0.01	-	0.10

The percent distribution of As across the various fractions are presented in Fig 2 below. Approximately 50 % of As concentration is in the residual fractions, followed by bonds to soil organic matters (i.e organic bonds). About 10 % is bound to amorphous Fe oxides, while about 8-9 % is bioavailable and mobile, bioavailable are the As content that are readily available for plant and mobile are those. About 1 % is associated with Fe oxides in the crystalline phase.

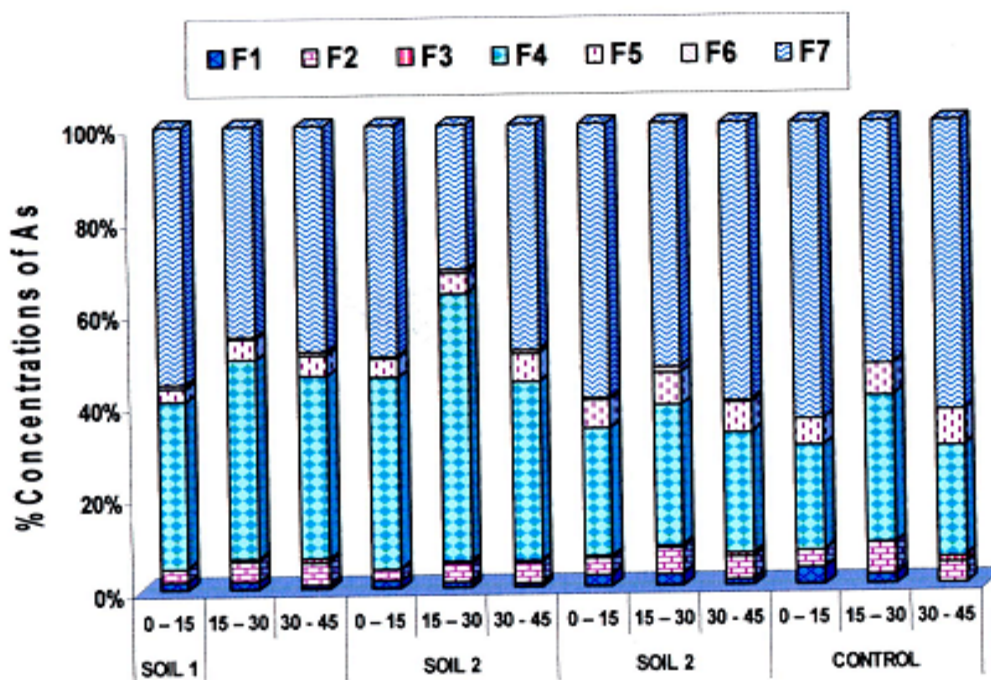


Figure 2. Percent distribution pattern of As across various fractions

In order to understand the extent of pollution, elemental contamination factors (CFs), soil enrichment factors (EFs) and geoaccumulation index (Igeo), results were determined using the formula described elsewhere (Likuku *et al.*, 2013; Loska *et al.*, 2003), The CFs of the entire study area ranges as follow 3.55-3.66, 4.04-4.26, 3.49-3.62 for top, middle and inner soil respectively. The highest is found in the middle soil which negate what was observed for total concentration of As. The CFs from all the sample is higher than that of the control which ranges between 0.53-0.77 (Table 6).

Table 6. Elemental contamination factors (CFs) in different soil layers

Element	Soil Layers	Soil 1	Soil 2	Soil 3	Natural Background Concentration
	0 – 15	3.64	3.55	3.66	0.69±0.25
	15 – 30	4.04	4.21	4.26	0.53±0.21
	30 – 45	3.49	3.52	3.62	0.77±0.13

^aAverage natural background concentration (±SD, n=3)

The results for EFs and Igeo can be found in Table 7. In this study, iron was used as a conservative tracer to differentiate natural from anthropogenic components (Ergin *et al.*, 1991) The mean EFs of As in soils under study ranged between 1.77 and 2.40. This according to Zhang and Liu (2000), points to As being deposited from the influence of mechanic workshop waste. Zhang and Liu classified EFs between 0.5 and 1.5 as the natural metal content, while any amount greater than 1.5 was probably due to anthropogenic sources. In this study, the anthropogenic source referred to is mechanical wastes. Since the presence of heavy metals in the soil does not necessarily constitute a pollution risk, Igeo as proposed by Muller (1969) was used to access the pollution of As in the soil of the mechanic workshop. The Igeo of all the soil samples under study ranged from 0.37- 0.39. This is an indication that the soil samples were uncontaminated to moderately contaminated (Muller, 1969).

Table 7. Mean EF and I_{geo} classes of As with respect to the natural background

ELEMENT	Soil 1	Soil 2	Soil 3
Enrichment Factor			
As	1.77	2.40	2.18
I_{geo}			
As	0.39	0.37	0.39

The normalizing element for calculation of the EF and I_{geo} is Fe with natural background value of 232.7 mg/kg. From both EF and I_{geo} , it is clear that the concentration of As in the soil is from the influence of auto-mechanic workshop waste, but it is not present in concentrations that pose a significant risk to the environment.

4. Conclusion

It is clear that the soils investigated were not contaminated with As, therefore plants and water in these areas are good for both residential and industrial purposes, although The CFs confirmed the influence of the auto-mechanic workshop's activities on the As mobility to the environment. The sequential extraction method adopted in this research provides dependable information on fractions of As in the soils of auto-mechanic workshops. The reagents were specific and selective for As in the phase examined. The fractions obtained from sequential extractions were small because the total As concentration in all soils were small. The results indicate that As is mainly associated with oxidizing and residual fractions, which allows us to predict their mobility. Hence periodic assessment of the mechanic workshops and waste sites is necessary to ensure the level is below the regulatory limit. This is of paramount importance since As from anthropogenic and geologic sources are considered one of the most toxic elements affecting millions of people around the world.

Acknowledgement

The effort of Barr William McCallig in proof reading this work is highly appreciated.

References

- Adamu, H., Luter, L., Musa, M. L., & Umar, B. A. (2013). Chemical Speciation: A strategic pathway for insightful risk assessment and decision-making for remediation of toxic metal contamination. *Environment and Pollution*, 2(4), 92-99.
- Awofolu, O. R., Mbolekwa, Z., Mtshenla, V., & Fatoki, O. S. (2005). Levels of trace metals in water and sediment from Tyume river and its effects on an irrigated farmland. *Water SA*, 31(1), 87-94. <http://dx.doi.org/10.4314/wsa.v31i1.5124>
- Baroni, F., Boscagli, A., Di Lella, L. A., Protano, G., & Riccobono, F. (2004). Arsenic in soil and vegetation of contaminated areas in southern Tuscany (Italy). *Journal of Geochemical Exploration*, 81(1), 1-14. [http://dx.doi.org/10.1016/S0375-6742\(03\)00208-5](http://dx.doi.org/10.1016/S0375-6742(03)00208-5)
- Bouyoucos, G. J. (1962). Hydrometer method improved for making particle size analyses of soils. *Agronomy Journal*, 5(5), 464-465. <http://dx.doi.org/10.2134/agronj1962.00021962005400050028x>
- Cai, Y., Cabrera, J. C., Georgiadis, M., & Jayachandran, K. (2002). Assessment of arsenic mobility in the soils of some golf courses in South Florida. *The science of the total Environment*, 291, 123-134. [http://dx.doi.org/10.1016/S0048-9697\(01\)01081-6](http://dx.doi.org/10.1016/S0048-9697(01)01081-6)
- Chemistry world. (2014). *Royal society of chemistry bulletin*, 11(4), 55-57. Retrieved from <http://www.chemistryworld.org>
- Cullen, W. R., & Reimer, K. J. (1989). Arsenic speciation in the environment. *Chemi. Rev.*, 89, 713-764. <http://dx.doi.org/10.1021/cr00094a002>
- Eisler, R. (1994). A review of arsenic hazards to plants and animals with emphasis on fishery and wildlife resources.
- Ergin, M., Saydam, C., Basturk, O., Erdem, E., & Yoruk, R. (1991). Heavy metal concentrations in surface sediments from the two coastal inlets (golden Horn Estuary and Izmit bay) of the northeastern sea of Marmara. *Chem., Geo.*, 91, 269-285. [http://dx.doi.org/10.1016/0009-2541\(91\)90004-B](http://dx.doi.org/10.1016/0009-2541(91)90004-B)
- Francis, O. (2004). ATrace metals contamination of soils and vegetation in the vicinity of livestock in Nigeria. *EJEAfche*, 4(2), 863-870.

- Gupta, S. K., Vollmer, M. K., & Krebs, R. (1996). The importance of mobile, mobilizable and pseudo total heavy metal fractions in soil for three-level risk assessment and risk management. *Science total environment*, 178, 11-20. [http://dx.doi.org/10.1016/0048-9697\(95\)04792-1](http://dx.doi.org/10.1016/0048-9697(95)04792-1)
- Jackson, M. L. (1958). *Soil chemistry analysis prentice Hall*. London, U.K, pp. 54-59.
- Kim, M. J., & Nriagu, J. (2000). Oxidation of arsenic in groundwater using ozone and oxygen. *Science total environment*, 247, 71-79. [http://dx.doi.org/10.1016/S0048-9697\(99\)00470-2](http://dx.doi.org/10.1016/S0048-9697(99)00470-2)
- Lee, D. Y., & Lee, C. (2011). Regulatory standard of heavy metal pollutant in soil and groundwater in Taiwan.
- Likuku, A. S., Gaboutloeloe, G. K., & Mmolawa, K. B. (2013). Determination and source apportionment of selected heavy metals in aerosol samples collected from Sebele. *American Journal of Environmental Science*, 9(2), 188-200. <http://dx.doi.org/10.3844/ajessp.2013.188.200>
- Loska, K., Wiechula, D., Barska, B., Cebula, E., & Chojnecka, A. (2003). Assessment of Arsenic Enrichment of Cultivated Soils in Southern Poland. *Polish Journal of Environmental Studies*, 12(2), 187-192.
- Muller, G. (1969). Index of geoaccumulation in sediments of Rhine river. *Geol. Journal*, 2 109-118.
- Ning, R. Y. (2002). Arsenic removal by reverse osmosis. *Desalination*, 143(3), 239-241.
- Ololade, I. A., Oloye, F. F., Adamu, H., Oluwole, O. D., Oluyede, O. P., Alomaja, F., & Ololade, O. (2014). *Distribution and Potential Mobility Assessment of Toxic Metals in Soils of Mechanic Workshops in Akoko, Ondo State Nigeria*. In press.
- Sadiq, M. (1997). Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations. *Water, air, and soil pollution*, 93(1-4), 117-136. <http://dx.doi.org/10.1007/BF02404751>
- Sager, M. (1992). Hazardous metals in the environment: Techniques and instruments in analytical chemistry. *Amsterdam: Elsevier.*, 133-175. [http://dx.doi.org/10.1016/S0167-9244\(08\)70106-9](http://dx.doi.org/10.1016/S0167-9244(08)70106-9)
- Shane Dever Whiteacre, B.S. (2009). Soil control on Arsenic bio accessibility, Arsenic fractions and soil properties, MSc thesis, Ohio state university.
- Shiowatana, J., McLaren, R. G., Chanmekha, N., & Samphao, A. (2001). *Journal of environmental quality*, 30, 1940-1949. <http://dx.doi.org/10.2134/jeq2001.1940>
- Tlustors, P., Szakova, J., Starkova, A., & Pavlikova, D. A. (2000). A comparison of sequential extraction procedures for fractionation of arsenic, cadmium, lead, and zinc in soil. *Central European journal of chemistry*, 3(4), 830-851. <http://dx.doi.org/10.2478/BF02475207>
- Ure, A. M., & Davidson, C. M. (1995). Chemical speciation in the environment. Blackie Glasgow.
- Uzairu, A., Harrison, G. F. S., Balarabe, M. L., & Nnaji, J. C. (2009). Concentration levels of trace metals in fish and sediment from Kubanni river, Northern Nigeria. *Bull. Chem. Soc. Ethiop.*, 23(1), 9-17. <http://dx.doi.org/10.4314/bcse.v23i1.21293>
- Wenzel, W. W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., & Adriano, D. C. (2001). Arsenic fractionation in soils using an improved sequential extraction procedure. *Analytica chimica acta*, 436, 309-323. [http://dx.doi.org/10.1016/S0003-2670\(01\)00924-2](http://dx.doi.org/10.1016/S0003-2670(01)00924-2)
- Zein, H., & Brummer, G. W. (1989). Mittiling. Dtsch. Bodenkundl, *Gesllsch*, 59, 505.
- Zhang, J., & Liu, C. L. (2000). Riverine composition and estuarine geochemistry of particulate metals in China-weathering features, anthropogenic impact and chemical fluxed. *Estuarine coastal shelves*, 54, 1051-1070. <http://dx.doi.org/10.1006/ecss.2001.0879>

Copyrights

Copyright for this article is retained by the author(s), with first publication rights granted to the journal.

This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).