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Determination of polyaromatic hydrocarbons and some selected heavy metals in an aluminium recycling contaminated soil of Atuwara-Igbheren, Sango-Ota, Ogun State

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs), both carcinogenic and hazardous, are common environmental contaminants. Soil samples were taken from three sites using a soil auger, air dried, and digested with the AODC method. HMs concentrations were measured using atomic absorption spectrophotometry, while PAHs were extracted with the USEPA method and analyzed by gas chromatography mass spectrophotometry. Descriptive and inferential statistics were applied to the data. HMs' mean concentrations in mg/kg were copper (Cu) (255 ± 33-356 ± 22), lead (Pb) (48 ± 4-213 ± 62), Mn (77 ± 10-101 ± 3), Na (49 ± 8-63 ± 19), and cadmium (Cd) (0.51 ± 0.05-4 ± 3), with Cu > Pb > Mn > Na > Cd. Cu, Pb, and Cd levels exceeded Dutch target values. PAHs concentrations ranged from 147,290 ± 120,340 to 265,090 ± 184,321 μg/kg, with six out of seven carcinogenic PAHs detected. Dibenzo[a,h]anthracene had the highest concentration (26,053 ± 18,465 μg/kg). All PAH levels exceeded the Dutch guideline of 50 μg/kg.

Keywords: contaminants, poly aromatic hydrocarbons, heavy metals, carcinogenic, contaminated soil, aluminum recycling

INTRODUCTION

Aluminum recycling is the process by which scrap aluminum can be reused in products after its initial production. The process involves simply re-melting the metal, which is far less expensive and energy-intensive than creating new aluminum through the electrolysis of aluminum oxide (Al_2O_3), which must first be mined from bauxite ore and then refined using the Bayer process. Recycling scrap aluminum requires only 5% of the energy used to make new aluminum. For this reason, approximately 31% of all aluminum produced in the United States comes from recycled scrap. Used beverage containers are the largest component of processed aluminum scrap, and most of it is manufactured back into aluminum cans (Al-Alimi et al., 2024). High smoke and gases generation with very low metal recovery rate and high energy consumption has been attributed to this process (Bai et al., 2024)

Thus, besides a direct economic problem that machining, and foundry companies have to face, waste prevention and recycling are becoming critical aspects of the aluminum industrial activities, arising as aggregate phases of the production cycle. During the last years, several recycling methods of machining chips and other aluminum wastes like beverage cans, for example, have been reported. They are based either in solid state transformation into extruded or sintered products (Li et al., 2020; Puga et al., 2009; Ruberti, 2024).

Urbanization, industrialization and population increase over the last few decades have enhanced the release of toxic organic pollutants, viz. polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) into the environment due to various anthropogenic activities such as fuel burning, industrial emissions, corrosion of metallic particles (Das et al., 2016). Soil systems are the long-term storehouse of such pollutants and are considered to be a steady index of the state of environmental pollution. The primary input of such organic pollutants into the soil surface is by air-to-surface precipitation and it persists in the top layer of the soil. Because of its toxicity, exposure to such pollutants in the environment is detrimental to human health and so has become the focus of much attention (Moradpour et al., 2023)

PAHs consist of at least two fused benzene rings and are classified as hydrophobic organic compounds (Zeng et al., 2000). Many of the PAHs have deleterious effects on mammals including humans such as respiratory, immunological, neurological, genotoxic, and reproductive. The United States Environmental Protection Agency has identified 16 most frequently occurring and/or dangerous PAHs as priority pollutants and has divided them into carcinogenic and non–carcinogenic groups (USEPA, 1997; Venkatraman et al., 2004). The seven compounds, namely benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a]anthracene, and indeno[1,2,3-c,d]pyrene, are considered human carcinogens. The remaining nine compounds, namely acenaphthene, acenaphthylene, anthracene, benzo[g,h,i]perylene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene, are considered non-carcinogens (Premnath et al., 2021).

Purpose of the Study

Several epidemiological studies have reported an increased risk of developing lung cancer or bladder cancer for workers in the aluminum industry, however, in all of these studies the risk has been attributed to the exposure to PAHs and HMs generated during aluminum melting process rather than from exposure to aluminum compounds. PAHs are harmful to the environment and health of human beings due to their high degree of mutagenicity and carcinogenicity when they enter the human body (Mwiganga & Kansiime, 2005)). Not all metals in soil are bioavailable and cause adverse effects to human health or the environment (Okereafor et al., 2020; Yang et al., 2022). However, even trace quantities of HMs, such as cadmium (Cd), arsenic, lead (Pb), and mercury, can cause adverse health effects (Ebrahimi et al., 2020). Organisms in different trophic levels are also believed to be suffering from metal toxicities; therefore, human health is under threat from the exposure to HMs through consumption of food grown on contaminated soil. Organic pollutants, such as PAHs, are also a major reason for deformity and cancer. The presence of some PAHs have shown increased incidence of skin, lung, bladder, liver and stomach cancers in laboratory animals (Mitra et al., 2022).

METHODS

Study Area

This study was conducted in Atuwara-Igberen, a residential neighborhood in Iyana-Iyesi, Sango-Ota, within the Ado-Odo/Ota Local Government Area of Ogun State, Nigeria. Sango Ota, with coordinates 6° 42’ 19” N and 3° 14’ 23” E, has an estimated population of 163,783 and is a key industrial hub, historically significant as the capital of the Awori Yoruba ethnic group.

Table 1. Concentration of HMs in soil samples (mg/kg)

Metals	Sample location A	Sample location B	Sample location C
Na	67.52 ± 5.96^{a}	48.69 ± 8.04^{c}	62.73 ± 18.51^{b}
Cu	355.65 ± 21.70^{a}	255.04 ± 33.07^{c}	295.77 ± 96.56^{b}
Pb	47.96 ± 3.60^{c}	174.45 ± 23.05^{b}	212.80 ± 61.58^{a}
Mn	101.16 ± 3.28^{a}	77.46 ± 10.25^{c}	93.32 ± 24.90^{b}
Cd	0.51 ± 0.05^{c}	1.35 ± 0.45^{b}	4.02 ± 2.62^{a}

Note. Number of samples = 9 & mean with the different superscript along the row are significantly different ($p < 0.05$)

Sample Collection

Soil samples

Nine soil samples were collected from three quadrants at a depth of 0 to 15 cm using a soil auger. Samples were stored in aluminum foil-covered containers and taken to the laboratory for analysis.

Sample preparation for soil samples

Soil samples were air-dried, sieved using a 2 mm sieve, and stored in amber bottles for PAHs determination and polythene bags for HMs analysis.

Extraction procedure for soil samples

Using the EPA3550B method, 20 g of air-dried soil was mixed with 20ml each of acetone and n-hexane. The mixture was agitated in an ultrasonic bath, and the extracts were filtered through Whatman No. 41 filter paper.

Cleanup procedure

A slurry of 10 g of activated silica gel in methylene chloride was placed in a chromatographic column and eluted with 40 ml of hexane. A sample extract was added and eluted with 25 ml of methylene chloride, then concentrated using a rotary evaporator.

Procedure for concentration of samples

Sample extracts were concentrated to around 2 ml using a Buchi R215 Rotary evaporator, with a water bath set to 60 °C and a chiller at 20 °C.

Heavy metals determination

1 g of air-dried and sieved soil was mixed with 20 ml of HNO^3 and heated at 120 °C for 30 minutes. The cooled samples were filtered and analyzed using an atomic absorption spectrometer at specific wavelengths for Cd, Pb, Na, Mn, and copper (Cu).

RESULT AND DISCUSSION

Heavy Metals in Soil Samples

HMs are persistent pollutants that can bio-magnify in the food chain, posing increasing dangers to humans and wildlife. The levels of Cd, Pb, sodium, manganese, and Cu in soil samples were analyzed and are shown in **Table 1**. The accumulation order of metals was Cu > Pb > Mn > Na > Cd. Cu had the highest concentration (355.65 ± 21.79 mg/kg) in sample A, followed by Pb (212.80 ± 61.58 mg/kg) in sample C. Cd had the lowest concentration (4.02 ± 2.62 mg/kg) in sample

Table 2. Concentration of PAHs in soil samples (µg/kg)

Metals	Sample location A	Sample location B	Sample location C
Naphthalene	1,497 ± 1,112[a]	333 ± 175[b]	210 ± 52[c]
Acenaphthylene	1,437 ± 441[a]	827 ± 559[c]	837 ± 289[b]
Acenaphthene	500 ± 70[a]	403 ± 121[c]	487 ± 175[b]
Fluorene	4,217 ± 1,270[a]	1,617 ± 675[b]	1,510 ± 485[c]
Phenanthrene	3,383 ± 1,356[a]	1,687 ± 756[c]	2,037 ± 1,199[b]
Anthracene	1,547 ± 1,161[a]	537 ± 223[c]	620 ± 470[b]
Fluoranthene	2,170 ± 416[a]	1,130 ± 879[c]	1,937 ± 1,340[b]
Pyrene	1,237 ± 370[b]	657 ± 441[c]	1,550.00 ± 597.33[a]
Benzo[c]phenanthrene	4,120 ± 2,675[a]	1070 ± 862[b]	770 ± 95[c]
Benz[a]anthracene	1,327 ± 854[a]	983.33 ± 451.00[c]	1,050 ± 745[b]
Chrysene	2,387 ± 1,044[a]	420 ± 220[c]	1,200.000 ± 826.135[b]
Benzo[e]pyrene	1,713 ± 374[c]	3,490 ± 2,231[a]	2,086.67 ± 473.00[b]
Benzo[k]fluoranthene	3,523 ± 1,040[b]	3,153.33 ± 660.00[c]	4,637 ± 3,432[a]
3-methylcholanthrene	18,560 ± 13,113[b]	15,743.33 ± 4,772.00[c]	26,053.33 ± 18,465.00[a]
Indeno[1,2,3-cd]pyrene	4,390 ± 3,653[b]	2,877 ± 1,963[c]	5,220 ± 1,977[a]
Dibenzo[a,h]anthracene	6,010 ± 2,125[b]	5,313 ± 3,218[c]	29,187 ± 17,728[a]
Benzo[g,h,i]perylene	4,070 ± 3,408[b]	2,487 ± 2,127[c]	4,703 ± 1,946[a]
Dibenzo[a,h]pyrene	5,203 ± 1,627[a]	1,453 ± 903[b]	780 ± 356[c]
Dibenzo[a,I]pyrene	6,247 ± 4,677[a]	1,397 ± 985[b]	577 ± 21[c]
Dibenzo[a,l]pyrene	4,457 ± 1,453[a]	1,553 ± 835[b]	1,213 ± 612[c]
Benzo[a]pyrene	703 ± 107[c]	1,967 ± 214[a]	1,700 ± 1,235[b]

Note. Number of samples = 9 & mean with the different superscript along the row are significantly different ($p < 0.05$)

C. These results contrast with Sanusi et al. (2017), which reported higher concentrations of Cu (267.70 ± 4.05 mg/kg), Pb (658 ± 0.28 mg/kg), and Cd (20.70 ± 0.01 mg/kg).

The concentrations of Cu, Pb, and Cd in this study exceeded the Dutch target of 36 mg/kg, 85 mg/kg, and 0.8 mg/kg, respectively, and the WHO standards of 30 mg/kg (Cu) and 35 mg/kg (Pb). The levels of Mn and Na were below these standards (Elzinga et al., 1999; Iordache et al., 2022). This indicates that the soil from the aluminum recycling site in Atuwara-Igbeheren is highly contaminated with Pb, Cu, and Cd, posing a significant risk of HM poisoning, particularly from Pb and Cd, which are prone to bioaccumulation and can cause neurological disorders.

PAHs in Soil Samples

The concentrations of PAHs in soil samples are presented in **Table 2**. A total of 21 PAHs were detected, including six of the seven carcinogenic PAHs. The total PAHs concentration ranged from 147,290 µg/kg to 265,090 µg/kg, which is much higher than the 3.33-34.81 µg/kg reported by (Bhupander et al. 2012). The high levels of PAHs are due to pollutants released during aluminum recycling at the site.

Dibenzo[a,h]anthracene, a high molecular weight and carcinogenic PAH, had the highest concentration (29,187 ± 17,728 µg/kg) across all samples, followed by the non-carcinogenic 3-methylcholanthrene (26,053 ± 18,465 µg/kg) in sample C. The lowest concentration was of acenaphthene, ranging from 403 ± 121 µg/kg to 500 ± 70 µg/kg. The other detected carcinogenic PAHs included chrysene, benzo[a]pyrene, benzo[a]anthracene, indeno[1,2,3-cd]pyrene, and benzo[k]fluoranthene, with concentrations exceeding the Dutch guideline of 50 µg/kg for polluted soil. These high concentrations of carcinogenic PAHs pose significant health risks, particularly cancer.

CONCLUSION AND RECOMMENDATION

The soil at the Atuwara-Igbheren aluminum recycling site is severely contaminated with Pb, Cu, and Cd. This poses a risk of HM poisoning to nearby residents. Additionally, six out of seven carcinogenic PAHs were detected at concentrations significantly above the Dutch guideline of 50 µg/kg. Long-term exposure to these contaminants may result in health issues such as cataracts, kidney and liver damage, jaundice, skin irritation, and immune system suppression. High levels of benzo[a]pyrene can also cause developmental and reproductive problems in animals (Bayowa, 2014).

Given the hazardous nature of Cd, Pb, Cu, and PAHs, it is crucial for both state and local governments to focus on activities addressing environmental contamination. Additionally, soil testing should be expanded to include residential areas, schools, streets, and markets to assess and mitigate risks from these toxic substances. For future research, the exploration to investigate innovative remediation technologies such as bioremediation, phytoremediation, or chemical treatments to reduce the levels of PAHs and HMs in contaminated soils from aluminum recycling activities. Understanding the efficiency of each method in this specific contamination setting can provide valuable insights. Also studying the combined toxicological effects of PAHs and HMs on soil microbial communities, plants, and aquatic systems. This could help in identifying synergistic or antagonistic interactions between these contaminants, which may influence ecosystem health.

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a study without the use of live subjects. Bench work and data collection using online resources involving information freely available in the public domain that does not collect or store identifiable data. The authors further stated that all related laws, rules, and regulations necessary for the execution of the study have been followed.

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