APPLICATION OF EDXRF IN THE DETERMINATION OF THE ABUNDANCE AND DISTRIBUTION OF ARSENIC ALONG A FEDERAL HIGHWAY IN NORTHERN NIGERIA

Abstract

The transmission-emission technique of EDXRF was used to determine the abundance and distribution of Arsenic in soil along a Federal Highway in northern Nigeria. The objective of the work is to investigate and quantify the presence of arsenic in soil so as to ascertain whether vehicular emission is responsible for the observed concentrations and distribution. Depth profile of the element was investigated. Subsequently, top soils within a depth of 5cm were collected along parallel and perpendicular transects and analyzed for arsenic. Samples were crushed and ground into fine, near-homogenous particle-sized powder and pelletized for irradiation and counting. Preliminary investigation revealed that within the depth considered, the concentration of arsenic was decreasing and increasing with increasing depth. The minimum level of arsenic of 17.7 ppm was detected in the study area at a distance of 100m from the road, while the maximum level of 110 ppm was detected by the roadside; and the mean concentration of the element ranged 21.6 – 101.9 ppm with a background loading factor (BLF) of between 1.1 and 5.0 which is suggestive of an environmental pollution. The data indicated initial decrease in arsenic concentration; however this pattern was reversed with increase in distance from the road. These data, in addition to that of the depth profile were clear indications that the observed arsenic concentrations were not due to vehicular emissions, rather, they have geochemical significance.

Key words: EDXRF, Arsenic, Environmental Pollution, and Vehicular Emission.

INTRODUCTION

Soil contamination is most often caused by the presence of xenobiotic chemicals or other materials that disturb the natural soil. Contamination of the natural soil is typically due to percolation of contaminated surface water to the substrata, discharge of industrial effluents to the soil or leaching of wastes from landfills, application of organic fertilizer and pesticides, and aerial deposition of contaminated particulate matter among others (Suciu *et al*., 2009; Chopin and Alloway, 2007; Yan *et al*., 2013).

The occurrence of soil pollution has been linked to increased industrialization and technological advancement. Elevated arsenic concentrations have been reported in the vicinity of mining sites which are not only reservoirs of arsenic but also serve as point sources of arsenic pollution to adjoining farmlands (Amonoo-Ntizer et al., 1996; Jones and Jarvis, 1981). Soil pollution/contamination is generally believed to be a threat to the environment, food safety and sustainable agriculture, human and environmental health (Peryea, 1999). Lead arsenate was a popular insecticide during the first half of the 20th century because of its low toxicity to plants and its effectiveness for controlling insect pests.

Soil contamination undoubtedly have significant deleterious consequences for ecosystems as this can cause radical soil chemistry changes which can arise from the presence of various hazardous chemicals even at low concentration of the contaminant. These changes can lead to elimination of some essential microbes in a given soil environment, with attendant adverse effects on crop yields. Though the lead and arsenic content of plants and most soils are not high enough to be acutely toxic to people, they

however contribute to overall lead and arsenic exposure (Peryea, 1999; Walsh *et al*., 1977).

The energy-dispersive x-ray fluorescence (EDXRF) has proved to be a powerful, nondestructive tool for multielemental determinations in geological, biological, and other environmental materials (Onoja *et al*., 2013; Constantinescu et al., 2009; Omotola and Onojah, 2009). The technique has been found to be sensitive with detection limits in the range of the order of parts per million (ppm) (Funtua, 1999; Singh and Saharan, 2010; Onoja *et al*., 2013;).

MATERIALS AND METHODS

The EDXRF unit is a system with an in-built 25 mCi ^{109}Cd annular isotopic source and a lithium-drifted Silicon [Si(Li)] detector (Canberra, model SL-12170) which has a resolution of 170 eV for the 5.90 keV line. The detector and the source are placed on the dewar which contained liquid nitrogen for the purpose of cooling the detector. There is also the molybdenum (Mo) target which serves as a source of monochromatic x-rays. The detector is in turn coupled to a computer-controlled analog-to-digital converter (ADC) card.

THEORY OF XRF

X-ray fluorescence spectrometry is one of the most versatile instrumental techniques for elemental determination in samples of various matrices. The method involves the use of high-energy x-rays (photons) or charged particles to excite the sample of interest. The excitation is followed by emission of characteristic x-rays from elements within the sample. The x-rays generated and detected by a high resolution

detector are processed for qualitative and quantitative determination of the various elements present in the sample. The technique is based on an aspect of the principle of interaction of radiation with matter known as photoelectric effect. In the interaction, an atom is bombarded with high energy photons, leading to ejection of an inner orbital electron following excitation. The hole thus created is subsequently filled by an outer electron.

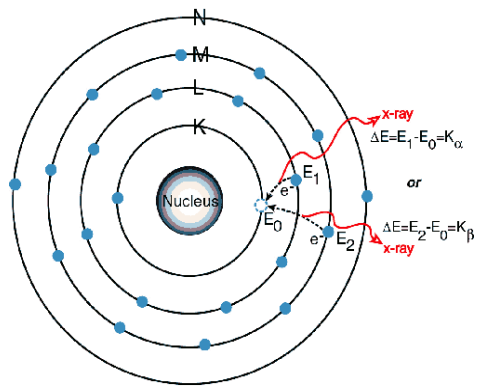

Fig. 1. Photoelectric Effect (Source: www.amptek.com/xrf.html on 9/5/2014)

The excitation is followed by emissions of characteristic x-rays whose energy is given by:

$$E_{\gamma} = E_{e-} + E_{b} \text{.....(1.1)}$$

where E_{e^-} is the energy of the ejected electron, E_{γ} is the energy of the bombarding

photon and E_b is the binding energy of the electron. In the above process, some characteristic peaks are revealed which leads to identification of the elements present in the sample.

SAMPLE COLLECTION AND PREPARATION

The study area is a segment of the Zaria – Sokoto highway in northern Nigeria that is seated on the basement complex. The road has a busy daily traffic of students and petty traders and also covers a distance of about 40 km partly through a vast farmland.

At each of the six sampling locations (Kwangila, Samaru, Shika 1, Shika 2, Giwa 1 and Giwa 2), a depth profile of the soil comprising of samples from depths of 0, 20, 40, 60 and 80cm was carried out. The samples were collected using a core sampler. The sampler was pushed into the soil and samples were collected at depths of interest. Also from each of these locations, surface soil samples (0-5cm) were collected from the parallel transects (at the edge of the road) and subsequently at about, 50, 100, 150, 200 and 250m from the highway along the perpendicular transects. The above depths and distances were chosen arbitrarily following the pattern of past studies (Al-Chalabi and Hawker, 2000; Ward et al, 1975 and Donisa *et al*, 2000). At each sampling point, samples were collected randomly from 10 neighboring points within about five meter radius and then properly mixed to get a good representation of the sampling point. Also, a remote area, about 5 km from the study area was chosen as a control and surface soil within the depth of 5 cm were in like manner collected for analysis. The soil samples were then oven- dried at 65°C for about 48 hours.

The first step in the sample preparation was to divide each of the soil samples into four portions; each portion was then crushed and properly mixed. Then from each of these four portions, little quantity (about 1g) was collected and mixed again and further crushed into very fine powder. Thereafter, an average of 0.5g of each sample was measured and pelletized at 10 tons per square inch with the hydraulic press (SPECAC P/N 15.011) after being properly mixed with 3 drops of a non-contaminating liquid binder (PVC dissolved in toluene). The pellets were finally weighed and then taken for analysis.

SPECTRA ANALYSIS

The spectra for each sample was collected for 3000s and recorded by the detector for subsequent evaluation and analysis. The molybdenum target is used for absorption correction and the absorption factor thus determined was then used by the software package (AXIL-QXAS) to quantify the concentration of the elements in the samples (AXIL-QXAS, 1993). The software is also used to correct for the contribution of the Zr-K to the Mo-K peaks by subtraction.

RESULTS AND DISCUSSION

In this work, EDXRF has again proved to be very useful in elemental determinations in geological samples. The results of investigation of soil arsenic at K_x energy of 10.53 keV are presented below. The depth profile is presented in figure 1, while the variation of arsenic concentrations with distance along the perpendicular transects at the four sampling locations are represented graphically in figures 2 – 7. Table 1 shows the variations of mean concentrations of arsenic at the sampling stations

along the parallel transects, while the mean background arsenic concentration, measured from five replicates was 20.5 ± 4.5 ppm.

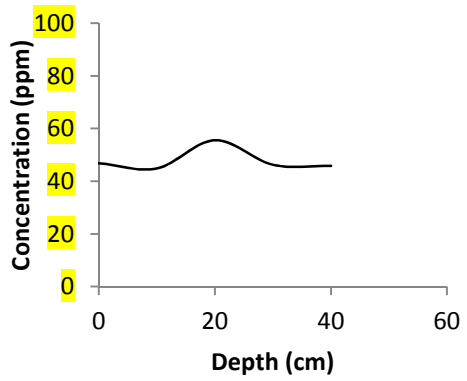

Fig. 1. Concentration of arsenic with depth

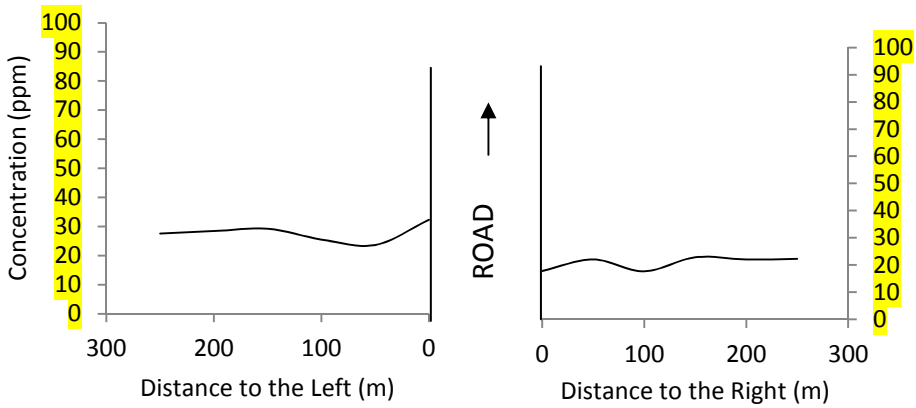

Figure 2. Distribution of arsenic from the road at Kwangila

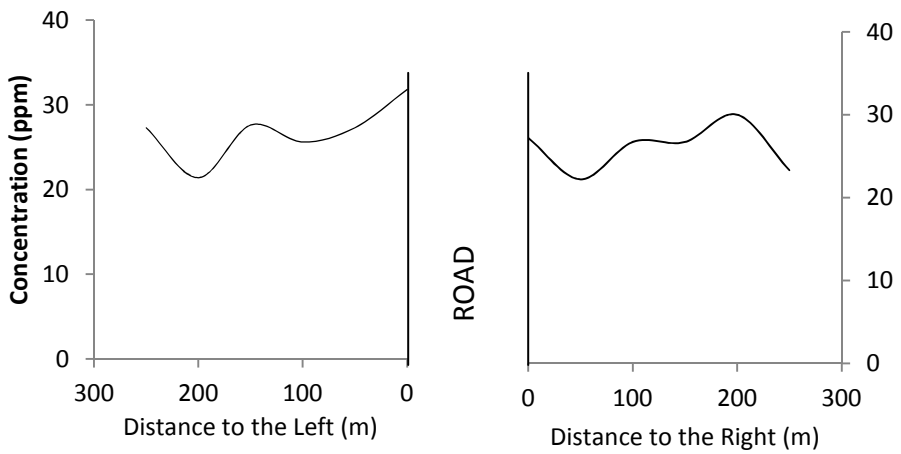

Fig. 3. Distribution of arsenic from the road at Samaru

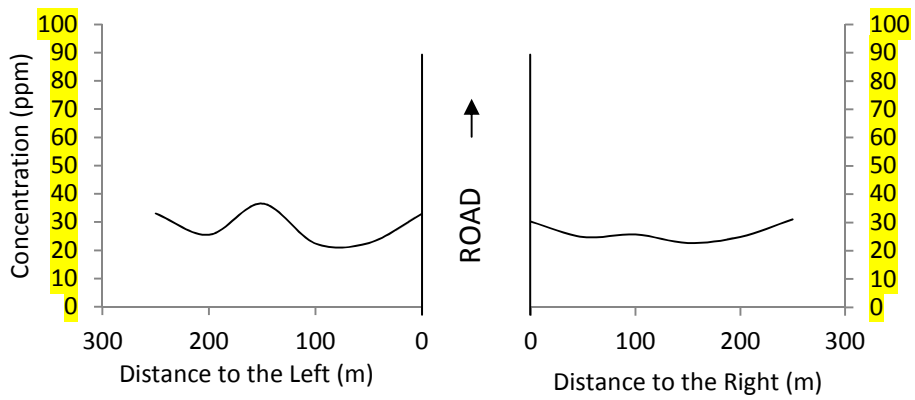

Fig. 4. Distribution of arsenic from the road at Shika 1

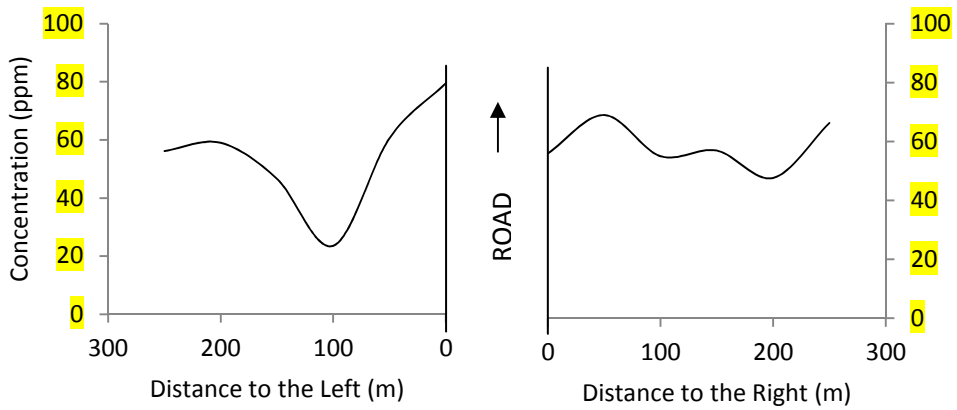

Fig. 5. Distribution of arsenic from the road at Shika 2

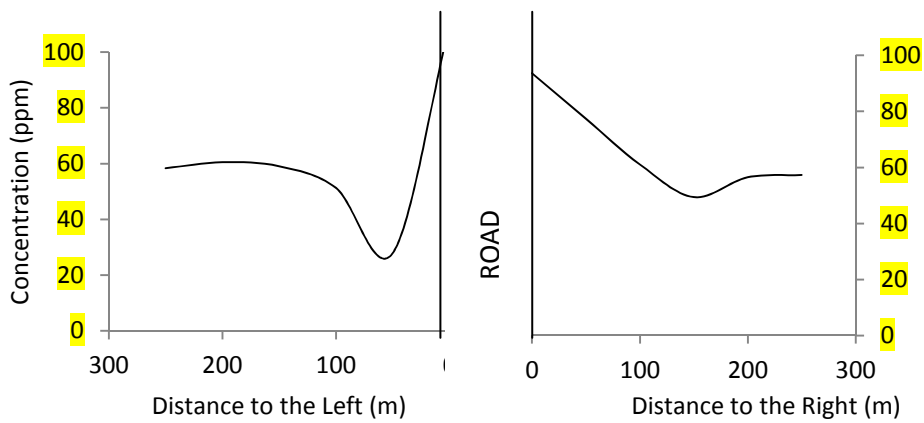

Fig. 6. Distribution of arsenic from the road at Giwa 1

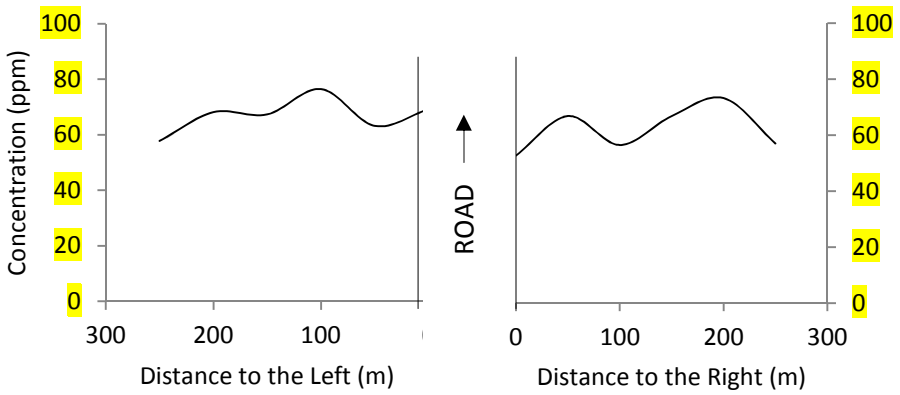

Fig. 6. Distribution of arsenic from the road at Giwa 2

The data recorded revealed that arsenic concentrations varied spatially at all the six samples stations. At Kwangila, the metal occurred in concentration between 17.7 and 32.3 ppm with a mean of 25.3 ± 2.4 ppm. At the other stations concentrations ranged between 22.2 and 30.0 ppm (24.8 ± 3.1 ppm) for Samaru; 22.4 and 36.5 (29.7 ± 3.3 ppm) for Shika 1; 23.6 and 79.5 ppm (51.8 ± 5.2 ppm) for Shika 2; 28.0 and 110.0 ppm (56.5 ± 8.4 ppm) for Giwa 1; and 52.7 and 93.2 ppm (63.2 ± 7.6 ppm) for Giwa 2. With a mean background concentration of 20.5 ± 4.5 ppm, the measured concentrations in the study area revealed a background loading factor (BLF) of between more than 1 and 5 except at the edge of the road at Kwangila where the metal occurred at background levels.

Table 1. Concentration of arsenic along the parallel transects

Sample Station	Concentration (ppm)	
	Left	Right
Kwangila	32.3	17.7
Samaru	31.8	27.2
Shika 1	32.9	30.3
Shika 2	79.5	55.9
Giwa 1	110.0	93.7
Giwa 2	69.2	52.7

Variation of arsenic concentration with depth

The depth profiles of arsenic revealed that the mean concentration decreased slightly with depth from the surface to about 10 cm, thereafter, it increased to a maximum of about 55 ppm at a depth of about 20 cm and decreased again. Jones and Jarvis (1981) reported that there were a number of physical and chemical properties of soil (pH, cation exchange capacity (CEC), organic matter content, soil granulometric fractions, and lithology) affecting As mobilization-immobilization processes, meaning that the above observation could have geochemical significance.

Variation of arsenic concentration with distance from the road

The concentration of arsenic from the road along the perpendicular transects, though varied did not decrease exponentially with increase in distance from the road as

observed of lead in previous related works (Ward *et al*., 1975; Jaradat and Momani, 1999; Onoja *et al*., 2013; Yan *et al*., 2013,); but rather existed with no particular trend, a result that agreed with that reported by Englund, 2004. However, at Samaru, Shika 1, and Giwa 1, the element showed initial decrease in concentration with distance from the road within the first 100m from the edge of the road. Along the parallel transects (table 1), the concentrations of arsenic were not all highest by the edge of the road. This observation further confirmed the fact that the distribution of the element did not take on any particular pattern as the distance from the road increased. The occurrence of arsenic above the background could therefore be linked to mixed sources, with the application of pesticides as a probable cause (Barringer *et al*., 1998). Also, Frost (1967) has reported that arsenic has a complex chemical behavior which enables it to bond with many different elements and also to react differently depending on the physico-chemical properties and water content of the soil which makes prediction of its stability rather difficult. This perhaps explains the distribution pattern of the element in this work. The overall ranking of the abundance of arsenic (As) in all the sample stations was: Giwa 1 (101.9 ppm) > Giwa 2 (80.7 ppm) > Shika 2 (67.7 ppm) > Shika 1 (32.1 ppm) > Samaru (29.5 ppm) > Kwangila (26.1 ppm).

Conclusion

The investigation being reported here have been able to reveal that arsenic occurred above background levels in the study area, but the concentration did not decrease monotonically with increase in distance from the edge of the road. It could therefore be concluded that the abundance and distribution of arsenic in the study area

could be due to contributions from different sources, agricultural activities being the most likely cause. However, the observed levels did not call for much health concern.

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