

Original Research Article**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. Top soil within a depth of 5cm was collected along the parallel transects and at intervals of about 50m along the perpendicular transects at six stations spanning across 40km along the road. Depth profile of the element was investigated. Subsequently, samples were collected from perpendicular transects on both sides of the road at each sampling station and analyzed for arsenic. Samples were crushed and ground into fine, near-homogenous particle-sized powder and pelletized for irradiation and counting. Data of preliminary investigation indicated that within the depth considered, the concentration of arsenic did not follow any particular trend as it was decreasing and increasing with increasing depth. The minimum level of arsenic of 17.7ppm was detected in the study area at a distance of 100m from the road, while the maximum level of 110ppm was detected by the roadside; and the mean concentration of the element ranged 21.6 – 101.9ppm 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 is a clear indication that the observed arsenic concentrations were not due to vehicular emission alone.

Key words: EDXRF, Arsenic, Environmental Pollution, and VehicularEmission.

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 (Suciuet *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. 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 (Onojaet *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; Onojaet *al.*, 2013;).

MATERIALS AND METHODS

The EDXRF unit is a system with an in-built 25 mCi¹⁰⁹Cd annular isotopic source and a Canberra lithium-drifted Silicon [Si(Li)] detector which has a resolution of 170 eV for the 5.90 keV line.

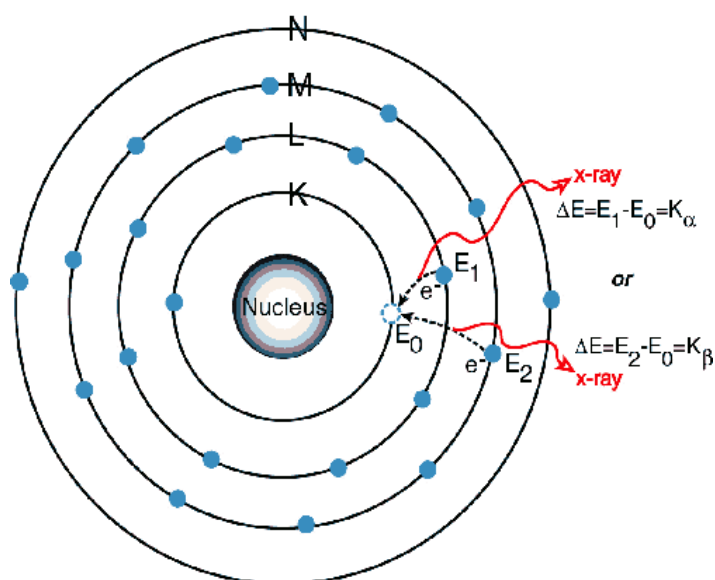
INSTRUMENTATION

An x-ray spectrometer requires an x-ray source and a means of dispersing the x-rays. The Cadmium source acts as an excitation source that emits Ag-K x-ray (22.1keV) in which all elements having characteristic energies lower than that quoted above were detectable in the samples. There is also the molybdenum (Mo) target which serves as a source of monochromatic x-rays. The x-rays are excited through the sample by primary radiation and they penetrate the sample on their way to the detector. The detector is in turn coupled to a computer-controlled analog-to-digital converter (ADC) card. The molybdenum target is used for absorption correction. The absorption factor thus determined is 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 peak by subtraction. The spectra for the samples were collected for 3000s and subsequently evaluated.

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. The hole thus created is subsequently filled by an outer electron.



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

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

$$74 \quad E_{\gamma} = E_{e^{-}} + E_b \dots\dots\dots(1.1)$$

75 Where $E_{e^{-}}$ is the energy of the ejected electron, E_{γ} is the energy of the bombarding

76 Photon and E_b is the binding energy of the electron.

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78 **Sample Collection and Preparation**

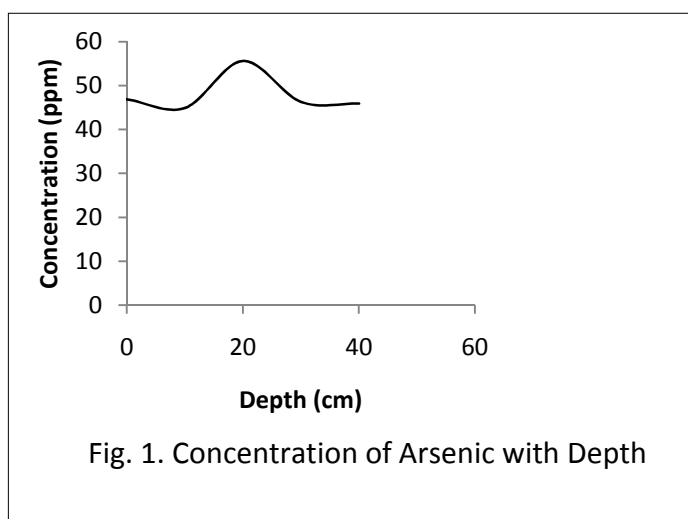
79 At each of the six sampling locations (Kwangila, Samaru, Shika 1, Shika 2, Giwa
80 1 and Giwa 2), a depth profile of the soil comprising of samples from depths of 0, 20,
81 40, 60 and 80cm was carried out. The samples were collected using a core sampler. The
82 sampler was pushed into the soil and samples were collected at depths of interest. Also
83 from each of these locations, surface soil samples (0-5cm) were collected from the
84 parallel transects at the roadside and subsequently at about, 50, 100, 150, 200 and 250m
85 from the highway along the perpendicular transects. The above depths and distances
86 were chosen arbitrarily following the pattern of past studies (Al-Chalabi and Hawker,
87 2000; Ward et al, 1975 and Donisaet *al*, 2000). At each sampling point, samples were
88 collected randomly from 10 neighboring points within about five meter radius and then
89 properly mixed to get a good representation of the sampling point. Also, a remote area,
90 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 with the hydraulic press (SPECAC P/N 15.011) after being properly mixed with 3 drops of liquid binder (PVC dissolved in toluene). The pellets were finally weighed and then taken for analysis.

Results and Discussion

The results of investigation of soil arsenic at K_{α} 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. Data revealed that background arsenic in the control area was 20.5 ± 4.5 ppm.



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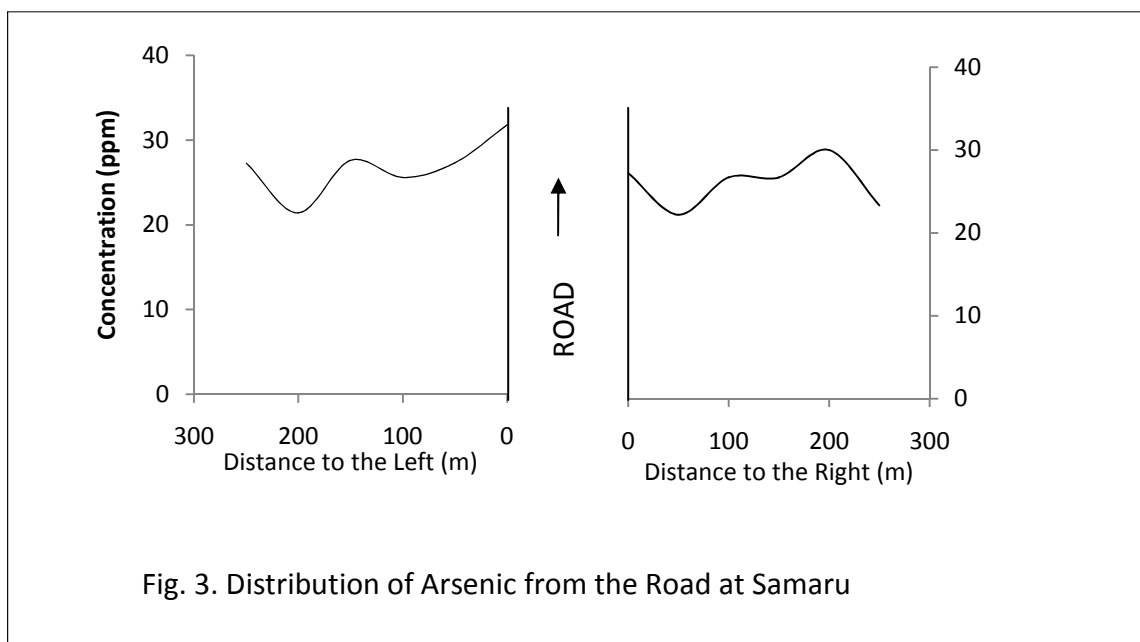
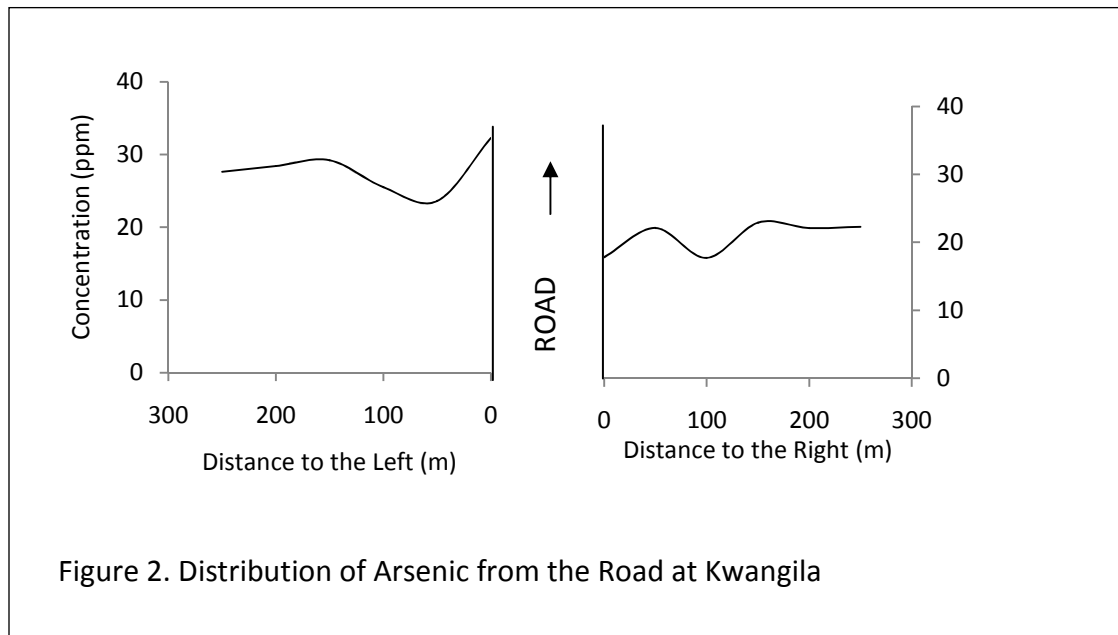
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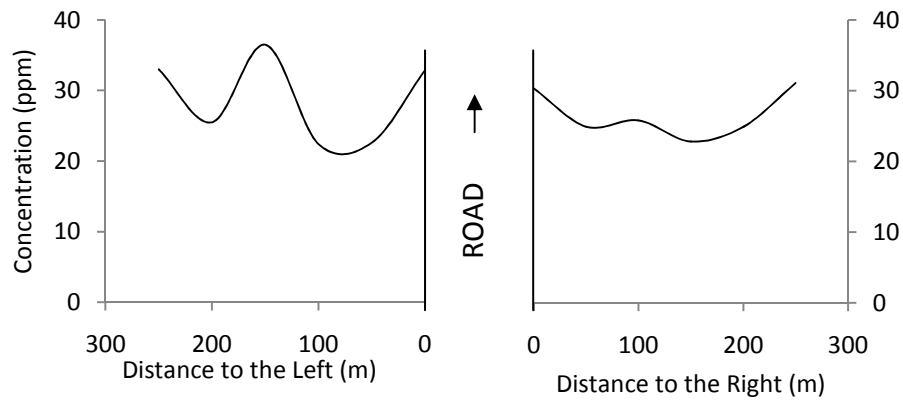


Fig. 4. Distribution of Arsenic from the Road at Shika 1

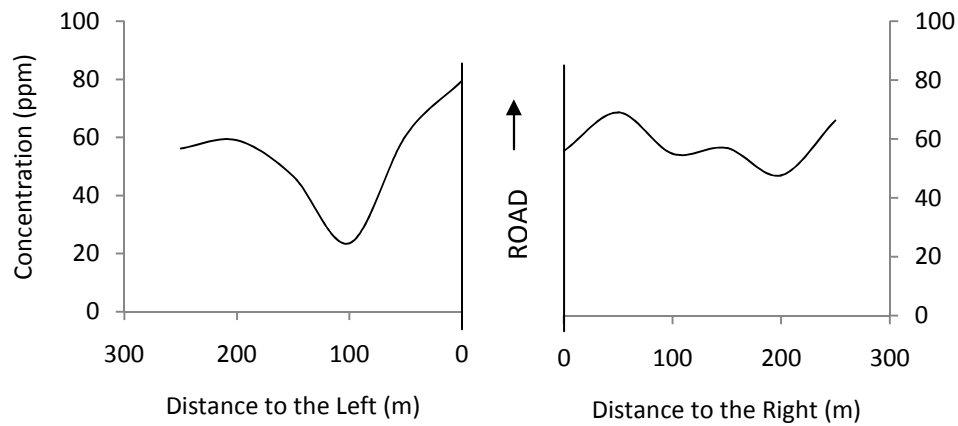


Fig. 5. Distribution of Arsenic from the Road at Shika 2

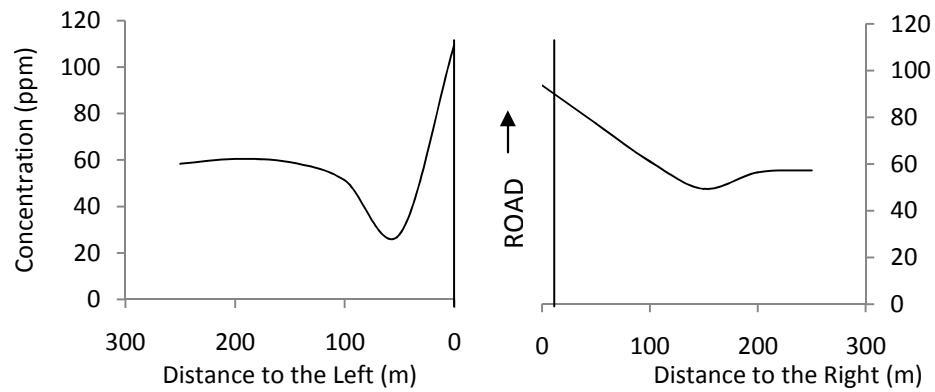


Fig. 6. Distribution of Arsenic from the Road at Giwa 1

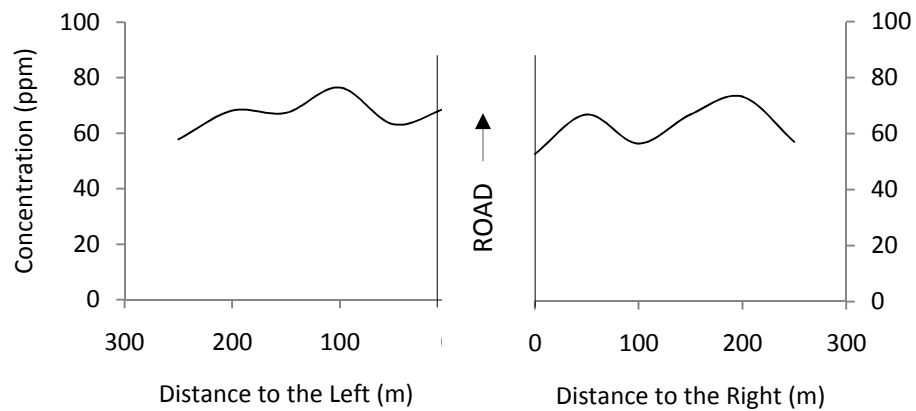


Fig. 7. Distribution of Arsenic from the Road at Giwa 2

In this work, EDXRF has again proved to be very useful in elemental determinations in geological samples. 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 32.3ppm with a mean of 25.3 ± 2.4 ppm. At the other stations concentration 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 concentration 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 below 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

210	Giwa 1	110.0	93.7
211	Giwa 2	69.2	52.7

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214 The concentration of arsenic from the road along the perpendicular transects,
215 though varied did not decrease exponentially with increase in distance from the road as
216 observed of lead in previous related works (Onojaet *al.*, 2013; Yan *et al.*, 2013, Ward *et*
217 *al.*, 1975); but rather existed with no particular trend, a result that agreed with that
218 reported by Englund, 2004. However, at Samaru, Shika 1, and Giwa 1, the element
219 showed initial decrease in concentration with distance from the road within the first
220 100m from the edge of the road. Along the parallel transects (table 1), the
221 concentrations of arsenic were not all highest by the edge of the road. This observation
222 further confirmed the fact that the distribution of the element did not take on any
223 particular pattern as the distance from the road increased. The occurrence of arsenic
224 above the background could therefore be linked with mixed sources, with the
225 application of pesticides as the most probable cause (Barringeret *al.*, 1998). The overall
226 ranking of the abundance of arsenic (As) in all the sample stations was: Giwa 1 (101.9
227 ppm) > Giwa 2 (80.7 ppm) > Shika 2 (67.7 ppm) > Shika 1 (32.1 ppm) > Samaru (29.5
228 ppm) > Kwangila (26.1 ppm).

229 **Conclusion**

230 The investigation being reported here have been able to reveal that arsenic
231 occurred above the background in the study area, but the concentration did not decrease
232 monotonically with increase in distance from the edge of the road. It could therefore be
233 concluded that the occurrence of the metal in the study area could be linked to

emissions 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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