Journal of
Agricultural, Food, and Environmental Sciences ISSN 1934-7235
Volume 1, Issue 2, 2007

Concentration and Speciation of Arsenic in South African Soil Contaminated by Historically Cattle Tick Dip Operations

Billy A. Moremedi, Student assistant, Department of Environmental, Water and Earth Sciences, Faculty of Science, Tshwane University of Technology, Private bag X680, Pretoria, South Africa. Email: MoremediBl@tut.ac.za

Jonathan O. Okonkwo, Professor, Research & Innovation, Department of Environmental, Water and Earth Sciences, Faculty of Science, Tshwane University of Technology, Private bag X680, Pretoria, South Africa. Email: OkonkwoOJ@tut.ac.za

Abstract

Concentration and speciation of arsenic in South African soil contaminated by historically cattle tick dip operations was determined. High total arsenic levels (1033-1369 mg/L) were detected in the soil. Two-Way ANOVA indicated a significant difference ($p<0.05$) between arsenic levels in soils obtained from the contaminated sites and control site (0.15 mg/L). A decrease in the total arsenic with increased depth was observed. The greatest arsenic value (1369 mg/L) was obtained at the surface, indicating that arsenic was still abundant at the surface even though the dip is no longer in operation. The total arsenic recorded for different depths were significantly higher than the target value of 40 mg/kg. The distribution of arsenic in the different fractions indicated that arsenic was mostly bound to Fe and Al hydroxides (21%) and in the residual fractions (52%). A low arsenic proportion was present in the most labile fractions, soluble (3%), exchangeable (14%) and carbonates (10%). The results obtained in the present study suggest that the study area is grossly contaminated by arsenic. This means that the site has the potential to contaminate groundwater over a period of time if no remediation or reclamation is carried out. However, the low total arsenic values obtained for the sites closer to the river suggest that arsenic movement towards the river has been slow. There is an urgent need, therefore, to conduct risk assessment of the site in order to ascertain the overall risk posed to the immediate environment, water resources and vegetation.

Introduction

Throughout most of the twentieth century, tick infestations on cattle were mainly controlled by chemicals, administered by plunge dipping or spraying, and more recently, in the form of parenteral injections and intra-ruminal boluses [16]. Arsenic was first used for tick control in South Africa in 1893 and since then, over a thousand cattle dipping vats were constructed throughout the country where arsenic was applied as the sodium salt of arsenous acid [2]. This may have resulted in soil contamination. The toxic nature of arsenic has prompted various studies on its environmental behaviour in grassland ecosystem [8], soils at cattle tick dips [9], sea [10], the areas surrounding metal smelters [14, 17], within soil/plant relationships [15] and exposure via potable water [21].

Upon the cessation of cattle the dipping programme in the late 1960s, disused vats were usually dismantled or they were allowed to colonize naturally with local plants and animals so that they eventually blend into the surrounding landscape. In other cases, the developed ecosystem, particularly, water resources are exposed to the toxic residue of the cattle tick dip substrate.
Development of rural areas containing cattle tick dips has triggered the need to assess the risk posed by arsenic contaminated sites. From the environmental point of view, it is important to assess the type, amount, mobility (since this can determine migration of metal from the

contaminated areas into water resources) and bioavailability of arsenic at these sites. Such data are helpful in developing strategies to manage risks associated with arsenic contaminated soil.

Determination of total metal concentration is important, but it does not differentiate between different metallic species, forms or phases; which determine the potential mobility and bioavailability of the metal. A comprehensive knowledge of interaction between the different species of the metal and environmental media such as soil is of importance in order to be able to predict their environmental impact. Sequential extraction techniques have been used to determine the concentration and the different species of arsenic and other elements in soil, sediment and street dust [6, 7, 11, 18, 20]. These studies attest that sequential extraction is still a much used extraction technique in elemental fractionation studies.

This study was conducted to establish the arsenic concentration in the soil and to assess the speciation of arsenic with the aim of establishing the pollution potential for mobilization of the metal from soil to water resources. This was conducted with the use of a single and sequential extraction techniques using contaminated soil samples from a historically cattle tick dip.

Materials and Methods

All glassware used were first soaked in dilute HNO_3, thoroughly rinsed with de-ionized water and dried in the oven at 100°C for 24 h. All reagents used in the present study were of analytical grade. Soil samples were taken at approximately 5 m intervals from the contaminated area as indicated in Fig. 1. Before collection, large objects such as stones were removed.

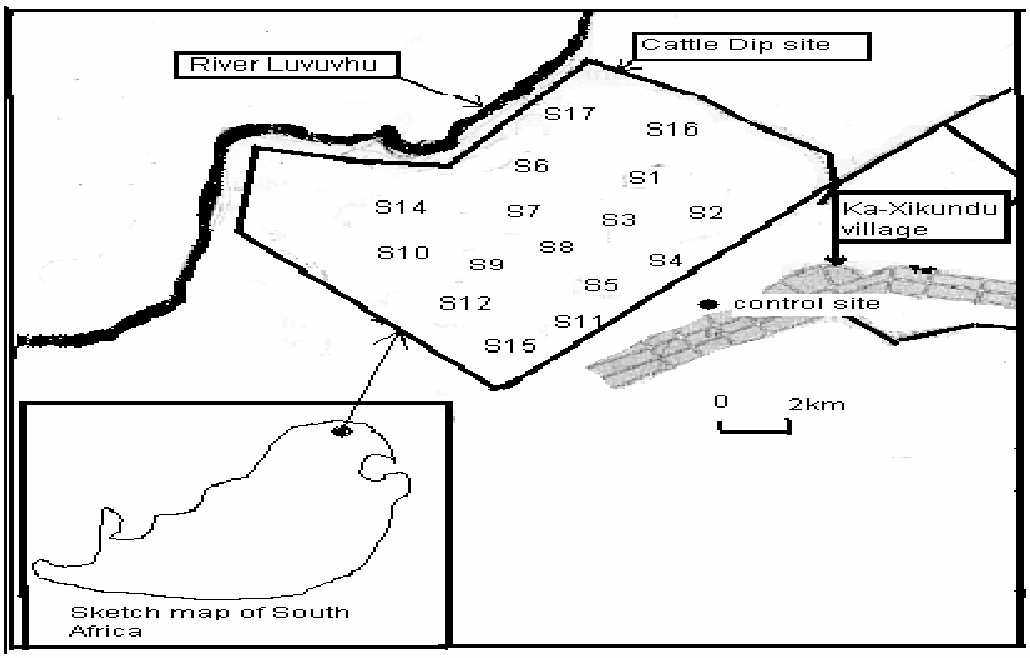

Fig. 1 Sketch map of the sampling sites

The samples (50 g from each sampling point) were collected at the surface, 5 and 10 cm depth with stainless steel and thoroughly cleaned trowel, placed in clean polyethylene bags, sealed and stored at 4°C in the laboratory until analysis. In order to avoid cross contamination during sampling, the trowel was cleaned after each sample. Soil was taken from a nearby control site (approximately 1km) which is within the same geological make-up was also sampled. Prior to use the samples were air dried for 48 h and homogenized using a mortar and pestle and then sieved through 1 mm sieve.

1 g and 10 g of air dried homogenized soil samples were added to 10 mL and 100 mL of de-ionized water, agitated for 1 h, filtered for pH and conductivity measurements respectively. Conductronic PC18 (IQ scientific instrument USA) was used for the measurement.

The sequential extraction method used was as described by Tessier et al [18] and modified by McLaren et al [11] for arsenic. The first extraction step involved leaching 2 g of the sample with de-ionized water, agitated for 24 h, and centrifuged at 3000 rpm. The supernatant was then decanted for soluble arsenic measurement. The precipitate obtained from the first step was subjected to 25 mL 0.5 M NaHCO treatment, agitated for 16 h, centrifuged for 5 min at 3000 rpm and the exchangeable arsenic determined in the supernatant. The precipitate was added to 25 mL 0.5 M NaOH, agitated for 16 h, centrifuged and the supernatant analyzed for Fe and Al bound hydroxides. The precipitate from the third step was treated with 25 mL of HCl (1.0 M) and agitated for 16 h, centrifuged and the supernatant analyzed for arsenic bound carbonate. The precipitate was thereafter treated with a mixture of 10 ml concentrated HF and 10 mL $HClO_4$ and heated to dryness at 120°C in a fume cupboard at room temperature. About 1 mL $HClO_4$ and 10 mL HF were added and heated again to near dryness at 120°C; and 1 mL $HClO_4$ added and heated (>120°C) until the appearance of white fumes. The precipitate obtained was dissolved in 12 M HCl and diluted to 25 mL de-ionized water and the concentration of residual arsenic determined in the solution.

To quantify total arsenic concentration, sieved soil samples were weighed (1.0 g) and subjected to a mixed acid digestion using hot HNO_3, H_2SO_4 and $HClO_4$ [11]. This method involved overnight digestion in HNO_3 at room temperature, followed by hot digestion at 120°C for 2 h. After cooling, 3 mL of $HClO_4$, (70%) and 1.25 ml of H_2SO_4 were added and the mixture heated gradually in a fume cupboard to 240°C and maintained for a further 2 h. The digested samples were thereafter cooled at room temperature, filtered through Whatman No 42 filter paper and the filtrates diluted to 25 ml with 7M HCl.

Analysis for arsenic was by hydride generation atomic absorption spectrometry [3, 4] with an instrument detection limit of 0.007 mg/L. Analysis was carried out in triplicate. The instrument was calibrated using 1% HNO_3 (Merck USA) solution as well as all the working calibration standards. For quality assurance, calibration and method blanks were prepared. Because of the unavailability of certified reference material, randomly selected samples were spiked with 1.0 mg/L of arsenic to validate the method suitability and sample preparation.

Microsoft EXCEL was used to calculate the means of each dataset. Dataset for arsenic concentration values were subjected to a Two-Way ANOVA using site and sample depth as effect terms. Where significant difference ($p<0.05$) were indicated, the least significant difference was calculated as described by Alder and Roessler [1]

Results and Discussion

The calibration of the instrument using different concentrations of arsenic standard gave a correlation coefficient of 0.97, and the percentage recovery of the spiked samples ranged between 80-120%. The high percentage recovery validated the method and sample preparation used in the present study. The results of the physical features, mineralogy, pH, conductivity and total arsenic are given in Table 1. As can be seen from Table 1, the pH is slightly alkaline a result of neutralization reaction of the calcite contents of the clay soil in the following reaction equation:

$$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$$

The observed high conductivity of the samples may suggest the occurrence of oxidation reactions. Two-Way ANOVA indicated significant differences ($p<0.05$) between the total arsenic values for the soils obtained from the contaminated sites versus control site. In addition, there is a general decrease in the total arsenic with increase in depth (Table 1). The highest total arsenic was obtained at the surface, indicating that arsenic is still abundant at the surface even though the dip is longer in operation. The total arsenic recorded for different depths are significantly higher than the target value of 40 mg/kg [5]. A similar study on the arsenic movement in cattle dip sites also recorded the highest arsenic concentration at 0-0.5 m, although the levels of total arsenic in the present study is higher than the values reported by Kimber et al [9]. The total arsenic concentrations reported in the present study are within the same range as reported by Milton and Johnson [13] in soil from a metalliferous mine tailings pond and far lower than values reported by Méndez and Armienta in soil from a tailings in Mexico [12].

Peak concentration of arsenic was recorded at the surface and this can be attributed to the high organic layer at this layer with a potent dung stench during sample collection. This may have adsorbed an appreciable amount of arsenic, in comparison to the lighter-cloured soil at the other depths. According to Thomas, a cattle dip vat sites that contain uncoated sand without clay or organics the arsenic is usually very mobile and consequently, the arsenic plume will be difficult to locate [19].

Table 1 Physical and chemical characteristics of soil from a historic cattle tick dip

Sampling depth cm	Physical features	Mineralogy	pH	Conductivity μS/cm ±SD	Total As (mg/kg)
			Mean values for all sites		
surface	Dark brown	clay/organic	7.7±0.2	1900±5.2	1369±12.4†
5	Light brown	clay	7.5±0.1	2130±9.3	1042±9.4†
10	Light brown	clay	7.3±0.3	2009±10.2	1033±7.2†
Control	Brown	loam soil	6.9±0.1	725±3.5	0.15±0.02‡

† significant (p<0,05)
‡ not significant

The total arsenic concentrations at different sampling sites are shown in Fig. 2. Sample sites 1-3 show even levels of arsenic. Thereafter, the level of arsenic dropped at sites 4 and 5. However, the level of arsenic increased at site 6 and peaked at 7 and thereafter the total arsenic was below 1000 mg/kg. The peak arsenic level at site 7 may suggest that most of the dipping may have taken place at this site. The very low levels of arsenic recorded for sites 16 and 17 suggest that the mobilization of arsenic has been slow, and therefore, the threat of runoff to water resources (River Luvuvhu) is low. It is worth noting that the total arsenic recorded for most of the sites are significantly higher than the target value of 40 mg/g [5].

The total arsenic values obtained at the surfaces of sites 1-14 are significant ($p<0.05$) except sites 16 and 17. At 5 cm depth the arsenic concentrations obtained at the following sites were found to be significant: 1, 2, 3, 6-12 and at 10 cm sites 1, 3, 7-9 and 11 exhibited significant ($p<0.05$) total arsenic concentrations.

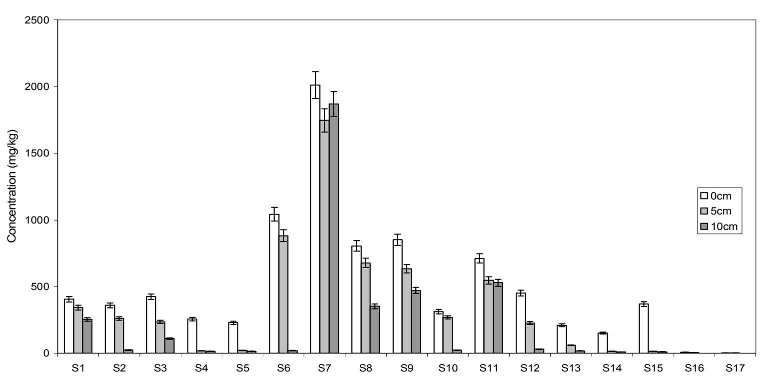

Fig. 2. Total arsenic concentrations in soil at different sampling sites taken from three depths (Error bars SEM n =3)

The speciation of arsenic in different fractions is shown in Fig. 3. Arsenic is mostly bound to Fe and Al hydroxides and in residual fractions. A low arsenic proportion was present in most labile fractions, soluble, exchangeable and carbonates. The residual fraction accounted for 52% of the total metal concentration. The overwhelming importance of this fraction illustrates clearly the difficulty in distinguishing between background and anomalous levels of trace metal contamination when only total metal analyses are performed. Similar percentage for arsenic, lead, cadmium, zinc and copper in soil and sediment samples respectively have been reported previously [12, 18].

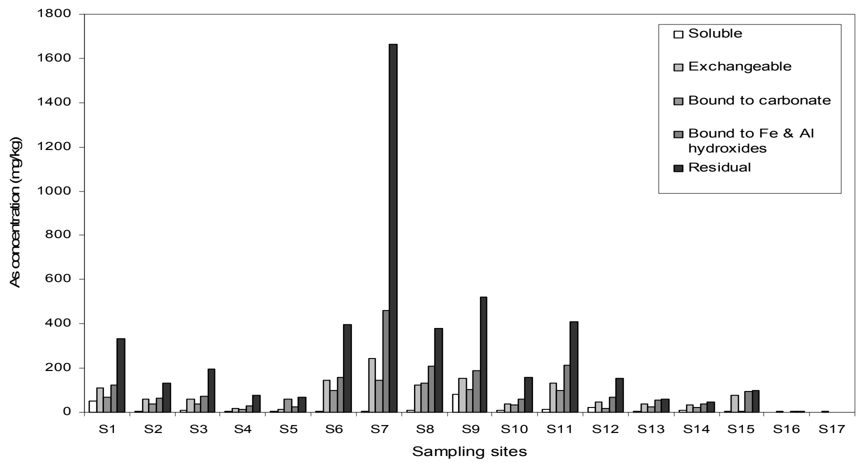

Fig. 3 Arsenic speciation in geochemical phases of soil from a historically cattle tick dip operation.

The percentages of arsenic in the hydroxide (21%) and carbonate (10%) fractions indicate that a portion of the arsenic released has been sorbed onto the Fe and Al hydroxide and on the carbonate. The exchangeable fraction accounted for 14% of the total arsenic concentration. According to Tessier et al [18], exchangeable metals are generally found to represent one of the minor fractions of the total metal concentration. That exchangeable fraction accounted for 14% of the total arsenic may suggest that arsenic existed in an oxidized form as arsenate, AsO_4^{3-}. Under this oxidizing condition, moderate leaching of arsenic will occur since arsenate is less mobile than arsenite, AsO_3^{3-}.

A previous study of cattle dipping vat sites found factors such as: hydrology of the site, Fe and Al hydroxide in the soil clay layers and the hydraulic conductivity of the soil can all influence the movement of arsenic [19]. These factors may have contributed to the results obtained in the present study.

Conclusion

The results obtained in the present study suggest that the study area is grossly contaminated by arsenic, with total arsenic levels higher than the target value, even though cattle tick dip operations stopped several years ago. However, the low total arsenic values obtained for the sites closest to the river suggest that arsenic movement towards the river has been slow. The adsorption of arsenic residues onto soil particles may appear as the more important transport mechanism than leaching. This is supported by the observed high association of arsenic with the residual fraction which has the ability to hold metals within its mineral crystal structure such as silicate minerals. Such mineral structure (although not determined in the present study) may hold arsenic within the crystal structure such that the release of arsenic may not be easy. It was also observed that the arsenic was predominantly in the arsenate, AsO_4^{3-} form which is less toxic than the arsenite, AsO_3^{3-}. A reclamation programme has been suggested in order to put this arsenic contaminated into better use.

Acknowledgements: The authors are indebted to the Department of Water Affairs and Forestry, South Africa, for assisting Mr Moremedi in sample collection.

References

1 Alder HI and Roessler EB (1976) Introduction to probability and statistics (6th Edn) Freeman, San Francisco (1979) p 426

2 Baker JAF (1982) Some thoughts on resistance to ixodicides by ticks in South Africa, Symposium on ectoparasites of cattle, 15-16 March 1982. South African Bureau of Standards, Pretoria, South Africa: 53-67.

3 Brooke PJ, Evans SJ (1981) Determination of total inorganic arsenic in fish, shellfish and fish products. *Analyst* 106: 514-520.

4 Crecelilius EA, Johnson CJ, Hofer GC (1974) Contamination of soils near a copper smelter by arsenic, antimony and lead. *Water, Air, soil Pollut* 3: 337-342.

5 Department of the Environment (1987) Interdeoartmental committee for the reclamation of contaminated land list of trigger concentrations for contaminantants. DOE, London.

6 Harrison, RM., Laxen, D.P.H and Wilson, S.J. (1981) Chemical Associations of Lead, Cadmium, Copper and Zinc in Street Dusts and Roadside Soils. *Environ. Sci. Technol*. 15: 1378-1383.

7 Hopke, PK. (1980) Multielemental Characterization of Urban Roadway Dust.*Environ. Sci. Technol.*, 14: (2) 164-172.

8 Jackson DR, Ausmus BS, Levin M (1979) Effeects of arsenic on nutrient dynamics of grassland microcosms and field plots. *Water, Air Soil Pollut* 11: 13-21.

9 Kimber SWL, Sizemore DI, Slavich PG (2002) Is there evidence of arsenic movement at cattle tick dip sites? *Aust J Soil Res* 40: 1103-1114.

10 Leah RT, Evans SJ, Johnson MS (1992) Arsenic in place (Pleuromoectes platessa) and whiting (Merlingus merlangus) from the North East Irish Sea. *Pollut Bull* 24: 544-549.

11 McLaren RC, Naidu R, Smith J (1998) Fractionation and distribution of arsenic in soils contaminated by cattle dip. *J Environ Qual* 27: 348-354.

12 Méndez M, Armienta MA (2003) Arsenic phase distribution in Zimapan mine tailings, Mexico. *Geofisica Intern* 42: 131-140.

13 Milton A, Johnson M (1999) Arsenic in the food chains of revegetated metalliferous mine tailings pond. *Chemosphere* 39 765-779.

14 Pilgrim W, Hughs RN (1994) Lead, cadmium, arsenic and zinc in the ecosystem surrounding a lead smelter*. Environ Monit Assess*, 32: 1-2

15 Sheppard SC (1992) Summary of phytotoxic levels of soil arsenic. *Water, Air soil Pollut* 64: 539-550.

16 Tatcheli RI, Easton E (1986) Ticks (Acariixodidea) ecological studies in Tanzania. *Bull Ento Res*, 76: 229-246.

17 Temple SN, Linzon L, Chai BL (1977) Contamination of vegetation and soil by arsenic emissions from secondary lead smelters. *Environ Pollut* 12: 311-320

18 Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate metals. *Anal Chem* 31: 844-851.

19 Thomas JE (1998) Distribution, movement and extraction of arsenic in selected Florida soils. PhD dissertation, University of Florida, 1998, 47-148.

20 Tokalioglu, S., Kartal, S. and Birol, G. (2003) Application of a Three-Stage Sequential Extraction Procedure for the Determination of Extractable Metal Contents in Highway Soils. *Tuk J. Chem.* 27: 33–346.

21 Valentine HK, Kang OT, Spivey G (1979) Arsenic level in human blood, urine and hair in response to exposure via drinking water. *Environ Res* 20: 24-32.