

Arsenic Status and Distribution in Soils at Disused Cattle Dip in South Africa

Jonathan Okechukwu Okonkwo

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Abstract The status and the distribution of arsenic in soils from a disused cattle dip were determined. Elevated total arsenic levels (1,033–1,369 mg/L) were detected in the soils. Significant difference ($p < 0.05$) between the values for the soils obtained from the contaminated sites and control site (0.15 mg/L) was observed. The level of total arsenic decreased with increase in depth. The peak total arsenic (1,369 mg/L) was obtained at 0 cm depth, indicating the abundance of arsenic at the surface despite the fact that the dip has been out of use for a long time. The total arsenic recorded for different depths were significantly higher than the trigger value of 40 mg/kg. The distribution of arsenic in the different phases showed that arsenic was mostly bound to the residual fractions (52%) and Fe and Al hydroxides (21%). The distribution of arsenic in the order phases was in the following order: exchangeable (14%), carbonates (10%) and soluble (3%).

Keywords Arsenic · Distribution · Soil · Cattle dip

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 (Tatcheli and Easton 1986). Arsenic was first used for tick control in South Africa in 1893 (Baker 1982). Between then and 1962, over a thousand cattle dipping vats were constructed throughout the country where arsenic was

applied as the sodium salt of arsenous acid. This may have resulted in soil contamination. The toxic nature of arsenic has prompted various studies on its environmental behaviour in grassland ecosystem (Jackson et al. 1979), the areas surrounding metal smelters (Crecelius et al. 1974; Temple et al. 1977; Pilgrim et al. 1994), within soil/plant relationships (Shephard 1992), potable water (Valentine et al. 1979) and soils at cattle dips (Kimber et al. 2002)

Upon the cessation of cattle dipping programme, disused vats are usually dismantled or they are allowed to decay naturally with local plants so that they eventually blend into the surrounding landscape. In other cases, the developed ecosystem, particularly, water resource is exposed to the toxic residue of the cattle dip substrate. From the environmental point of view, it is important to know whether, in this case, arsenic in the soil is potentially mobile or not since this can determine off-site migration of the metal from the contaminated area to, say, water resources. This study was conducted to first, establish the arsenic status of the soil at a disused cattle dip and secondly, to assess the pollution potential for mobilization of arsenic from soil to water resources. In this paper, the usefulness of sequential extraction method was evaluated using contaminated soil samples from a disused cattle dip.

Materials and Methods

All glassware used were thoroughly washed with soap, 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.

J. O. Okonkwo (✉)
Environmental, Water and Earth Sciences, Tshwane University
of Technology, 175 Nelson Mandela Avenue, Arcadia, Pretoria,
Gauteng 0001, South Africa
e-mail: OkonkwoOJ@tut.ac.za

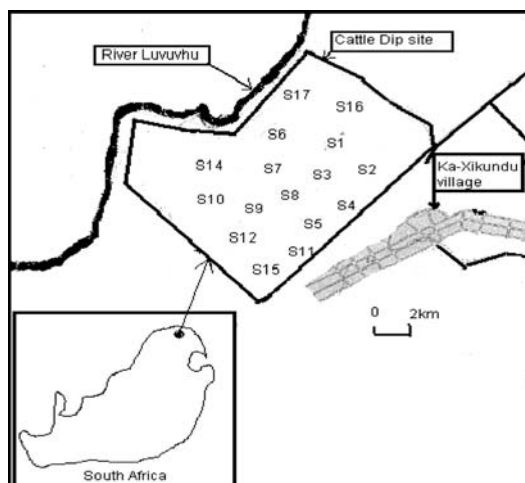


Fig. 1 Sketch map of the sampling sites

The samples (about 50 g from each sampling point) were collected at 0, 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 ready to use. In order to avoid cross contamination during sampling, the trowel was cleaned after each sample. A nearby control site which is within the same geological make-up was also sampled. Before use the samples were air dried for 48 h and thereafter, ground using mortar and pestle and then sieved through 1 mm sieve.

One gram and 10 g of air dried ground soil samples were added to 10 and 100 mL of de-ionized water, agitated for 1 h, filtered for pH and conductivity measurements respectively. Conductronic PC18 was used for the measurement.

The sequential extraction method used was as described by Tessier et al. (1979) and modified by McLaren et al. (1998) for arsenic. The first extraction step involved leaching 2 g of the sample with deionised water, agitated for 24 h and centrifuged at 3,000 rpm. The supernatant was collected for soluble arsenic measurement. The residue obtained from the first step was subjected to 25 mL 0.5 M NaHCO treatment, agitated for 16 h, centrifuged and the exchangeable arsenic determined in the supernatant. The residue 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 residue 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 residue was thereafter treated with a mixture of 10 ml concentrated HF and 10 mL HClO₄ and heated to dryness in a fume cupboard. About 1 mL HClO₄ and 10 mL HF were added and heated again to near dryness; and 1 mL HClO₄ added and heated until the appearance of white fumes. The residue obtained was dissolved in 12 M HCl

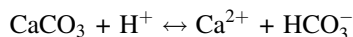
and diluted to 25 mL deionised water and the concentration of residual arsenic determined in the solution.

For total arsenic concentration, sieved soil samples were weighed (1.0 g) and subjected to a mixed acid digestion using hot HNO₃, H₂SO₄ and HClO₄ (Leah et al. 1992). This method involved overnight cold digestion in HNO₃, followed by hot digestion at 120°C for 2 h. After cooling, 3 mL of HClO₄, (70%) and 1.25 ml of H₂SO₄ 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 7 M HCl.

Analysis for arsenic was by hydride generation atomic absorption spectrometry (Brooke and Evans 1981) with an instrument detection limit of 0.007 mg/L. Analysis was carried out in triplicate. The instrument was calibrated using 1% HNO₃ (Merck) 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.

Results and Discussion

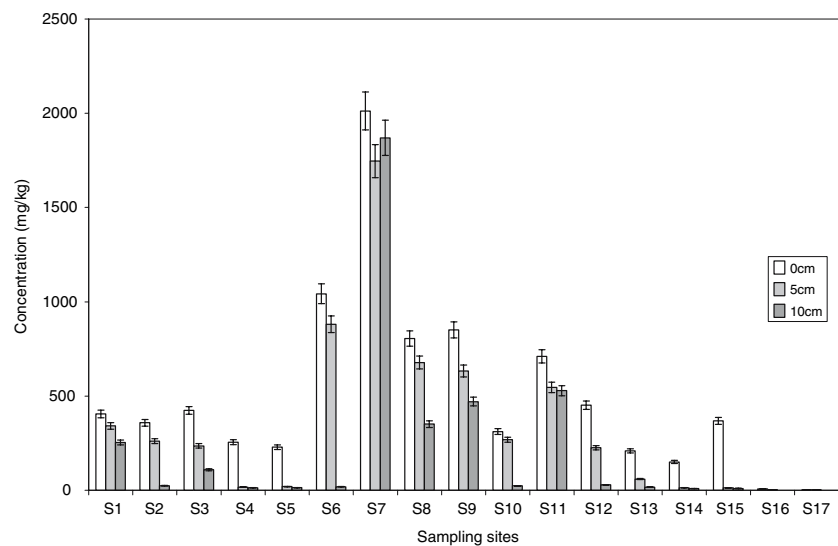
The calibration of the instrument using different concentrations of arsenic standard gave a correlation coefficient of 0.97, and the percentage recovery of the spiked samples ranged between 80–120%. The high percentage recovery validated the method and sample preparation used in the present study. The 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:



The observed high conductivity of the samples may suggest the occurrence of oxidation reactions. Two-way ANOVA indicated significant difference ($p < 0.05$) between the total arsenic values for the soils obtained from the contaminated sites and control site. Also from Table 1, there is a general decrease in the total arsenic with increase in depth. The highest total arsenic was obtained at 0 depth, indicating that reasonable amount of arsenic is still abundant at the surface considering the fact that the dip has been abandoned for a long time. The total arsenic recorded for different depths are significantly higher than the trigger value of 40 mg/kg (DOE 1987).

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

Sampling depth (cm)	Physical features	Mineralogy	pH	Conductivity ($\mu\text{S}/\text{cm} \pm \text{SD}$)	Total As (mg/kg)
0	Dark brown	Clay/organic	7.7 ± 0.2	$1,900 \pm 5.2$	$1,369 \pm 12.4$
5	Light brown	Clay	7.5 ± 0.1	$2,130 \pm 9.3$	$1,042 \pm 9.4$
10	Light brown	Clay	7.3 ± 0.3	$2,009 \pm 10.2$	$1,033 \pm 7.2$
Control	Brown	Loam soil	6.9 ± 0.1	725 ± 3.5	0.15 ± 0.02

Fig. 2 Total arsenic concentration from soil taken from three depths (*Error bars SEM = 3*)

The report by Kimber et al. (2002) 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 by far higher than the values reported by Kimber et al. (2002). The total arsenic concentrations reported in the present study are within the same range as reported by Milton and Johnson (1999) in soil from a metalliferous mine tailings pond but far lower than the values reported by Méndez and Armienta (2003) in soil from a tailings in Mexico.

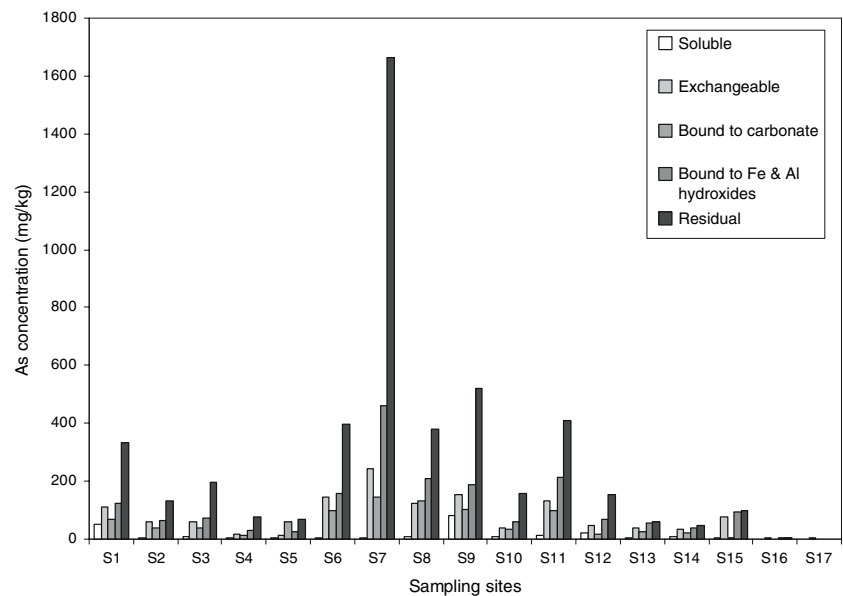
That the peak concentration of arsenic was recorded at 0 depth can be attributed to the high organic layer at this depth which was very obvious with dung stench during sample collection. This may have adsorbed an appreciable amount of arsenic, in comparison to the lighter-cloured soil at the other depths. According to Thomas (1998) a cattle dip vat sites that contain only uncoated sand, without clay or organics, the arsenic is usually very mobile and consequently, the arsenic plume will be difficult to locate.

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 1,000 mg/kg. The peak arsenic level at site 7 may suggest

that most of the spraying may have taken place at this site. The very low levels of arsenic recorded for sites 16 and 17 suggests that the mobilization of arsenic has been slow, and therefore, the threat to water resource (River Luvuvhu) is not imminent. It is worth noting that the total arsenic recorded for most of the sites are by far higher than the trigger value of 40 mg/g (DOE 1987).

The distribution of arsenic in different fractions is shown in Fig. 3. As can be seen from Fig. 3, arsenic is mostly bound to Fe and Al hydroxides and in the residual fractions. A low arsenic proportion was present in the most labile fractions, soluble, exchangeable and carbonates. The residual fraction accounted for 52% of the total metal concentration. This 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. Méndez and Armienta (2003) and Tessier et al. (1979) reported similar percentage for arsenic and lead, cadmium, zinc and copper in soil and sediment samples respectively. The percentage of arsenic in the hydroxide (21%) and carbonate (10%) fractions indicate that part 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.

Fig. 3 Arsenic distribution in geochemical phases of soil from a disused cattle dip



According to Tessier et al (1979), 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 study of cattle dipping vat sites by Thomas (1998) concluded that several factors such as: hydrology of the site, Fe and Al hydroxide found in the soil clay layers and the hydraulic conductivity of the soil can all influence the movement of arsenic. These factors may have contributed to the results obtained in the present study. The results obtained in the present study suggest that the study area is grossly contaminated with arsenic, with total arsenic levels higher than the trigger value. However, the low total arsenic values obtained for the sites closer to the river suggest that arsenic movement towards the river has been moderate. It was also observed that the arsenic was predominately in the arsenate, AsO_4^{3-} form which is less toxic than the arsenite, AsO_3^{3-} .

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