

Doi: [HTTPS://DOI.ORG/10.23910/IJBSM/2017.8.5.1829](https://doi.org/10.23910/IJBSM/2017.8.5.1829)

Fractionation and Speciation of Arsenic in Agricultural Soils in West Bengal, India

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Article History

Article ID: AR1829

Received in 18th July, 2017Received in revised form 19th September, 2017Accepted in final form 4th October, 2017

Abstract

Arsenic a toxic trace metalloid is of great environmental concern due to its presence in soil, water, plant and human continuum. Its high toxicity and increased appearance in biosphere has triggered public and political concern. Widespread arsenic (As) contamination in West Bengal, India is of great concern as it affects millions of people due to its toxicity. Arsenic in ground water, soil present as dissolved oxyanions namely arsenate and arsenite. Groundwater, when used for irrigation, helps entry of arsenic into the food chain via a soil-plant-animal continuum. In this study the extent of geo accumulation is measured in order to assess the degree of arsenic contamination in soil. A sequential fractionation study of arsenic revealed that out of all the fractions, the Fe/Mn bound arsenic has emerged to be most predominant fraction in all the experimental soils, sharing 38.2 to 73.3% of total soil arsenic recovered from the soils under study while the least proportions were retrieved from water soluble fractions. The variation in fractions may be attributed to the mineralogical make-up of soils along with some physicochemical factors. Arsenic speciation study showed that As-V appeared to be the major species while As (III) was found at a minor concentration.. The extraction efficiency of the selected reagent was observed to be substantially low in a number of soils as the majority of As is strongly bonded to Fe, Al and Mn particles of the soil.

Keywords: Arsenic, soil, fractionation, speciation

1. Introduction

Arsenic (As) is a widely occurring toxic metalloid in natural ecosystems. It is drawing global concern because of its indiscriminate contamination affecting millions in many countries including the state of West Bengal, India. The entry of arsenic into the soil-plant system occurs through either natural process of weathering of arsenic bearing rocks and/or use of arsenic-contaminated groundwater for irrigation, or else through a host of anthropogenic activities such as mining operations, smelting of base metal ores, Arsenic held by solid phases within the sediments, especially iron oxides, organic matter and sulphides may constitute the primary arsenic sources in groundwater under conditions conducive to arsenic release from these solid phases. These include abiotic reactions (oxidation/reduction, ion exchange, chemical transformations) and biotic reactions (microbial methylation) (Mok and Wai, 1994). Arsenic contamination in groundwater and elsewhere, causing human exposure, has been reported at different times from West Bengal, India and countries like U.S.A., U.K., Argentina, Chile, Mexico, Taiwan, Hungary, Finland, Inner Mongolia, Thailand, Ghana, China, Nepal and Bangladesh (Thornton and Farago, 1997). Arsenic-rich soil can affect human health by entering the food chain through plant uptake. The consumption of arsenic even at low levels

through the food chain may lead to carcinogenesis (Mandal and Suzuki, 2002). Among the different oxidation states of As, arsenite [As(III)] and arsenate [As(V)] are the main inorganic forms in most contaminated soils and sediments (Smith et al., 1999). According to the literature, As(III) is ten times more soluble, mobile and toxic than As(V) (Van Herreweghe et al., 2003). After a critical evaluation of the available literature, it was seen that most of the research outcomes were on total soil arsenic, as it reflects the geological origins of soils as well as the anthropogenic inputs. However, the use of arsenic total concentration as a criterion to assess the potential effects of soil contamination implies that all forms of a given element have an equal impact on the environment; such an assumption is clearly untenable (Tessier et al., 1979).

Therefore, fractionation of soil arsenic is an important tool of chemical characterization and can provide useful information on its bioavailability (McLaren et al., 1998). To the best of our knowledge, research on arsenic has mainly been focused on the transfer of As from soil to the major most common plants (or crops), considering highly As-contaminated soils (Ma et al., 2001; Lu et al., 2010). Nevertheless, most of the food consumption originates from crops grown in countryside agricultural fields that are not heavily contaminated with arsenic, but may contain meaningful concentrations of this



element, which may be harmful if transferred to the food chain.

A relatively simple method to estimate arsenic fractions of differential relative lability in soil is the chemical sequential extraction procedure. Laboratory studies on coupled transport of aqueous arsenic across and down the plugs/columns of soils from the affected zone revealed that the soils acted as effective sink for arsenic through accumulation and relative hold-up of arsenic from irrigation water contaminated with arsenic (Mukhopadhyay and Sanyal, 2002). Thus, a thorough understanding of soil-arsenic interaction is necessary in order to adjudge as to how good a sink the soil is or whether it can also act as a source of toxin. In course of several attempts to fractionate soil arsenic in different fractions, the 'freely exchangeable' arsenic (anion exchange resin-extractable arsenic) rather than total arsenic in soil, has been found to provide a satisfactory index of potential bioavailability and mobility, and hence phytotoxicity of arsenic in soil (McLaren et al., 1998). Furthermore, As in soil is predominantly associated with inorganic soil constituents. The organic forms of arsenic do not substantially contribute to the plant-available pool of As in soil. In such a background, the present study was undertaken to evaluate different fractions of As and their distribution in the arable soils, receiving arsenic-contaminated groundwater from shallow and deep tube-wells for irrigation.

2. Materials and Methods

Soil samples were collected from the areas, namely Ghentugachhi, Mitrapur, Mondalhut and Polba (District-Nadia, West Bengal, India) after a preliminary survey of the arsenic contamination. The first three sites were located within the arsenic-affected zone, whereas the last mentioned site was located within relatively less arsenic contaminated zone. The soil samples were air dried at room temperature to constant weight. The coarse litter and plant roots were carefully removed. The soil samples were then crushed carefully by hand and passed through a 2-mm sieve. These samples were stored into properly marked acid-washed container for further experiments. The important physico-chemical properties of the soils were determined following the standard methodologies.

2.1. Fractionation study

To fractionated different arsenic, by following the method of Tessier et al., 1979 a 1 g portion of each soil sample was treated sequentially with 20 ml of Water, 1 M NH_4OAc (pH 7.0), 1 M NaOAc , 0.4 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% acetic acid and 0.02 M HNO_3 (5 ml) and 10 ml of 30% H_2O_2 at 85 °C+15 ml of 3.2 M NH_4OAc in 20% HNO_3 (v/v) along with intervening washings at most of the stages with 8 ml of water. After addition of each extractant to the soil, contained in a 100ml tube, the soil-extractant mixture was shaken on a mechanical shaker and centrifuged to obtain clear extract. Sequential extraction of soil for determination of different fractions of arsenic has been done as per the method followed by Tessier et al., 1979.

2.2. Speciation study

All of the solutions were prepared with Mili-Q (Millipore, Bedford, MA, USA) water. For the speciation studies, standard

solution (100mg/l) of As compounds were prepared as follows: i) arsenite (NaAsO_2 , Perkin Elmer, USA) ii) arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, Perkin Elmer, USA) iii) monomethyl arsonate ($\text{CH}_3\text{AsNa}_2\text{O}_3$, Sigma-Aldrich Corp St. Louis, MO USA) iv) dimethyl arsenate ($(\text{CH}_3)_2\text{AsO}(\text{OH})$, Sigma) arsenobetaine (As B; Sigma) were dissolved in water.

All of the standard solutions were standardized with respect to As and kept at 4°C at dark until use. Dilutions of these standard solutions were prepared daily for analysis. Concentrated nitric acid and concentrated hydrochloride acid (Supra pure; Merck KGaA, Darmstadt, Germany) were used for the aqua regia digestion method. Orthophosphoric acid (Merck Chemical, 85% purity), was used for microwave extraction. A microwave digestion system (Multiwave 3000, Anton Par) with a rotor of 48 Teflon digestion vessels was used for sample digestion and extraction. We collected five agricultural soil samples from different location of arsenic affected area of West Bengal, India that have been exposed to contaminated irrigation water.

The EPA 3051 method was followed for sample digestion (method 3051, USEPA, 1997). For determining total arsenic in soil samples 0.5 g dried finely powered soil sample was weighed into a dry, clean teflon digestion vessel and 5 ml of aqua regia was added. The vessel was then closed, placed into the rotor. The loaded rotor was then placed into the microwave oven.

The microwave conditions for digestion were followed the sequence

Stage 1: Microwave power 1200W, 300PSI and ramp for 2 minute, Stage 2: microwave power 1200W, 300PSI and ramp for 3 minutes and Stage 3: 5 minute hold and cooling for 30 minutes.

The resultant digest was transferred to a 50 ml volumetric flask and analyzed for total arsenic through a Perkin Elmer ELAN DRcE 6100 ICP-MS. The 6100 was equipped with nickel cones, and the DRC was equipped with platinum cones. Sample introduction system components were similar for both instruments: a cyclonic spray chamber (GlassExpansion, Inc., West Melbourne, Australia) and a Meinhard® type A nebulizer. For speciation analysis selected soil sample and selected extractant solutions namely orthophosphoric acid (1M H_3PO_4 , pH 1.39) was taken to extract different species of arsenic from soil. About 0.5 g of dried finely powered soil sample and 10ml of extractant solutions was placed in a microwave teflon vessel and the mixture was maintained at 60W for 10 minutes. Then the mixture was transferred to a 50 ml volumetric flask for analysis in a HPLC hyphenated Perkin Elmer ELAN DRcE 6100 ICP-MS the LC-ICP-MS. For the isocratic method, a Perkin Elmer Series 200 Micro Pump was used instead of the quaternary pump. The isocratic mobile phase was 30 mM $\text{NH}_4\text{H}_2\text{PO}_4$ at pH 5.6. The flow rate was 1.0 mL/min with 100 μL sample injections. The effluent from the LC column was directly connected to the nebulizer with PEEK tubing (1.59 mm o.d.) and a low dead volume PEEK connector (Part No.:WE024375).

3. Results and Discussion



Physicochemical properties of soil: The soil samples selected for the study had a neutral soil pH (7.20-7.76). Soils are mostly silty clay in texture, low to medium in organic matter (oxidizable organic C ranges from 0.44–0.56%), low in available nitrogen (126.0–220.0 kg ha⁻¹), medium in available P₂O₅ (44.0–57.0 kg ha⁻¹) and moderate in available K₂O (142.0–190.0 kg ha⁻¹) content (Table 1).

Fractionation and speciation of arsenic: The experimental soils were characterized for different fractions of arsenic (both organic and inorganic fractions). In general, the Fe/

Mn bound As has emerged to be most predominant fraction in all the experimental soils, sharing 38.2 to 73.3% of total soil As recovered from the soils under study while the least proportions were retrieved from water soluble fractions. Such observation, however, are in quite good agreement with findings obtained earlier by (Saha and Sanyal, 2005) who reported the predominance of soil arsenic in iron bound forms in Bengal delta basin and several endemic areas of USA (Woolson et al., 1971). In some Florida soils contaminated with arsenical pesticides, soil arsenic was primarily found to be associated with the amorphous hydrous oxide-bound (Fe/Mn) fraction, ranging from 40 to 59% of the total recovery of the toxic metalloid (Gonzaga et al., 2008).

Chiang et al., 2010 have also reported high percentages of As in soil profiles remaining bound to amorphous Fe and Al oxyhydroxides and residual minerals in a seriously contaminated agricultural rice soils in the Guandu Plain, Taiwan. The other major soil As fractions appeared in an order of organically bound < water soluble < exchangeable < carbonate bound, with a very few exceptions noticed in control (non-contaminated Polba soil) and low-As contaminated (Mondalhut) soils where water soluble As fractions exceeded the exchangeable fraction (Table 2).

The observations were recorded in Table 3 showed that As-V appeared to be the major species while As (III) was found at a minor concentration. It indicates that Cl⁻ in sample did not interfere with the determination of As species. No methylated arsenic species were detected in these soils probably due to poor organic fractions and low microbial activity. In temperate regions with organic rich soils however contrasting findings were obtained. Giacomino et al., 2010 reported that AsV prevails over AsIII whereas more than 40% of total arsenic has been recovered in organic form. The study revealed that AsV was the predominant species in soil solution. However As III

Table 1: Physico-chemical properties of experimental soils

Properties	Ghentugachhi	Polba	Mitrapur	Mandalhut
pH	7.51	7.20	7.76	7.40
Organic C (%)	0.56	0.48	0.44	0.51
Textural class	Silty clay	Silty clay	Silty clay	Silty clay
%Sand	3.5	8.6	8.0	9.0
% Silt	46.7	42.9	44.6	46.9
% Clay	49.8	48.5	47.4	44.1
CEC c mol(p+) kg ⁻¹	24.1	30.2	22.1	17.1
Available nitrogen (kg ha ⁻¹)	220.0	200.0	178.0	126.0
Available phosphorus (kg ha ⁻¹)	57.0	44.0	46.0	54.0
Available potassium (kg ha ⁻¹)	190.0	156.0	162.0	142.0
Total arsenic (µg kg ⁻¹)	19400.9	7900.9	15300.3	11800.2

Table 2: Sequential extraction of arsenic to identify different arsenic fractions in the experimental soils (Tessier et al., 1979)

Extractants	Volume (ml)	Time shak- en (hr)	Forms of arsenic	Soil samples			
				S ₁	S ₂	S ₃	S ₄
				Arsenic extracted (mg kg ⁻¹)			
Water	20	0.5	Water soluble	0.21	0.28	0.40	0.11
1 M NH ₄ OAc (pH 7.0)	20	0.5	Exchangeable	0.25	0.39	0.13	0.03
1 M NaOAc	20	5.0	Carbonate bound	0.40	0.64	0.41	0.39
0.4 M NH ₂ OH.HCl in 25% acetic acid	20	6.0	Fe/Mn bound	2.80	2.21	1.07	0.36
0.02 M HNO ₃ (5 ml) and 10 ml of 30% H ₂ O ₂ at 85 °C+15 ml of 3.2 M NH ₄ OAc in 20% HNO ₃ (v/v)	30	2.0	Organically bound	0.16	0.15	0.13	0.05

S₁: Ghentugachhi soil; S₂: Mitrapur soil, S₃: Mondalhut soil; S₄: Polba soil

was detected in some soil samples. This may be due to the fact that the pH of the extracting solution influences the speciation of arsenic (AsIII, pka: 9.2 and AsV. Pka₁: 2.8, pka₂: 6.3, pka₃: 11.8) in soil and the phosphate (Pka₁: 2, pka₂: 7, pka₃: 12) in the extractant (Gallardo et al., 2001). This in turn impacts on the ion exchange between As species in soil and phosphate in the

extractant, leading to different recoveries for arsenic species from different soils. The extraction efficiency of the selected reagent was observed to be substantially low in a number of soils as the majority of As is strongly bonded to Fe, Al and Mn particles of the soil.

Table 3: Recovery of different arsenic species from experimental soils

Sample id	Extractant	Arsenic species					Sum of species (ppb)	Total As after aqua regia extraction (ppb)	Recovery (%)
		As B (ppb)	As III (ppb)	DMA (ppb)	MMA (ppb)	As V (ppb)			
Ghentugachhi soil	1M H ₃ PO ₄	n.d.	900.15± 14.17	n.d.	n.d.	13300.70± 122.75	14200.85± 136.91	19400.9± 205.53	73.29±1.48
Mitrapur soil	1M H ₃ PO ₄	n.d.	n.d.	n.d.	n.d.	7500.89± 145.18	7500.89± 145.18	15300.3± 163.66	49.50±0.51
Polba soil	1M H ₃ PO ₄	n.d.	n.d.	n.d.	n.d.	2700.88± 126.24	2700.88± 126.24	7900.9± 81.65	34.89±1.33
Mandalhut soil	1M H ₃ PO ₄	n.d.	300.37± 64.50	n.d.	n.d.	7900.29± 187.94	8200.66± 222.32	11800.2± 133.73	69.93±1.49

n.d.- Not detectable

4. Conclusion

Fe/Mn bound As has emerged to be most predominant fraction in all the experimental soils, sharing 38.2 to 73.3% of total soil As recovered from the soils under study while the least proportions were retrieved from water soluble fractions. Arsenic speciation study showed that As-V appeared to be the major species in soils under study while As (III) was found at a minor concentration.

5. Acknowledgement

This work was supported by the ICAR, NAIP (Component-4), Bidhan Chandra Krishi Viswavidyalaya, Kalyani, Nadia, West Bengal, India.

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