

Distribution of different inorganic forms of arsenic in selected arsenic affected soils of the Bengal Delta Basin

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Manuscript received 16 April 2004, revised 1 November 2004, accepted 19 January 2005

Inorganic soil arsenic (As) fractions from three representative arsenic affected surface soils of West Bengal, collected from Ambikanagar, Chakla, Iajpur (Block-Deganga, District-North 24-Parganas) as well as the control site at Gayespur (Block-Chakdah, District-Nadia), were fractionated into different soil arsenic pools by following the sequential extraction methodology. These soils were also subjected to extraction of As by using several individual extracts in order to adjudge their efficacy in extracting soil arsenic fractions. The findings suggested that the inorganic fractions of soil arsenic were in the order of $W\text{-As} < \text{Al-As} < \text{Ca-As} < \text{Fe-As}$. The Fe-As contributed 44.7% to 74.7% towards arsenic sequential sum. Soils of Iajpur had the highest sum of As fractions followed by those from Ambikanagar and Chakla. As regards the individual extractants used, the efficacy of the latter in extracting soil arsenic fell in the order, $(\text{NH}_4)_2\text{CO}_3 \approx \text{CH}_3\text{COONH}_4 < \text{Na}_2\text{CO}_3 < \text{NaHCO}_3 < \text{NaOH} = \text{NH}_4\text{F} < \text{HCl} + \text{H}_2\text{SO}_4 < \text{KH}_2\text{PO}_4 < \text{HCl} < \text{H}_2\text{SO}_4$. Among these extractants used, 0.5 N H_2SO_4 (pH 0.9) proved superior to others in releasing acidic and alkaline cation-bound arsenic in soils, while the 0.1 N NaOH (pH 13.0) also showed promise in releasing arsenic bound by the sesquioxides of the given soils, in agreement with the findings from the sequential extraction scheme followed in these soils. A careful perusal of these results suggested that iron components played dominant role in facilitating accumulation of arsenic in these soils.

Arsenic (As), a toxic trace element, is of great environmental concern due to its presence in soil, water, plant and animal continuum. Arsenic in terrestrial environment may have had its origin in natural and anthropogenic sources. Arsenic contamination of groundwater in the Gangetic alluvial zones of West Bengal has assumed the proportion of a drinking water-related disaster in recent years with reports of arsenic related health hazards for millions of people¹.

Soil, though an important sink for arsenic, may nevertheless facilitate its access to plant through leaching, methylation or erosion. The clay fraction, iron and aluminium oxide and organic carbon pool in soil have frequently been implicated in the sorption of different species of arsenic by soils². Sequential extraction of soil arsenic helps one to differentiate between arsenic that is readily labile and accessible to plant uptake, and that which is bound strongly by the soil components in soil matrix.

The toxicity of arsenic compounds in groundwater/soil environment depends largely on its oxidation state, and hence on redox status and pH, as well as whether arsenic is present in organic combinations¹. The toxicity follows the order : arsine [AsH_3 ; valence state of arsenic (As) : -3].

> organo-arsine compounds > arsenites (As^{3+} form) and oxides (As^{3+} form) > arsenates (As^{5+} form) > arsonium metals (+1) > native arsenic metal (0). The arsenites are much more soluble, mobile, and toxic than arsenates in aquatic and soil environments.

The objective of the present investigation was to study the various inorganic As fractions in selected arsenic-affected soils and also the efficiency of different extractants to extract arsenic from these soils. While doing so, the standard sequential extraction scheme was employed³, which, however, measures the total arsenic loading in different fractions of soil pools, *irrespective* of the valency state of inorganic arsenic species in soil, *notwithstanding* what is stated above. We have also determined the total arsenic content in different fractions of the given soils following such standard procedure, without attempting any speciation.

Results and discussion

The physico-chemical properties of four surface soils indicated that the soil reaction (pH) was neutral to slightly alkaline, ranging from 7.2 to 7.7, while the organic carbon varied from 6.8 to 18.9 g/kg (Table 1). The cation exchange

Note

Table 1. Important physico-chemical properties of the experimental soils

Soil taxonomy	Gayespur	Ambikanagar	Chakla	Iajpur
	Typic Haplustepts	Typic Haplaquepts	Typic Haplaquepts	Typic Haplaquepts
Sand (%)	16.2	18.5	55.7	17.3
Silt (%)	58.6	50.4	32.2	66.6
Clay (%)	21.2	31.1	12.1	16.1
Texture	Silty clay loam	Silty clay loam	Sandy loam	Silty loam
pH (1 : 2.5)	7.25	7.42	7.85	7.77
EC (1 : 5) (dS/m)	0.33	0.30	0.38	0.60
Organic C (g/kg)	6.80	11.6	11.2	18.9
Specific surface area (m ² /g)	86	107	69	82
Amorphous Fe (%)	0.25	0.43	0.32	0.61
Amorphous Al (%)	0.24	0.39	0.31	0.29
CEC [cmol(p ⁺)/kg]	12.5	15.6	17.2	16.7
Exchangeable cations [cmol(p ⁺)/kg]				
Na	0.50	0.13	0.16	0.14
K	0.30	0.46	0.32	0.30
Ca + Mg	11.8	14.7	16.3	16.0
Olsen extractable (mg/kg)				
As	0.63	2.90	6.50	19.4
P	39.2	40.0	38.0	37.0

Table 2. Sequential extraction of arsenic (mg/kg) by extractants to identify inorganic arsenic fractions in the experimental soils

Extractant	Volume/ ml	Time shaken/ h	Soil sample			
			Gayespur	Ambikanagar	Chakla	Iajpur
1 N NH ₄ Cl	100	0.50	0.10	0.66	0.36	0.75
0.5 N NH ₄ F	100	1.00	0.24	1.12	1.25	0.81
Sat. NaCl	25	0.25	0.005	0.10	0.13	0.31
Sat. NaCl	25	0.25				
0.1 N NaOH	100	18.0	1.44	6.63	5.52	7.42
Sat. NaCl	25	0.25	0.006	0.11	0.13	0.18
Sat. NaCl	25	0.25				
0.5 N NH ₄ F	100	1.00	0.003	0.47	0.23	0.19
Solvent-extractable soil arsenic fractions						
NH ₄ Cl ext. As (Ws-As)*			0.10 (5.15)**	0.66 (4.37)	0.36 (4.28)	0.75 (4.54)
NH ₄ F ext. As (Al-As)*			0.25 (12.9)	1.69 (11.2)	1.61 (19.2)	1.31 (7.94)
NaOH ext. As (Fe-As)*			1.45 (74.7)	6.80 (45.0)	5.67 (67.5)	7.54 (45.7)
H ₂ SO ₄ ext. As (Ca-As)*			0.14 (7.22)	5.99 (39.7)	0.76 (9.05)	6.88 (41.7)
Sum of arsenic-fractions			1.94	15.1	8.40	16.5

*Ws-As : Water soluble As; Al-As : Al-bound As; Fe-As : Fe-bound As; Ca-As : Ca-bound As.

**The numbers in the parentheses denote the percent loading of each arsenic fraction in the present soils.

capacity of these soils ranged from 12.5 to 17.2 cmol (p⁺)/kg. Generally two types of textural variations (silty clay loam and sandy loam) were noted in these soils where the clay content varied from 12.1 to 31.1%. As regard the

exchangeable cationic composition, the exchangeable sodium plus potassium content was the highest in Gayespur soil, while the lowest in Iajpur soil, whereas the exchangeable calcium plus magnesium content was maximum in

Chakla soil and lowest in Gayespur soil. The soil loading of the acid cationic components, mainly iron and aluminium oxides, in their amorphous state, was in the following order (Table 1) :

Gayespur (0.25% + 0.24%) < Chakla (0.32% + 0.31%) < Ambikanagar (0.43% + 0.39%) < Iajpur (0.61% + 0.29%).

Table 3. Individual solvent extraction of As (mg/kg) from the experimental soils

Extractants	Arsenic extracted (mg/kg)			
	Gayespur	Ambikanagar	Chakla	Chakla
1 M CH ₃ COONH ₄	ND ⁺	ND	ND	ND
0.5 M NH ₄ F (pH 8.2)	0.98	4.17	4.88	4.60
0.5 M NaHCO ₃ (pH 8.5)	0.34	2.74	0.872	2.78
0.5 M Na ₂ CO ₃ (pH 11.7)	ND	0.655	0.822	1.03
0.1 N NaOH (pH 13.0)	1.70	5.09	1.06	4.25
0.05 N HCl + 0.025 N H ₂ SO ₄ (pH 1.2)	1.07	1.41	1.07	2.33
0.5 M HCl (pH 0.7)	0.72	3.06	2.26	3.86
0.5 M KH ₂ PO ₄ (pH 4.5)	0.65	3.27	1.53	3.31
0.5 N H ₂ SO ₄ (pH 0.9)	2.10	10.15	5.30	15.33
0.5 M (NH ₄) ₂ CO ₃ (pH 8.9)	ND	ND	ND	ND

⁺ND : Not detectable.

The different fractions of As, viz. water soluble (Ws-As), Al bound (Al-As), Fe bound (Fe-As) and Ca bound (Ca-As) fractions in the given surface soils were sequentially extracted as stated above, and the following trend was observed : NH₄Cl ext. As (Ws-As) < NH₄F ext. As (Al-As) < H₂SO₄ ext. As (Ca-As) < NaOH ext. As (Fe-As) (Table 2) excepting Gayespur soil where the calcium-bound arsenic was lower than the aluminium-bound arsenic pool (Table 2).

In general, iron bound arsenic was found high, contributing about 45.0 to 74.7% to the total soil As fractions. In terms of the absolute amounts, the soils of Iajpur had the highest Fe-bound arsenic fraction, followed by Ambikanagar and Chakla (Table 2). Gayespur soil being the control site, showed such arsenic fraction in lowest proportion. There is a good correlation between amorphous iron content of these soils and the iron-bound arsenic in these soils ($r = 0.830$). Similar observations were also reported by several workers^{2,3}. Hence the relatively large amount of these reactive As fractions in soil would facilitate the accumulation of the toxin in these soils which thereby act as effective sink for As. Also the Olsen extractable arsenic loading in these soils (Table 1) was highly and positively correlated with the soil attributes, namely pH ($r = 0.697$), EC ($r = 0.979^*$), organic C ($r = 0.956^*$), CEC ($r = 0.617$) and amorphous Fe content ($r = 0.880$), whereas negatively correlated with Olsen P ($r = -0.874$).

The efficiency of the individual extractants to extract soil As followed the order (Table 3) :

(NH₄)₂CO₃ ≈ CH₃COONH₄ < Na₂CO₃ < NaHCO₃ < NaOH ≈ NH₄F < HCl + H₂SO₄ < HCl < H₂PO₄ < H₂SO₄.

Thus, 0.5 N H₂SO₄ (pH 0.9) seemed to be the best extractant for soil As in the given soils (Table 3). This may possibly be attributed to the dissolution of soil minerals, chiefly iron and aluminium sesquioxides, at this low pH, thereby releasing large amounts of arsenic held by these components. Besides the acidic extractants used, ammonium fluoride (0.5 M NH₄F, pH 8.2) appeared to be another useful extractant, possibly by virtue of its dissolving the Fe- and Al-bound As fractions (in soil) which are relatively dominant fractions in the arsenic affected alluvial soils of the Bengal delta basin. Further, the 0.1 N NaOH (pH 13.0) showed promising results as it also dissolves the iron- and aluminium-bound fractions. Thus, the given acidic extractants, and to some extent, the alkaline extractants used proved efficient in extracting soil arsenic fractions.

The present study suggested that arsenic in the given soils was present chiefly in forms held by oxides and oxyhydroxides of Fe. Along with this, the soil organic matter pool also tended to contribute towards such arsenic retention in soils under study. The latter turned out to be a function of soil pH as well. As regards the individual extractants, 0.5 N H₂SO₄ (pH 0.9) seemed to be the best one in releasing arsenic through partial dissolution of iron and aluminium sesquioxides which are effective binders of arsenic oxyanions in soil. The Olsen extractable arsenic, another important indicator of plant-extractable pool of soil arsenic, was, however, generally low in these soils.

Experimental

For the present study, three surface (0–0.20 m) soil samples were collected from arsenic affected areas of the Deganga Block (namely Ambikanagar, Chakla and Iajpur) of North 24-Parganas District of West Bengal, while another soil sample was obtained from an arsenic unaffected area (namely Gayespur, Chakdaha Block of Nadia District, West Bengal). Several relevant physico-chemical properties of these soil samples were measured by following the standard methodologies.

Soil pH was measured in 1 : 2.5 (w/v) soil-water mixture using a combined electrode⁴. Organic carbon in soils was determined by the Walkley and Black method⁵. Soil clay content was determined by the Buoycos hydrometer method⁶. Amorphous iron and aluminium fractions were extracted with 0.3 M ammonium oxalate, pH 3.25⁷. Iron and aluminium in these soil extracts were determined by employing Atomic Absorption Spectrophotometry. The other chemical properties of the given soil samples like EC, total nitrogen, calcium and magnesium and available phosphorus were measured by following the standard proce-

Note

dures⁴. The specific surface area of the soil samples was measured by the ethylene glycol retention method⁸.

To fractionate the inorganic soil arsenic pools, a five g portion of each soil sample was treated sequentially with 100 ml of 1 N NH₄Cl, 0.5 N NH₄F, 0.1 N NaOH and 0.5 N H₂SO₄ along with intervening washings at most of the stages with saturated NaCl, in order to extract, respectively, water-soluble As fraction, As associated with Al components, As associated with Fe components, and that associated with Ca components in soil³. After addition of each extractant to the soil, contained in a conical flask, the soil-extract mixture was shaken on a reciprocating shaker. The actual sequence of extractions, washings and shaking times are given below :

Extractant used	Volume/ml	Time shaken/h
1 N NH ₄ Cl	100	0.50
0.5 N NH ₄ F	100	1.00
Sat. NaCl	25	0.25
Sat. NaCl	25	0.25
0.1 N NaOH	100	18.0
Sat. NaCl	25	0.25
Sat. NaCl	25	0.25
0.5 N H ₂ SO ₄	100	1.00
Sat. NaCl	25	0.25
Sat. NaCl	25	0.25
0.5 N NH ₄ F	100	1.00

Individual soil extractions were performed by shaking for two hours five g soil with 100 ml of each of the nine extractants [0.5 M NH₄F, pH 8.2; 0.5 M NaHCO₃, pH 8.5; 0.5 M (NH₄)₂CO₃, pH 8.9; 0.5 M Na₂CO₃, pH 11.7; 0.1 N NaOH, pH 13.0; 0.5 N HCl + 0.025 N H₂SO₄, pH 1.2; 0.5 M HCl, pH 0.7; 0.5 M KH₂PO₄, pH 4.5 and 0.5 N H₂SO₄, pH 0.9] to detect the efficiency of the latter to extract soil arsenic fractions. The arsenic content in various extracts was measured by employing an atomic absorption spectrophotometer (Model : GBC 932B) coupled with a hydride generator unit (Model : HG 3000).

Finally the simple linear correlation analysis of different arsenic fractions with relevant physicochemical properties of the experimental soils was performed by the standard statistical procedure⁹.

Acknowledgement

The authors would like to thank the State Water Investigation Directorate, Government of West Bengal and the Indian Council of Agricultural Research, New Delhi for providing the financial support during the entire course of the study.

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