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## Evaluation of inorganic fractions of arsenic in relation to soil properties in affected areas of West Bengal, India

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Inorganic soil arsenic (As) in three soils was fractionated adopting phosphorus fractionation schemes. Among these fractions, iron-bound arsenic (Fe-As) was found highest, followed by aluminium-bound arsenic (Al-As). The freely exchangeable arsenic was relatively small compared to the arsenic held by internal surfaces of soil aggregates. The arsenic fractions exhibited positive correlation with phosphorus content presumably due to the fact that high P in soil releases more arsenic from soil adsorption sites owing to the competition for the same adsorption sites. Predominantly, negative correlation of arsenic with organic carbon confirms the fact of lowering of arsenic mobility in presence of organics in soil.

**Keywords:** Arsenic fractions, arsenic extractants, soil properties, resin extractable arsenic.

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, combustion of coal and application of arsenicals as agricultural pesticides<sup>1–5</sup>.

Arsenic is the twentieth abundant element in the earth's crust<sup>1</sup>. It is distributed in soils in various forms associated with different soil constituents, namely iron, aluminium, calcium compounds, etc. forming varieties of compounds having different solubility and mobility in soil–water system<sup>6</sup>. Arsenic is also present in soil in adsorbed phases on clays, ferromanganese oxides and organic matter<sup>7</sup>. The amount of plant available arsenic is very limited compared to the total arsenic content in soil<sup>8</sup>. Thus, the total concentration of As in soil may be a good indicator of the degree and extent of contamination but is insufficient for evaluation of its environmental impact without considering the speciation<sup>9</sup>. Therefore, the

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fractionation of different forms of arsenic from soil using sequential extraction protocol was used to assess the abundance of the different forms in which arsenic is associated in order to estimate the distribution and bioavailability of arsenic.

Arsenic fractionation which is indeed extraction of arsenic from different soil solid pools can be performed by using different reagents, having varying dissolution capacity, sequentially. Several attempts have been made to fractionate soil arsenic in various forms. Although there are a large number of sequential extraction procedures available for metal cations, there are very few studies on oxyanions such as those of As. Arsenic chemistry in soil closely parallels phosphorus chemistry, particularly in respect of its association with hydrated Fe/Aloxides<sup>10</sup>. Therefore, often the fractionation schemes in usage for soil phosphorus have been used to fractionate As from soil<sup>11</sup>. In the 1970s, researchers used the adaptation of the Chang and Jackson's<sup>12</sup> soil phosphorus fractionation procedure to explore arsenic chemistry in contaminated soils<sup>13</sup>. However, the applicability of sequential extraction schemes, designed for transitional metals, in fractionating soil arsenic has been questioned<sup>14</sup>. Some attempts were made to fractionate arsenic into different soil arsenic pools, namely water soluble arsenic, arsenic associated with Al compounds in soil, the so-called aluminium-bound arsenic, iron-bound arsenic and calcium-bound arsenic, by following the sequential extraction methodology as proposed by Johnston and Barnard<sup>13</sup> in selected arsenic-affected soils of West Bengal, India<sup>15</sup>. In recent years, the limitations of Chang and Jackson's procedure in regard to interpretational problems for soil phosphorus, and hence of soil arsenic has been pointed out. McLaren et al.14 had recourse to an alternative phosphorus fractionation scheme to fractionate arsenic from soils contaminated with cattle dip sites. These authors noted that anion exchange membrane resin-extractable arsenic might provide a satisfactory index of potential arsenic bioavailability and mobility, and hence its toxicity. 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 inorganic fractions of As with respect to soil properties in the arable soils, receiving arsenic-contaminated groundwater from shallow and deep tube-wells for irrigation, by way of employing two fractionation schemes, proposed by Johnston and Barnard<sup>13</sup> and McLaren *et al.*<sup>14</sup>. The extractability of arsenic by different individual extractants was also ascertained.

Surface (0–0.15 m) soil samples were collected from the areas, namely Nonaghata Uttarpara, Mollabelia (Haringhata Block, District-Nadia, West Bengal, India) and Kalyani (Sub-Division, District-Nadia, West Bengal, India) after a preliminary survey of the arsenic contamination in irrigation water. The first two sites were located within the arsenic-affected zone, whereas the last mentioned site was located within relatively less arseniccontaminated zone. The first site was a shallow tube-well (STW) (100-120 feet) dominated highly arseniccontaminated zone, whereas the second one was a deep tube-well (DTW) (>400 feet) command area with relatively lower As contamination. The soil samples were airdried 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<sup>16,17</sup>. The available pool of soil arsenic was extracted using Olsen extractant (0.5 M NaHCO<sub>3</sub>, pH 8.5). For estimation of total arsenic, the soil samples were digested on a sand bath with tri-acid mixture (HNO<sub>3</sub>:  $H_2SO_4$ : HClO<sub>4</sub>:: 10:1:4, by volume). The arsenic content in both the soil digest and the soil extracts was measured employing the atomic absorption spectrophotometer coupled with a hydride generator (AAS-HG) unit (Model: GBC 932B and HG 3000; GBC Scientific Equipment, Australia). For QA/QC (quality assurance/quality control) programme for analysis of arsenate in AAS-HG, standard reference material (170303 Arsenate ICP standard traceable to SRM from NIST H<sub>3</sub>AsO<sub>4</sub> (1000 mg/l) in HNO<sub>3</sub> 2-3% As CertiPUR®; Merck, Germany) was used.

To fractionate the inorganic arsenic, by following the method of Johnston and Barnard<sup>13</sup>, a 5 g portion of each soil sample was treated sequentially with 100 ml of 1 N NH<sub>4</sub>Cl, 0.5 N NH<sub>4</sub>F, 0.1 N NaOH and 0.5 N H<sub>2</sub>SO<sub>4</sub>, along with intervening washings at most of the stages with saturated NaCl. After addition of each extractant to the soil, contained in a conical flask, the soil-extractant mixture was shaken on a reciprocating shaker. The actual sequence of extractions, washings and shaking times are given in Table 1.

Following shaking, each sample was immediately centrifuged for 10 min at 2000 rpm and the supernatant decanted into another conical flask; the remaining solid

Tab	le 1	<b>l.</b> /	Actual	sequence	of	extractio	ns,	time	of	wasł	ning	and	sha	kin	g
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Extractant	Volume/ml	Time shaken/h
1 NH <sub>4</sub> Cl	100	0.5
0.5 N NH <sub>4</sub> F	100	1.0
Saturated NaCl	25	0.25
Saturated NaCl	25	0.25
0.1 NaOH	100	18.0
Saturated NaCl	25	0.25
Saturated NaCl	25	0.25
0.5 N H <sub>2</sub> SO <sub>4</sub>	100	1.0
Saturated NaCl	25	0.25
Saturated NaCl	25	0.25
0.5 N NH <sub>4</sub> F	100	1.0

		I I I I I I I I I I I I I I I I I I I						
	Soil samples							
	Mollabelia	Nonaghata	Kalyani					
Soil taxonomy	Typic haplustepts	Typic haplustepts	Typic haplustepts					
Sand (%)	16.2	14.2	18.4					
Silt (%)	45.1	53.2	44.4					
Clay (%)	38.7	32.6	37.2					
Texture	Silty clay loam	Silty clay loam	Silty clay loam					
pH (1:2.5)	6.12	6.85	7.12					
EC $(1:2.5)$ (dS m <sup>-1</sup> )	0.28	0.36	0.27					
Organic C (g kg <sup>-1</sup> )	6.94	3.25	3.62					
Specific surface area $(m^2 g^{-1})$	112	121	90					
Amorphous Fe (%)	0.26	0.25	0.22					
CEC $[\text{cmol} (p^+) \text{kg}^{-1}]$	22.6	23.4	20.2					
Exch. Na $[\text{cmol}(p^+) \text{kg}^{-1}]$	0.21	0.14	0.11					
Exch. K [cmol $(p^+)$ kg <sup>-1</sup> ]	0.26	0.45	0.23					
Exch. Ca + Mg $[\text{cmol}(p^+) \text{ kg}^{-1}]$	7.90	7.65	13.2					
Total arsenic (mg $kg^{-1}$ )	7.22	14.7	2.69					
Olsen extractable As (mg kg <sup><math>-1</math></sup> )	1.98	3.85	0.39					
Olsen extractable P (mg kg <sup><math>-1</math></sup> )	48.9	56.2	52.6					

 Table 2.
 Physicochemical properties of the experimental soils

residue was then treated with the next extractant or washing.

In another fractionation method, proposed by McLaren et al.<sup>14</sup> to fractionate the inorganic arsenic, a 2 g portion of each soil sample was taken in a polypropylene centrifuge tube in a suspension with 30 ml of deionized water. Five gram of anion exchange resin was taken in a dialysis paper bag, which was immersed in the suspension. The latter was shaken for 24 h, and then centrifuged, followed by filtration. The anion exchange resin, with its adsorbed (exchanged) arsenic load, was extracted with 30 ml of 0.1 M HCl. The soil residue was re-suspended in 30 ml of NaHCO<sub>3</sub> (0.5 M, pH 8.5) and shaken for 16 h. The supernatant was collected and kept for analysis. The residual soil was again re-suspended in 30 ml of 0.1 M NaOH and shaken for 16 h with the simultaneous collection of the supernatant for analysis. After such extraction with NaOH, the soil residue was sonicated by using an ultrasonic probe (Branson sonifier operated at 20 kHz) for 3 min in 0.1 M NaOH solution. The system was centrifuged and the supernatant solution was filtered through Whatman No. 42 filter paper. Once again, the soil residue was treated with 30 ml of 0.1 M HCl solution and shaken for 16 h. The supernatant solution was collected and the residual soil was finally digested with the tri-acid mixture of HNO<sub>3</sub>, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> in the ratio of 10:1:4 by volume. The supernatant and the centrifuged solution from each corresponding step were collected separately and the arsenic content of each such solution was measured by using the atomic absorption spectrophotometer, coupled with the hydride generator.

Nine extractants (0.5 M NH<sub>4</sub>F, pH 8.2; 0.5 M NaHCO<sub>3</sub>, pH 8.5; 0.5 M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, pH 8.9; 0.5 M Na<sub>2</sub>CO<sub>3</sub>, pH 11.7; 0.1 N NaOH, pH 13.0; 0.5 N HCl + 0.025 N H<sub>2</sub>SO<sub>4</sub>,

pH 1.2; 0.5 M HCl, pH 0.7; 0.5 M KH<sub>2</sub>PO<sub>4</sub>, pH 4.5 and 0.5 N H<sub>2</sub>SO<sub>4</sub>, pH 0.9) were used for extraction of arsenic from the given soils. Each soil solution (1 : 20) mixture was shaken for a period of 2 h and then filtered through a Whatman No. 42 filter paper. Arsenic in the extract was determined by AAS employing arsine generation<sup>13</sup>.

The physico-chemical properties of three surface soils (Table 2) indicated that the soil reaction (pH) was slightly acidic to neutral, whereas the organic carbon content varied from 3.25 to 6.94 g kg<sup>-1</sup>. The cation exchange capacity of these soils ranged from 20.2 to 23.4 cmol ( $p^+$ ) kg<sup>-1</sup> and the clay content varied from 32.6% to 38.7%. As regards the exchangeable cationic composition, the exchangeable sodium content was higher in Mollabelia than Nonaghata and Kalyani soils, whereas potassium content was higher in Nonaghata, followed by Mollabelia and Kalyani soils. The total arsenic content was highest in Nonaghata soil (14.7 mg kg<sup>-1</sup>), followed by Mollabelia  $(7.22 \text{ mg kg}^{-1})$  and Kalyani  $(2.69 \text{ mg kg}^{-1})$  soils. This also reflects itself in the Olsen extractable arsenic, i.e. highest in Nonaghata and lowest in Kalyani. The Olsen extractable arsenic loading in these soils was positively correlated with the soil attributes, namely EC (r = 0.930), CEC (r = 0.940), amorphous Fe content (r = 0.687) and Olsen extractable P (r = 0.533), whereas negatively correlated with organic carbon (r = -0.137). The total arsenic content was also positively correlated with amorphous Fe content (r = 0.616) and Olsen extractable P (r = 0.610). The arsenic in soil is predominantly contributed by the ironcontaining minerals in the parent material (e.g. pyritic)<sup>4</sup>. Relatively lower iron content in Kalyani soil as well as much lower arsenic concentration in the groundwater (less than 0.04 mg l<sup>-1</sup>) may have led to less arsenic loading in this soil. The arsenic loading in groundwater of

#### **RESEARCH COMMUNICATIONS**

	V - 1	T:	Soil samples				
Extractants	(ml)	shaken (h)	Mollabelia	Nonaghata	Kalyani		
Arsenic extracted (mg kg <sup>-1</sup> )							
1 N NH <sub>4</sub> Cl	100	0.50	0.36	0.49	0.09		
0.5 N NH <sub>4</sub> F	100	1.00	1.28	3.41	0.23		
Saturated NaCl	25	0.25					
Saturated NaCl	25	0.25	0.08	0.08	0.01		
0.1 N NaOH	100	18.0	2.46	4.64	0.94		
Saturated NaCl	25	0.25					
Saturated NaCl	25	0.25	0.10	0.09	0.008		
0.5 N H <sub>2</sub> SO <sub>4</sub>	100	1.00	1.24	1.28	0.31		
Saturated NaCl	25	0.25					
Saturated NaCl	25	0.25	0.08	0.08	0.003		
0.5 N NH <sub>4</sub> F	100	1.00	0.62	0.92	0.18		
Solvent extractable arsenic fractions (mg $kg^{-1}$ )							
NH <sub>4</sub> Cl extractable As (Ws-As)			0.36 (5.79)	0.49 (4.46)	0.09 (5.06)		
NH <sub>4</sub> F extractable As (Al-As)			1.98 (30.84)	4.41 (40.13)	0.42 (23.60)		
NaOH extractable As (Fe-As)			2.56 (41.15)	4.73 (43.04)	0.95 (53.37)		
H <sub>2</sub> SO <sub>4</sub> extractable As (Ca-As)			1.32 (21.22)	1.36 (12.37)	0.32 (17.98)		
Sum of soil arsenic fractions			6.22	10.99	1.78		

Table 3. Sequential extraction of arsenic by extractants to identify inorganic arsenic fractions in the experimental soils<sup>13</sup>

\*Numbers in parentheses denote the percentage loading of each arsenic fraction in the present soils.

Table 4. Simple linear correlation coefficient (r) between different arsenic fractions and some soil properties

	Soil arsenic fractions									
Properties of soils	Ws-As	Al-As	Fe-As	e Ca-As	Resin xtractable As	0.5 M NaHCO <sub>3</sub> extractable As	0.1 M NaOH extractable As	Sonicated 0.1 M NaOH extractable As	1 M HCl extractable As	Residual As
Olsen-As	0.970	0.997*	0.999**	0.859	0.947	0.956	0.999**	0.992*	0.974	0.946
Clay	-0.572	-0.804	-0.779	-0.314	-0.924	-0.913	-0.776	-0.671	-0.882	-0.926
рН	-0.447	-0.138	-0.177	-0.684	0.106	0.079	-0.182	-0.331	0.007	0.112
Organic C	0.108	-0.215	-0.176	0.388	-0.445	-0.421	-0.171	-0.018	-0.354	-0.450
Amorphous Fe	0.844	0.628	0.659	0.962	0.421	0.445	0.662	0.769	0.508	0.415
CEC	0.997*	0.919	0.934	0.978	0.731	0.749	0.895	0.952	0.795	0.727
Exch. Ca + Mg	-0.960	-0.820	-0.842	-0.999*	* -0.656	-0.678	-0.844	-0.917	-0.728	-0.652
Olsen extractable P	0.311	0.598	0.565	0.026	0.774	0.757	0.561	0.423	0.708	0.778
Specific surface	0.999**	0.935	0.948	0.968	0.821	0.836	0.949	0.986*	0.873	0.817

\*Significant at 5% and \*\*Significant at 1% probability level.

Nonaghata and Mollabelia was much higher, namely 0.18 to 0.75 and 0.12 to 0.21 mg  $I^{-1}$  respectively. Furthermore, the varying specific surface area and hence the corresponding adsorption capacity was also observed in these soils, being the highest in Nonaghata and the lowest in Kalyani, which directly correlates with the total and Olsen-extractable arsenic in these experimental soils.

Table 3 summarizes the findings obtained from the sequential extraction of soil arsenic pools from the given three soils, treated sequentially with the extractants (as per the scheme developed by Johnston and Barnard<sup>13</sup>) in the order listed. In the lower part of the table, the data have been appropriately summed up (extractants and washings) to identify the arsenic fractions in the given soils that were conventionally interpreted as being water soluble (Ws-As) and those associated with Al (Al-As), Fe (Fe-As) and Ca (Ca-As) compounds in soil.

The NH<sub>4</sub>Cl extractable arsenic, i.e. water soluble arsenic (Ws-As) was observed to be lowest and the highest was iron-bound arsenic (Fe-As), followed by Al-As fraction in all the three soils (Table 3). The Ca-As fraction was generally smaller compared to the Fe-As or Al-As fractions. The sum of the soil arsenic fractions was the highest in Nonaghata soil, followed by that in Mollabelia and Kalyani soils, in this order. This agrees with the order of groundwater loading of arsenic in these locations as stated earlier.

All the arsenic fractions had a good correlation with the Olsen-extractable arsenic in soil (Table 4). There was also a good correlation between amorphous iron content

Table 5.	Sequential extraction o	f arsenic (mg kg <sup>-1</sup>	<ol> <li>by extractants to identif</li> </ol>	fy different arsenic	fractions in soils under study <sup>14</sup>
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		Soil samples	
Extractants	Mollabelia	Nonaghata	Kalyani
Arsenic extracted (mg kg <sup>-1</sup> )			
Resin extractable arsenic	1.35	3.45	0.94
0.5 M NaHCO <sub>3</sub> (pH 8.5) extractable arsenic	1.02	2.98	0.56
0.1 M NaOH extractable arsenic	1.32	2.46	0.46
Sonicated 0.1 M NaOH extractable arsenic	2.56	4.12	0.55
1 M HCl extractable arsenic	1.2	3.06	0.55
Residual arsenic	0.84	2.76	0.48
Solvent – extractable arsenic (mg kg <sup>-1</sup> ) fractions from experimental soils			
Soil arsenic fractions	Mollabelia	Nonaghata	Kalyani
Freely exchangeable arsenic	1.35 (16.3)	3.45 (18.3)	0.94 (26.6)
Non-exchangeable but readily available/labile As associated with soil mineral surfaces	1.02 (12.3)	2.98 (15.8)	0.56 (15.8)
Arsenic held by strongly chemisorbed Fe and Al components	1.32 (15.9)	2.46 (13.1)	0.46 (13.0)
Arsenic held by internal surfaces of soil aggregates	2.56 (30.9)	4.12 (21.9)	0.55 (15.5)
Calcium associated arsenic	1.2 (14.5)	3.06 (16.3)	0.55 (15.5)
Residual recalcitrant arsenic	0.84 (10.1)	2.76 (14.7)	0.48 (13.6)
Sum of soil arsenic – fractions	8.29	18.83	3.54

\*Numbers in parentheses denote the percentage loading of each arsenic fraction in the present soils.

and the iron-bound arsenic in these soils (r = 0.659) as shown in Table 4. The soil in this zone originated from the alluvium sediments rich in iron-containing minerals. Such relatively larger iron content would facilitate the accumulation of arsenic in the soil forming Fe-As compound. Thus, the soil may act as effective sink for arsenic. The relatively higher kaolinite clay content in Nonaghata soil<sup>5</sup> may have also facilitated chemisorptions of As with iron and aluminium on clay surfaces, resulting in relatively higher arsenic loading in this soil<sup>5</sup>. The clay fraction of the Kalyani soil was predominantly montmorillonitic-illitic<sup>5</sup> in nature which is not known to possess high arsenic retention capacity. Further, the given trends of the arsenic content in the experimental soils is in agreement with the observations reported earlier that arsenic in the affected belt of the Bengal-delta basin is generally associated with iron-bearing minerals<sup>4,5</sup>.

Table 5 records data from the fractionation scheme (according to McLaren et al.<sup>14</sup>) which dealt with the soil colloidal surfaces and subsequently their capacity to hold arsenic in their matrices. The resin extractable arsenic form varied from 0.94 mg kg<sup>-1</sup> in Kalyani soil to  $3.45 \text{ mg kg}^{-1}$  in Nonaghata soil, in agreement with the earlier observation that Nonaghata soil was from a highly arsenic-contaminated zone (Table 2). The amount of resin extractable arsenic, which is assumed to be freely exchangeable arsenic, accounts from 16.3% to 26.6% of total arsenic in these soils. Resin-extractable arsenic may be considered as an indicator of potential bio-availability and/or mobility of contaminant arsenic in soil<sup>14</sup>. This was confirmed by the relatively high correlation (r = 0.947)between the resin extractable arsenic and Olsen extractable arsenic in the present contaminated zone (Table 4). This is negatively correlated with the soil organic carbon (r =-0.445) (Table 4). The latter may cause a higher degree of complexation of arsenic leading to its lower extractability. The freely exchangeable arsenic was positively correlated with the Olsen extractable P content of the soils (r = 0.774), presumably because high P releases more arsenic from the soil absorption sites due to the stronger competition offered by phosphate (compared to arsenate) for the same adsorption sites in soil<sup>4</sup>. The 0.5 M NaHCO<sub>3</sub> (pH 8.5) extractable arsenic content varied from 0.56 to 2.98 mg As kg<sup>-1</sup>, whereas 0.1 M NaOH extractable arsenic varied from 0.46 to 2.46 mg As kg<sup>-1</sup> (Table 5). Further, the extractability was improved in all the three soils when treated with sonicated 0.1 M NaOH. This probably was due to dispersion and dissolution of arsenic bound by the internal surface of soil aggregates. The extractable arsenic by the extractant 1 M HCl varied from 0.55 to 3.06 mg As kg<sup>-1</sup>. The dissolution of Ca and Mg-bound arsenic in these soils by hydrochloric acid might have resulted in slight increase in arsenic extractability as compared to the amount of arsenic extracted by 0.5 M NaHCO<sub>3</sub>.

Regarding different fractions of arsenic, the resin extractable form corresponds to the freely exchangeable form of arsenic. The sodium bicarbonate extractable arsenic represents the non-exchangeable but readily available arsenic, i.e. labile arsenic associated with soil mineral surfaces. Arsenic held by internal surface of soil aggregates, extracted by the sonicated 0.1 M NaOH, was found to be higher (varying from 0.55 to 4.12 mg As kg<sup>-1</sup>) which may be attributed to the high clay content of these soils (Table 2).

Table 4 shows the simple linear correlation coefficient (r) values of such arsenic fractions and the important physicochemical properties of the given soils. The Olsen extractable arsenic and P, as well as CEC were positively correlated with all the forms of soil arsenic. In all the cases, clay content of soil was found to be generally highly negative in correlation with soil arsenic fractions,

	Soil samples					
Extractants	Mollabelia	Nonaghata	Kalyani			
Arsenic extracted (mg kg <sup>-1</sup> )						
0.5 M NH <sub>4</sub> F (pH 8.2)	1.12	2.22	0.42			
0.5 M NaHCO <sub>3</sub> (pH 8.5)	1.92	3.16	0.37			
0.5 M (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> (pH 8.9)	2.10	3.85	0.40			
0.5 M Na <sub>2</sub> CO <sub>3</sub> (pH 11.7)	2.45	4.22	0.64			
0.1 N NaOH (pH 13.0)	2.16	3.92	0.73			
0.5 N HCl + 0.025 N H <sub>2</sub> SO <sub>4</sub> (pH 1.2)	1.98	3.69	0.47			
0.5 M HCl (pH 0.7)	3.22	7.68	0.98			
0.5 M KH <sub>2</sub> PO <sub>4</sub> (pH 4.5)	5.32	9.53	2.21			
0.5 N H <sub>2</sub> SO <sub>4</sub> (pH 0.9)	6.56	10.32	2.41			

 Table 6. Individual solvent extraction of arsenic (mg kg<sup>-1</sup>) from the experimental soils

illustrating the fact that soil clay can assist the soil to act as an effective sink for arsenic, thereby reducing its mobility and phyto-availability in the soil. The arsenic held by strongly chemisorbed Fe and Al components had positive correlation with amorphous iron content of the soils. The positive correlation of Olsen-extractable P with arsenic fractions was observed, and may be due to release of arsenic by P in soil resulting from competition for same sorption sites by these two chemically analogous anions<sup>4</sup>. The specific surface area of the soils had positive correlation with all the arsenic fractions. The significant positive relation  $(r = 0.986^*)$  between specific surface area and sonicated 0.1 M NaOH extractable arsenic confirms the higher accumulation of arsenic on the clay surface. Organic carbon content of the soils showed the negative relationship with almost all forms of soil arsenic, thereby confirming that formation of possible organo-arsenic complexes in soil leading to the lowering of the arsenic extractability. The exchangeable Ca and Mg content of the soils showed negative correlation with all the fractions of arsenic extracted by both the methods applied.

Nine extractants were used for arsenic extraction from the given soil samples. The effectiveness (in general) of the individual extractants to extract arsenic from the given soils followed the order:

Thus,  $0.5 \text{ N H}_2\text{SO}_4$  (pH 0.9) seemed to be the best extractant for soil arsenic in the given soils (Table 6). This may possibly be attributed to the dissolution of soil minerals, chiefly iron and aluminium sesquioxides (besides the amorphous Fe and Al fractions), at this low pH, thereby releasing large amounts of arsenic held by these components. Besides the acidic extractants used, ammonium fluoride (0.5 M NH<sub>4</sub>F, pH 8.2) appeared to be another useful extractant, possibly by virtue of its dissolving the Fe- and Al-bound arsenic fractions in soil which are relatively dominant fractions in the arsenic-affected alluvial soils of the Bengal delta basin, in agreement with the present observations. The extracting ability of 0.5 M NaHCO<sub>3</sub> was rather low compared to that of most other extractants used. The NaHCO3-extractable arsenic indicates the non-exchangeable but readily labile arsenic, associated with soil mineral surfaces. If such association is strong, then the corresponding extract would be rather poor in arsenic. The efficiency of 0.1 N NaOH (pH 13.0) for extraction of arsenic was more than that of the other basic extractants except Na<sub>2</sub>CO<sub>3</sub>. arsenic one would expect, NaOH-extractable arsenic is held in soil strongly by chemisorption by Fe and Al components of soil surfaces. In the present study, OH<sup>-</sup> ions appeared to dissolve readily the Fe-As, and slowly the Al-As fractions. Further, the 0.05 N HCl + 0.025 N H<sub>2</sub>SO<sub>4</sub> (pH 1.2) solution extracted less arsenic from the soils than did the other acidic extractants such as 0.5 M KH<sub>2</sub>PO<sub>4</sub> (pH 4.5) and 0.5 N H<sub>2</sub>SO<sub>4</sub> (pH 0.9). This is in agreement with earlier observations<sup>13</sup>. Thus, the given acidic extractants, and to some extent, the alkaline extractants used proved efficient in extracting the soil arsenic fractions.

The present study reveals the association of the fractions of arsenic with different soil constituents. The following trend was observed for different fractions of soil arsenic: NH<sub>4</sub>Cl extractable arsenic (Ws-As) < H<sub>2</sub>SO<sub>4</sub> extractable arsenic (Ca-As) < NH<sub>4</sub>F extractable arsenic (Al-As) < NaOH extractable arsenic (Fe-As) from a fractionation scheme<sup>13</sup>. Another fractionation study<sup>14</sup> was also followed to examine the relative preponderance of arsenic held in different portions of clay moieties. The findings revealed that resin extractable or freely exchangeable arsenic was very small compared to the arsenic held by the internal surfaces of soil aggregates or the strongly chemisorbed arsenic held by Fe and Al components. The negative and positive correlation of arsenic fractions with soil organics and clay respectively, supports the function of soil as an effective sink of arsenic. Phosphorus has some role in the release of arsenic in the soil available pool. The acids were more efficient in extracting arsenic from soil than the basic extractants.

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## Synthesis of nano-porous carbon from cellulosic waste and its application in water disinfection

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The present study deals with the preparation of new cellulosic catalyst materials, viz. paper and textile industry waste. Activated nano-carbons were prepared from these waste materials using thermo-chemical method. Nano-silver particles (AgNP) were embedded into the synthesized carbons to incorporate antimicrobial properties. The catalyst materials were characterized using FESEM-EDX, XRD, FTIR, etc. The characterization results showed that the materials were nanoporous and silver was uniformly distributed throughout the catalyst. The suitability of the catalyst as an antimicrobial agent was studied using pour plate technique. The main advantages of the disinfecting materials over conventional materials were: (i) only small quantities (mg) of catalysts are required to deactivate microorganism for up to 1 litre of water; (ii) time required for more than 99% disinfection is less (60 min); (iii) carbon has been synthesized from cellulosic wastes which otherwise would pollute the environment, hence it is a waste recycling process. The carbons exhibited more than 99% E. coli removal within 60 min.

**Keywords:** Cellulosic waste recycling, disinfection, *E. coli*, nano-carbon, nano-silver.

SAFETY of drinking water is taken for granted in most developing countries. Water pollution caused by faecal contamination is a serious problem. *E. coli* contaminated waters when used as drinking water, cause severe diarrhoea, abdominal cramps and in some cases may cause severe anaemia or kidney failure. Approximately 12 million people die yearly due to water-borne diseases. Most diseases occurring in developing countries are due to consumption of contaminated water<sup>1–3</sup>. In the past few decades, clean-water received much attention<sup>4,5</sup>. Water is disinfected through different techniques such as chlorination, UV treatment, ozonization, etc. However, these disinfection routes have limitations due to their cost and difficulties in large scale implementation<sup>6–9</sup>.

Water purification using nanotechnology utilizes nanoscopic materials such as nano-carbon, carbon nanotubes,

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