RESEARCH ARTICLE

Arsenic Fractionation in Paddy Field Soil of Middle and Lower Ganga Plain in Relation to Soil Physico-chemistry

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Abstract

Arsenic (As) pollution in paddy fields through geogenically contaminated irrigation water is a big challenge in many countries. Soil physico-chemistry is crucial in As accumulation in soil as well as its release in soil solution. To assess the potential toxic effect of As on crops and humans, it is essential to determine the availability of As in soil solution. In this study, fractionation of As was performed in As-contaminated paddy field soils from Uttar Pradesh, i.e., Middle Ganga Plain (MGP) and West Bengal, i.e., Lower Ganga Plain (LGP) and analyzed in relation to soil properties. The percent of total As extracted was 0.87 to 6.5% as water soluble, 0.13 to 4.8% exchangeable, 6.8 to 14% specifically sorbed and 11 to 21% associated with amorphous Fe oxide. Most of the As (57–79%) was found in crystalline Fe oxide and residual fraction, i.e., incorporated in minerals. The concentration of As in soil and its release in different fractions was strongly correlated to the soil properties. A high content of clay, Fe and Ca and low P and S seem to be the main factors for the accumulation of As in the soil of LGP. The primary causes of the higher release of As, particularly in water-soluble and amorphous Fe oxide-associated As in soils of LGP, appeared to be high TOC and EC and alkaline pH. Conversely, the soils of MGP were more sandy, low in TOC and OM, and had relatively higher levels of available P and S, causing more release of exchangeable and specifically sorbed As. Although amorphous Fe oxide was the primary As binding fraction in both soils, it would be a substantial source of accessible As in a reducing environment.

Keywords*:* Arsenic, Arsenic fractionation, Organic carbon, Paddy soil, Sequential extraction.

Highlights:

- The concentration of arsenic (As) in paddy soil and its release was strongly correlated to the soil properties.
- Relatively high clay, Fe and Ca and low P and S in the soil of the lower Ganga plain (LGP) resulted in more As retention in soil.
- High TOC, alkaline pH, and high EC were the primary causes of As release in soils of LGP.
- Soils of Middle Ganga Plain (MGP) were relatively sandy have low TOC and high P and S.
- In soil of MGP release of exchangeable and specifically sorbed As was higher than LGP.
- Amorphous Fe oxide was the primary mobile As-bearing fraction in MGP and LGP soils.

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Introduction

Arsenic (As) is the most prevalent toxic metalloid in the biosphere, posing a global threat to all living organisms. The level of As varies from 1.5–2 in the upper and 1 to 1.8 $mgkg^{-1}$ in bulk Earth's crust and from 0.5 to >7000 µg/l in aquatic environments (Mishra *et al*., 2023a). Arsenic gets into the food chain mostly via polluted drinking water and through crops that absorb arsenic from soil or from arsenic-laden irrigation water. Soil As contamination now constitutes a chronic global issue. It has been estimated that annually, $5.2x10^4$ to $1.12 x10^6$ tons of As are released into the environment through mining and industrial activities (Liao *et al*., 2005). Nevertheless, contaminated groundwater through natural geogenic reasons is the major source of soil As contamination in many parts of the world (Mandal and Suzuki, 2002; Mondal *et al*., 2006; Mishra *et al.* 2016). Bangladesh and West Bengal (India) situated in Bengal Delta Basin have been recognized as worst As affected regions, with millions of people have developed arsenicosis-related diseases. Recent reports show that the As contamination incidents are increasing in other parts of India (Mishra *et al*., 2016). Middle Ganga plain being the second hot-spot, is already showing symptoms of arsenicosis in many villages in this region (Dwivedi *et al*., 2023). In most of the As affected regions, paddy rice is the main crop, which requires flooded conditions for most of the cropping duration that needs

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a lot of irrigation. In turn several thousand tons of As goes into the agricultural fields every year through irrigation water in these areas. In soil, various chemical forms of As have been identified that differ in plant uptake, translocation and toxicity. Inorganic arsenate (AsV) and arsenite (AsIII) are the most prevalent in soil and irrigation water, whereas methylated pentavalent forms, monomethylarsonic Acid (MAV) and dimethylarsinic acid (DMAV) have been detected in small to significant quantities in soils of various regions of the world (Mishra *et al*., 2017; Mestrot *et al*., 2011). The accumulation and toxic effect of As on plants strongly depend on As availability and its chemical speciation (Mishra *et al*. 2017). Further, the total retention of arsenic in soil, its availability to plants and its chemical speciation depends on several edaphic and environmental factors, such as pH, texture (clay mineralogy), CEC, organic matter, amorphous oxides of Fe–Al, sulfur, phosphorus and nitrogen content, and redox conditions of soil (Adriano, 2001, Golui *et al*., 2017, Grimm *et al*., 2024). For instance, soil having higher organic matter also has higher availability of As, particularly in the form of organic As (Norton *et al*., 2013). Soil pH may significantly impact As mobility, in general, As is less mobile at neutral pH. However, both high and low pH may cause the dissolution of As. At high pH, desorption of sorbed oxyanions of As may take place, while at lower pH the proton competition and dissolution of minerals may increase As in solution. Soil organic matter greatly affects As accumulation in rice and its chemical speciation in grain (Jia *et al*., 2012). It might be pertaining to the depletion of oxygen by organic matter, leading to an anoxic environment. Similarly, the level and availability of elements, particularly Fe, Mn, Ca, P, S, etc., also affect the solubility of As in soil solution and availability to plants. Thus, these soil properties play an important role in net As buildup in soil as well as its availability to the plants and accumulation in grain. In India, As contamination in the lower Ganga plain has been long known and now severe contamination has been recognized in the middle Ganga plain as well. Both are agriculture-intensive regions and paddy rice is an important crop. However, in the lower Ganga plain, paddy rice is grown in both Rabi and Kharif seasons dependent primarily on groundwater irrigation and monsoon, respectively. Whereas in the middle Ganga plain wheat and rice are consecutively grown in Rabi and Kharif seasons, respectively. Paddy rice requires flooded anaerobic conditions until the maturity of crop, while wheat is grown aerobically and irrigated only at specific growth stages mostly through groundwater. Further, West Bengal receives higher rainfall, an average of >200 mm to 400 in northern hilly areas, while Uttar Pradesh receives 84 to 170 mm rainfall. Soil moisture and periodic drying and rewetting may directly affect soil enzyme and microbial activity (Huang *et al*., 2024). These factors may significantly contribute to soil biogeochemistry and As buildup, fractionation and bioavailability. In the current study, the distribution of As in different soil fractions was studied in the paddy field soil of As-contaminated regions of West Bengal, i.e., Lower Gana Plain and Uttar Pradesh, i.e., Middle Ganga Plain.

Material and Methods

Study area

Paddy field soil and irrigation water samples were collected from two districts i.e., Nadia and North 24 Parganas of West Bengal (lower Ganga Plain) and three districts i.e., Ballia, Prayagraj and Lakhompur Khiri of Uttar Pradesh (middle Ganga plain) on the basis of our previous experience and other reports of As contamination in water. The climatic conditions in these districts are tropical in Nadia, North 24 Parganas and Ballia, humid subtropical in Prayagraj and subhumid continental in Lakhimpur. The groundwater in the studied areas is reported to contain As from geogenic origin, which has led to soil As contamination. No other sources of anthropogenic pollution of As were identified in the region.

Sampling of paddy field soil and irrigation water

The soils from the selected paddy fields were collected just prior to the harvesting of the crops. Six to ten samples from different paddy fields of each district were taken and for each field, ten soil cores (0–45cm depth) were randomly collected and mixed together to create a single composite sample. The samples were placed in polyethylene bags and transported to the laboratory for further analysis of various parameters. The soil samples were air-dried, homogenized and sieved for physicochemical analysis. Bore well water samples used for irrigation of respective paddy fields were also sampled in two sets: one for physicochemical parameters and another for metal estimation. The second set of water samples was preserved on site by adding 1-mL of nitric acid.

Physico-chemical analysis of paddy field soil

The physicochemical properties of the soil, including pH and electrical conductivity (EC), were analyzed in a 1:2 (w/v) soil solution using a portable pH/EC meter (Hanna pH/EC meter, model number HI5522). The water holding capacity (WHC) of the soil was estimated by gravimetric method and moisture content was determined by subtracting the dry weight from wet weight and normalized by the soil dry weight. Soil bulk density was measured by dividing the dry weight of the soil material by the volume of the soil. Soil texture was determined by the pipette method. Total organic carbon (TOC) and total organic matter (TOM) were determined using the Walkley and Black method (1934). Available calcium (Ca), sodium (Na), potassium (K), phosphorous (P) and sulfure (S) were analyzed using a flame photometer (ESICO, model 1385, India) after extraction of soil.

Analysis of micro-elements and arsenic in soil

The analysis of multi-elements was conducted after sieving the powdered soil samples from paddy and wheat fields (<2 mm). Oven-dried soil samples (0.2 g) were digested in a mixture of HNO_3 and HF (1:1) at 120°C for 2 hours, followed by digestion at 140°C for 4 hours (Dwivedi *et al*., 2020). After digestion, the samples were filtered and diluted to 10 mL with Milli-Q water and the concentrations of various elements viz., Fe, Mn, Zn and As were analyzed using inductively coupled plasma mass spectrometer (ICP-MS iCAP-RQ, Thermo Scientific, USA).

Arsenic fractionation in soils

The fractionation of As in soil samples was performed using a five-step sequential extraction procedure modified from Wenzel *et al*., (2001). Briefly, 1 g soil was placed in 50 ml centrifugation tubes and extracted with 25 ml of water (step 1) to determine water soluble As. Afterwards, the soil was extracted with various reagents stepwise in 1:25 (soil to solution) ratio. The subsequent steps involved extraction with 0.05 M ammonium sulfate [$(NH_4)_2SO_4$] (step 2) to determine exchangeable fraction, 0.05M ammonium phosphate ($NH_4H_2PO_4$) (step3) to release specifically sorbed As, 0.2 M ammonium oxalate in oxalic acid [$(NH_4)_2C_2O_4/H_2C_2O_4$)] (step 4) to release As associated with amorphous Fe oxides and (0.2 M ammonium oxalate buffer and 0.1 M ascorbic acid [$(NH_4)_2C_2O_4/H_2C_2O_4$ + 0.1 M $C_6H_8O_6$] (step 5) to dissolved As bound to crystalline Fe oxides. The samples were centrifuged at 5000 rpm for 10 minutes and filtered and supernatant was collected carefully. A washing step with 5 mL of water was performed after each step and pooled with the previous fraction. After fractionation, the soil was digested in HNO_3 and H_2O_2 to determine residual As. The extracted bioavailable arsenic fractions and the residual As in soil samples were estimated using ICP-MS as described above.

Quality control

An inductively coupled plasma mass spectrometer (ICP-MS) was utilized for the estimation of various multi-elements and As. Rhodium served as an internal standard, and the multi-element calibration custom standard 1725 from VHG (LGC Standards, USA) was used for ICP-MS calibration. Quality assurance for each analytical batch was ensured by repeated analysis of certified reference materials (n = 5). Recovery rates were 96-99% for Fe, 92-98% for Mn, 97-104% for Zn, and 96-101% for As, with an overall range of 96-104%. The detection limit for each element was 1 μgL^{-1}

Results and Discussion

Soil properties and elemental composition of paddy soil

For all the soil samples studied the pH was > 7, ranging from 7.2 to 8.25. The clay content was relatively higher in the soil of West Bengal (i.e. Lower Ganga Plain hereafter LGP) than Uttar Pradesh (i.e. Middle Ganga Plain hereafter MGP). The total organic carbon (TOC) and organic matter was also substantially higher in the soils of LGP than MGP (Table 1). The level of available Na, K, Ca, P, S and level of total Fe, Mn and Zn were determined in soil of paddy fields (Table 2). Sodium and K are important for soil and plant health and soil enzyme and Ca, P, and S essential plant macronutrients as well as relevant to As geochemistry in soil. Level of Na was relatively higher in soils of Nadia and North 24 Parganas in comparison to the paddy soils of Uttar Pradesh while K was higher in soils of Prayagraj and Nadia followed by Ballia, North 24 Pargana and Lakhimpur. In contrast to organic C, the paddy soils of MGP were richer in available P and S, with average values ranging from 83 -101 and 50- 175 $mgKg^{-1}$, respectively in comparison to LGP (41-46 $mgKg^{-1}$available P and 19-23 $mgKg^{-1}$available P) in the studied districts. Whereas, level of available Ca was higher in the paddy soil of LGP than in MGP. The level of Fe, Mn and Zn did not show any clear trend among the paddy fields of MGP and LGP. The level Fe and Mn was maximum in Ballia followed by Nadia and least in in the paddy soil of Lakhimpur. Level of Zn was maximum in the soils of Ballia then Prayagraj and Nadia, lowest in Lakhimpur.

Total As in irrigation water and paddy soil

The total As in borewell waters used for irrigation of the studied paddy fields showed higher level in samples from LGP than in MGP (Table 3). In Nadia district, nine out of ten samples contained As >100 μgL^{-1}, of which five samples contained As >400 μgL^{-1}. The average As concentration in Nadia was 340 μgL^{-1}. Similarly, all the borewell water samples from North 24 Pargnas contained >200 μgL^{-1} As, with average value >310 μgL^{-1}. The level of As contamination in water samples from MGP was relatively lower. However, most of the samples from MGP also contained >100 μgL^{-1} As, with average level of contamination 115, 113 and 70 μgL^{-1} As in Prayagraj, Ballia and Lakhimpur, respectively. Thus, the ground water of the studied areas in LGP and MGP are significantly As contaminated, as has been reported earlier (Mishra *et al*., 2016; Dwivedi *et al*., 2023). Most of the borewell water samples exceeded the FAO guideline value for irrigation water, which is 100 µg As L^{-1} (FAO, 1985). The borewell waters are used to irrigate the paddy fields mostly during the cultivation of Rabi rice (boro) in West Bengal, while in Uttar Pradesh both Rabi (wheat) and Kharif (rice) is irrigation as and when required to compensate the low rainfall.

The total As concentration in soil samples from paddy fields of Nadia ranged from 9.8 to 31. 34 $mgKg^{-1}$ with average level 24.8 $mgKg^{-1}$ and in soil of North 24 Parganas ranged from 15 to 24.65 $mgKg^{-1}$ with average 22.8 $mgKg^{-1}$. Soil As level in Uttar Pradesh ranged from 5.25 to 25.74 $mgKg^{-1}$ with average As level of about 18 $mgKg^{-1}$ in all three districts. Thus, paddy field soils of both MGP and LGP contain significantly higher As than the normal background level i.e. <10 or 5$mgKg^{-1}$ (Kabata-Pendias and Pendias 2000, Punshon *et al*., 2017). Many of the samples contained As higher than the FAO guideline value 20 $mgKg^{-1}$ for agriculture soil (FAO, 2006). Though the level of

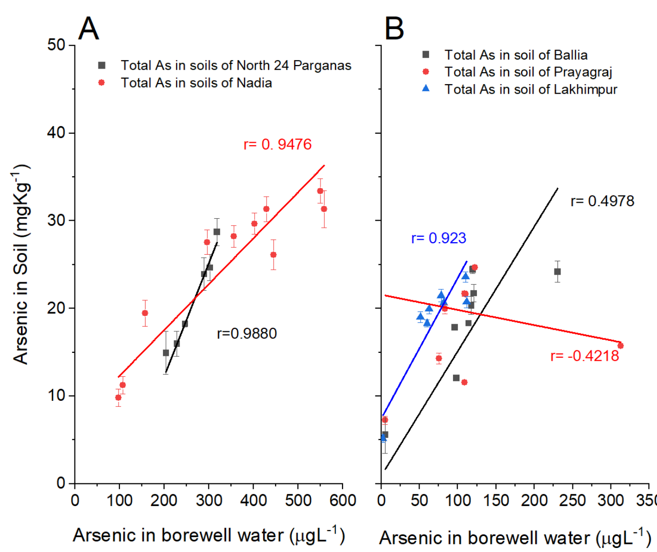

Fig. 1: Arsenic contamination in paddy field soils in relation to arsenic concentration in borewell water used to irrigate the respective paddy fields in selected districts of (A) Lower Ganga Plain (Nadia and North 24 Parganas districts of West Bengal) and (B) Middle Ganga Plain (Ballia, Prayagraj and Lakhimpur districts of Uttar Pradesh. Data is mean ±SD.

Table 1: Physico-Chemical properties of soil samples collected from arsenic contaminated paddy fields of West Bengal and Uttar Pradesh

District	*Sample*	*Bulk Density (gm cm^{-3})*	*WHC (%)*	*Moisture (%)*	*Texture*			*pH*	*EC (us cm^{-1})*	*TOC (%)*	*OM (%)*
					Clay (%)	*Sand (%)*	*Silt (%)*				
Nadia (West Bengal)	1	1.19^{d} ± 0.31	53^{b} ± 3.6	51^{a} ± 2.8	40	32	28	7.71^{b} ± 0.12	256^{d} ± 0.40	2.98^{b} ± 0.03	5.55^{b} ± 0.15
	2	1.24^{d} ± 0.24	55^{b} ± 3.2	25^{d} ± 3.4	43	37	20	7.62^{b} ± 0.09	242^{d} ± 0.45	3.52^{a} ± 0.06	5.68^{a} ± 0.11
	3	1.25^{d} ± 0.33	69^{a} ± 1.4	24^{d} ± 2.6	50	32	18	7.74^{b} ± 0.04	260^{d} ± 0.35	3.94^{a} ± 0.05	6.9^{a} ± 0.08
	4	1.31^{c} ± 0.25	55^{b} ± 1.5	28^{d} ± 2.5	38	35	27	7.31^{c} ± 0.03	311^{c} ± 0.41	3.73^{a} ± 0.05	6.14^{a} ± 0.08
	5	1.23^{d} ± 0.14	77^{a} ± 2.6	38^{b} ± 3.2	52	31	17	7.66^{b} ± 0.03	190^{e} ± 0.35	2.42^{c} ± 0.15	4.33^{c} ± 0.14
	6	1.39^{b} ± 0.26	57^{b} ± 3.2	28^{d} ± 2.7	40	35	15	8.11^{a} ± 0.06	380^{a} ± 1.01	3.72^{a} ± 0.05	6.35^{a} ± 0.08
	7	1.32^{c} ± 0.35	58^{b} ± 2.8	28^{d} ± 3.2	42	31	17	8.15^{a} ± 0.21	320^{b} ± 0.92	3.85^{a} ± 0.05	6.34^{a} ± 0.08
	8	1.41^{b} ± 0.29	59^{b} ± 3.4	27^{d} ± 2.7	44	31	15	8.14^{a} ± 0.33	350^{b} ± 0.28	3.67^{a} ± 0.11	6.61^{a} ± 0.20
	9	1.34^{c} ± 0.32	56^{b} ± 2.6	27^{d} ± 1.4	43	31	16	8.19^{a} ± 0.05	360^{b} ± 0.06	3.45^{a} ± 0.04	5.56^{b} ± 0.04
	10	1.45^{b} ± 0.28	61^{b} ± 1.5	27^{d} ± 1.5	40	32	18	8.21^{a} ± 0.04	340^{b} ± 0.40	3.21^{b} ± 0.06	6.36^{a} ± 0.11
North 24 parganas (West Bengal)	1	1.3^{c} ± 0.27	58^{b} ± 3.2	41^{b} ± 2.6	45	34	21	7.47^{c} ± 0.03	253^{d} ± 0.45	3.65^{a} ± 0.05	6.5^{a} ± 0.08
	2	1.3^{c} ± 0.34	59^{b} ± 2.7	43^{b} ± 3.3	47	35	18	8.15^{a} ± 0.06	243^{d} ± 0.35	3.46^{a} ± 0.05	5.2^{b} ± 0.08
	3	1.3^{c} ± 0.31	58^{b} ± 1.5	38^{b} ± 2.8	46	35	19	8.11^{a} ± 0.28	267^{d} ± 0.41	3.16^{b} ± 0.15	6.3^{a} ± 0.14
	4	1.4^{b} ± 0.17	59^{b} ± 2.8	35^{c} ± 3.4	46	34	20	8.07^{a} ± 0.03	220^{d} ± 0.35	4.1^{a} ± 0.05	6.4^{a} ± 0.08
	5	1.2^{d} ± 0.36	63^{b} ± 2.8	45^{a} ± 2.6	48	33	19	8.12^{a} ± 0.06	260^{d} ± 1.01	3.34^{b} ± 0.05	5.8^{b} ± 0.08
	6	1.3^{d} ± 0.13	66^{b} ± 3.2	45^{a} ± 3.8	50	33	17	8.07^{a} ± 0.04	255^{d} ± 0.92	3.57^{a} ± 0.11	6.3^{a} ± 0.20
Ballia (Uttar Pradesh)	1	1.47^{a} ± 0.34	43.35^{d} ± 2.9	31^{c} ± 2.6	15	45	40	7.55^{b} ± 0.04	179.11^{e} ± 2.65	0.71^{e} ± 0.06	1.22^{e} ± 0.10
	2	1.49^{a} ± 0.37	45.75 ± 3.5^{d}	35^{c} ± 1.5	20	50	30	7.94^{b} ± 0.03	192.03^{e} ± 5.29	0.72^{e} ± 0.11	1.24^{e} ± 0.18
	3	1.35c ± 0.25	45^{d} ± 2.6	32^{c} ± 3.3	24	49	27	7.96^{b} ± 0.07	118.2^{e} ± 16.50	0.49^{e} ± 0.06	0.84^{e} ± 0.10
	4	1.43^{b} ± 0.23	42^{d} ± 3.8	33^{c} ± 3.6	26	50	24	7.21^{c} ± 0.04	127.33^{d} ± 9.54	0.63^{e} ± 0.15	1.08^{e} ± 0.31
	5	1.46^{b} ± 0.13	45^{d} ± 1.5	29^{d} ± 2.6	19	45	36	7.43^{c} ± 0.02	118.45^{e} ± 0.58	0.9^{e} ± 0.25	1.42^{e} ± 0.18
	6	1.37^{b} ± 0.33	46^{d} ± 3.6	34^{c} ± 2.8	26	47	27	7.22^{c} ± 0.07	125.33^{e} ± 3.51	0.55^{e} ± 0.19	0.92^{e} ± 0.25
	7	1.42^{b} ± 0.23	49^{c} ± 3.3	32^{c} ± 2.9	23	39	38	7.78^{b} ± 0.03	321.03^{b} ± 2.52	0.69^{e} ± 0.06	1.28^{e} ± 0.10
	8	1.34^{bc} ± 0.17	43^{d} ± 2.6	37^{b} ± 2.1	25	44	31	7.95^{b} ± 0.02	109.7^{e} ± 5.51	0.53^{e} ± 0.07	0.92^{e} ± 0.08
Prayagraj (Uttar Pradesh)	1	1.36^{b} ± 0.38	56.15^{c} ± 2.8	43^{b} ± 2.8	35	40	25	8.47^{a} ± 0.03	238.39^{d} ± 3.03	0.39^{e} ± 0.13	0.67^{e} ± 0.23
	2	1.16^{d} ± 0.25	57.24^{c} ± 2.9	41^{b} ± 2.8	37	43	20	7.82^{b} ± 0.05	229.3^{d} ± 1.49	0.45^{e} ± 0.09	0.77^{e} ± 0.16
	3	1.37^{b} ± 0.32	51.03^{c} ± 2.1	41^{b} ± 3.2	28	45	27	8.19^{a} ± 0.02	200.7^{e} ± 1.07	0.44^{e} ± 0.08	0.75^{e} ± 0.13
	4	1.33^{c} ± 0.37	69.12^{a} ± 3.8	43^{b} ± 2.9	32	41	27	8.03^{a} ± 0.03	150.46^{e} ± 0.50	0.34^{e} ± 0.09	0.58^{e} ± 0.16
	5	1.3^{c} ± 0.15	40.9^{d} ± 2.4	46^{a} ± 3.5	36	39	25	8.03^{a} ± 0.07	171.43^{e} ± 0.49	0.35^{e} ± 0.05	0.60^{e} ± 0.08
	6	1.29^{c} ± 0.19	45^{d} ± 2.4	44^{a} ± 2.6	43	47	10	8.05^{a} ± 0.10	161.66^{e} ± 1.64	0.58^{e} ± 0.12	0.99^{e} ± 0.21
	7	1.32^{c} ± 0.36	49^{c} ± 3.6	37^{b} ± 3.8	34	43	23	7.53^{c} ± 0.11	212.53^{e} ± 0.29	0.82^{e} ± 0.08	1.41^{e} ± 0.13
	8	1.36^{c} ± 0.24	43^{d} ± 3.4	32^{c} ± 2.1	35	44	21	8.02^{a} ± 0.03	218.16^{e} ± 0.96	0.41^{e} ± 0.03	0.70^{e} ± 0.05
Lakhimpur (Uttar Pradesh)	1	1.2^{d} ± 0.28	67^{b} ± 2.3	47^{a} ± 3.8	51	35	14	7.79^{b} ± 0.05	168.58^{e} ± 0.03	0.44^{e} ± 0.06	0.76^{e} ± 0.06
	2	1.56^{a} ± 0.23	44^{d} ± 1.4	51^{a} ± 2.4	45	43	12	8.22^{a} ± 0.07	226.03^{d} ± 0.62	0.67^{e} ± 0.05	1.15^{e} ± 0.08
	3	1.45^{b} ± 0.34	45^{d} ± 2.7	43^{b} ± 2.4	41	45	14	8.01^{a} ± 0.03	413.06^{a} ± 0.44	0.64^{e} ± 0.12	1.10^{e} ± 0.21
	4	1.51^{a} ± 0.24	36^{d} ± 1.5	45^{a} ± 3.6	37	41	22	8.05^{a} ± 0.05	163.8^{e} ± 1.16	0.55^{e} ± 0.12	0.94^{e} ± 0.21
	5	1.48^{a} ± 0.18	35^{d} ± 3.4	36^{c} ± 3.4	34	39	27	8.41^{a} ± 0.05	228.66^{d} ± 2.29	0.52^{e} ± 0.09	0.89^{e} ± 0.16
	6	1.24^{d} ± 0.14	41^{d} ± 3.2	38^{b} ± 2.3	42	47	11	7.98^{b} ± 0.02	421.83^{a} ± 0.47	0.59^{e} ± 0.15	1.01^{e} ± 0.26
	7	1.43^{b} ± 0.31	42^{d} ± 2.4	43^{b} ± 2.4	38	43	19	8.15^{a} ± 0.04	169.73^{e} ± 0.40	0.49^{e} ± 0.12	0.84^{e} ± 0.21
	8	1.34^{c} ± 0.36	36^{d} ± 1.5	42^{b} ± 3.6	35	44	21	8.25^{a} ± 0.04	231.8^{d} ± 0.25	0.79^{e} ± 0.12	1.36^{e} ± 0.22

Data = mean ± SD, Different letters indicate significant difference within each parameter ($p<0.05$)

Table 2: Level of various elements (available/ total) in soil of arsenic contaminated paddy fields of West Bengal and Uttar Pradesh

District	*Sample*	*Available P (mg Kg^{-1})*	*Available S (mg Kg^{-1})*	*Available Na (mg Kg^{-1})*	*Available K (mg Kg^{-1})*	*Available Ca (mg Kg^{-1})*	*Fe (mg Kg^{-1})*	*Zn (mg Kg^{-1})*	*Mn (mg Kg^{-1})*
Nadia (West Bengal)	1	$51.35^{e} \pm 0.65$	$13.98^{e} \pm 1.01$	$88^{b} \pm 1.66$	$83.0^{e} \pm 3.48$	$3300^{d} \pm 305.58$	$11556.45^{e} \pm 968.67$	$67.82^{c} \pm 6.65$	$350.00^{e} \pm 23.06$
	2	$46.23^{e} \pm 4.22$	$14.23^{e} \pm 1.22$	$56^{c} \pm 2.48$	$71.0^{e} \pm 1.72$	$4500^{c} \pm 206.6$	$18717.5^{d} \pm 1278.01$	$53.47^{d} \pm 4.91$	486.00d± 41.45
	3	$39.59^{e} \pm 0.52$	$15.15^{e} \pm 1.09$	$159^{a} \pm 15.23$	$115.0^{d} \pm 5.72$	$7250^{a} \pm 355.29$	$24201.15^{b} \pm 1130.41$	$72.75^{c} \pm 5.04$	$536.87^{c} \pm 18.79$
	4	$42.78^{e} \pm 2.79$	$21.11^{e} \pm 0.31$	$145^{a} \pm 4.24$	$133.0^{c} \pm 2.36$	$6716^{a} \pm 612.08$	$22213.75^{c} \pm 1425.48$	$65.75^{cd} \pm 0.85$	$541.17^{c} \pm 13.21$
	5	$53.12^{e} \pm 1.25$	$18.6^{e} \pm 1.17$	$56^{c} \pm 1.33$	$88.0^{e} \pm 3.54$	$3300^{d} \pm 119.72$	$29852.74^{a} \pm 723.79$	$58.15^{d} \pm 1.89$	$410.75^{d} \pm 36.60$
	6	$42.98^{e} \pm 3.72$	$23.55^{e} \pm 2.21$	$14^{e} \pm 0.27$	$132.0^{c} \pm 1.34$	$6712^{a} \pm 183.7$	$31145.35^{a} \pm 2632.53$	$59.12^{d} \pm 0.66$	$578.92^{c} \pm 21.65$
	7	$45.12^{e} \pm 3.74$	$22.34^{e} \pm 1.9$	$145^{a} \pm 13.65$	$132.56^{c} \pm 10.58$	$6715^{a} \pm 122.63$	$22645.51^{c} \pm 1837.78$	$70.07^{c} \pm 2.54$	$648.35^{b} \pm 18.16$
	8	$44.23^{e} \pm 2.82$	$22.21^{e} \pm 0.48$	$144^{a} \pm 11.33$	$156.0^{c} \pm 3.51$	$6723^{a} \pm 536.32$	$15742.58^{d} \pm 227.16$	$68.25^{c} \pm 1.67$	$510.32^{c} \pm 45.97$
	9	$47.31^{e} \pm 2.86$	$21.53^{e} \pm 1.01$	$145^{a} \pm 9.17$	$134.0^{c} \pm 1.56$	$6736^{a} \pm 123.67$	$14655.63^{de} \pm 577.92$	$57.3^{d} \pm 2.01$	$489.89^{cd} \pm 22.58$
	10	$48.22^{e} \pm 2.17$	$21.34^{e} \pm 1.15$	$145^{a} \pm 13.39$	$145.0^{c} \pm 6.18$	$6823^{a} \pm 274.68$	$17718.15^{d} \pm 1660.58$	$65.66^{c} \pm 4.7$	$540.76^{c} \pm 15.29$
North 24 parganas (West Bengal)	1	$40.23^{e} \pm 3.42$	$23.67^{e} \pm 1.56$	$137^{a} \pm 2.33$	$83.0^{e} \pm 4.85$	$5800^{b} \pm 425.75$	$16143.74^{d} \pm 288.67$	$51.32^{d} \pm 2.51$	$456.42^{d} \pm 28.99$
	2	$38.43^{e} \pm 0.7$	$24.54^{e} \pm 0.25$	$137^{a} \pm 5.46$	$86.0^{e} \pm 7.46$	$5796^{b} \pm 243.21$	$18612.47^{d} \pm 560.53$	$57.58^{d} \pm 2.37$	$455.37^{d} \pm 30.42$
	3	$42.44^{e} \pm 2.9$	$23.98^{e} \pm 0.77$	$138^{a} \pm 9.9$	$87.0^{e} \pm 4.96$	$5845^{b} \pm 184.91$	$13837.71^{e} \pm 1265.32$	$71.26^{c} \pm 2.55$	$447.95^{d} \pm 11.02$
	4	$43.23^{e} \pm 0.69$	$27.1^{e} \pm 2.05$	$137^{a} \pm 9.96$	$87.0^{e} \pm 1.42$	$6034^{ab} \pm 86.68$	$14847.95^{e} \pm 993.16$	$49.45^{de} \pm 3.12$	$520.73^{c} \pm 51.83$
	5	$33.89^{e} \pm 0.61$	$22.73^{e} \pm 2.05$	$139^{a} \pm 4.36$	$87.0^{e} \pm 6.11$	$5546^{b} \pm 411.19$	$13486.47^{e} \pm 1176.86$	$48.74^{de} \pm 3.77$	$486.51^{d} \pm 26.46$
	6	$37.23^{e} \pm 2.24$	$24.5^{e} \pm 1.71$	$140^{a} \pm 12.03$	$76.0^{e} \pm 0.9$	$5626^{b} \pm 374.96$	$12977.65^{e} \pm 545.36$	$61.09^{d} \pm 4.48$	$462.07^{d} \pm 32.04$
Ballia (Uttar Pradesh)	1	$55.65^{d} \pm 1.3$	$39.33^{e} \pm 3.07$	$61.13^{c} \pm 4.97$	$83.36^{e} \pm 1.57$	$3452.36^{d} \pm 323.82$	$11632.25^{e} \pm 550.66$	$88.25^{c} \pm 1.2$	$382.3^{de} \pm 32.9$
	2	$121.97^{a} \pm 10.0$	$32.57^{e} \pm 2.64$	$44.67^{d} \pm 1.01$	$64.0^{e} \pm 5.52$	$2383.33^{e} \pm 91.49$	$15373.53^{de} \pm 594.37$	$72.75^{c} \pm 6.31$	$296.92^{ef} \pm 27.42$
	3	$125.33^{a} \pm 7.12$	$79.8^{c} \pm 7.16$	$35.67^{d} \pm 3.41$	$84.67^{e} \pm 1.9$	$2253.33^{e} \pm 95.34$	$21636.87^{c} \pm 669.82$	$62.72^{d} \pm 5.19$	$450.12^{d} \pm 13.67$
	4	$89.84^{c} \pm 1.84$	$29.61^{e} \pm 0.66$	$23.33^{e} \pm 0.42$	$44.33^{f} \pm 0.49$	$2066.67^{e} \pm 119.27$	$11750.87^{e} \pm 1126.08$	$104.62^{a} \pm 7.31$	$327.23^{c} \pm 7.99$
	5	$134.36^{a} \pm 4.28$	$55.45^{d} \pm 0.81$	$41.0^{c} \pm 3.36$	$101.65^{d} \pm 6.81$	$4167.96^{c} \pm 330.32$	$24636.23^{b} \pm 328.91$	$110.56^{a} \pm 10.54$	$415.11^{d} \pm 33.62$
	6	$43.69^{e} \pm 3.76$	$157.36^{b} \pm 10.75$	$18.36^{e} \pm 0.63$	$69.72^{e} \pm 1.93$	$6712.42^{a} \pm 197.57$	$16074.48^{d} \pm 647.27$	$72.41^{c} \pm 1.32$	$515.78^{c} \pm 42.62$
	7	$133.36^{a} \pm 7.75$	$41.31^{e} \pm 1.94$	$29.55^{d} \pm 2.33$	$184.35^{b} \pm 11.92$	$6415.25^{a} \pm 473.6$	$22507.87^{c} \pm 1578.04$	$101.92^{a} \pm 5.66$	$789.22^{a} \pm 38.91$
	8	$105.3^{b} \pm 1.82$	$39.7^{e} \pm 1.06$	$39.0^{d} \pm 1.0$	$57.0^{e} \pm 4.4$	$1910.0^{e} \pm 154.35$	$13227.53^{e} \pm 376.62$	$83.06^{b} \pm 2.11$	$350.8^{e} \pm 17.3$
Prayagraj (Uttar Pradesh)	1	$88.26^{c} \pm 7.97$	$165.28^{b} \pm 4.86$	$41.27^{d} \pm 2.26$	$125.28^{d} \pm 4.62$	$4367.01^{c} \pm 229.48$	$12655.36^{e} \pm 837.51$	$47.28^{e} \pm 1.71$	$478.26^{d} \pm 32.34$
	2	$61.33^{d} \pm 1.29$	$287.3^{a} \pm 21.42$	$29.33^{d} \pm 2.23$	$52.33^{e} \pm 3.35$	$3903.33^{cd} \pm 84.28$	$17871.05^{d} \pm 287.86$	$43.74^{e} \pm 0.91$	$370.45^{e} \pm 4.92$
	3	$49.14^{e} \pm 0.76$	$246.46^{a} \pm 11.66$	$37.67^{d} \pm 3.33$	$112.33^{d} \pm 5.86$	$6196.67^{a} \pm 402.23$	$30852.57^{a} \pm 1789.62$	$82.99^{b} \pm 7.83$	$556.78^{c} \pm 18.85$
	4	$89.84^{c} \pm 8.44$	$240.81^{a} \pm 9.06$	$21.17^{d} \pm 2.08$	$87.33^{e} \pm 1.73$	$1853.33^{e} \pm 134.88$	$23221.98^{bc} \pm 319.28$	$55.68^{d} \pm 2.21$	$501.42^{c} \pm 49.58$
	5	$66.79^{d} \pm 2.7$	$95.26^{c} \pm 1.51$	$31.67^{d} \pm 2.36$	$115.67^{d} \pm 4.83$	$5523.33^{b} \pm 165.64$	$17542.89^{d} \pm 1567.11$	$68.61^{c} \pm 6.14$	$760.72^{a} \pm 60.8$
	6	$86.79^{c} \pm 1.19$	$132.48^{b} \pm 3.51$	$24.0^{e} \pm 2.01$	$173.33^{b} \pm 14.05$	$6500.0^{a} \pm 130.48$	$30845.24^{a} \pm 979.98$	$69.12^{c} \pm 5.79$	$678.09^{a} \pm 65.69$
	7	$105.33^{b} \pm 4.36$	$125.17^{b} \pm 10.81$	$48.67^{d} \pm 4.64$	$103.33^{d} \pm 9.49$	$2950.0^{de} \pm 203.77$	$23901.01^{cb} \pm 2231.83$	$80.07^{bc} \pm 6.98$	$548.04^{c} \pm 35.78$
	8	$101.08^{b} \pm 1.26$	$229.98^{a} \pm 2.42$	$34.0^{d} \pm 0.35$	$219.67^{a} \pm 5.73$	$6960.0^{a} \pm 234.94$	$24265.52^{b} \pm 2029.35$	$58.58^{d} \pm 1.6$	$390.25^{dc} \pm 21.58$

Lakhimpur (Uttar Pradesh)	1	$66.39^{d} \pm 4.19$	$51.3^{d} \pm 2.4$	$18.44^{e} \pm 0.31$	$33.67^{f} \pm 2.18$	$1736.02^{e} \pm 103.84$	$11643.47^{e} \pm 978.07$	$61.32^{d} \pm 2.28$	$429.22^{d} \pm 20.71$
	2	$86.79^{c} \pm 3.23$	$61.28^{d} \pm 5.51$	$27.67^{d} \pm 2.32$	$35.0^{f} \pm 1.51$	$3770.0^{d} \pm 49.49$	$15337.47^{de} \pm 1100.45$	$47.58^{e} \pm 0.6$	$444.64^{d} \pm 19.72$
	3	$67.49^{d} \pm 5.02$	$37.76^{e} \pm 2.36$	$59.0^{c} \pm 3.79$	$249.67^{a} \pm 6.26$	$4133.33^{c} \pm 330.57$	$12862.75^{e} \pm 1078.45$	$71.26^{c} \pm 4.76$	$479.7^{d} \pm 38.86$
	4	$90.67^{c} \pm 1.01$	$72.85^{d} \pm 4.68$	$9.23^{e} \pm 0.71$	$30.33^{f} \pm 1.01$	$2063.33^{e} \pm 195.17$	$12847.39^{e} \pm 829.06$	$44.48^{e} \pm 1.27$	$411.76^{d} \pm 23.35$
	5	$29.14^{e} \pm 1.28$	$32.39^{e} \pm 0.7$	$19.2^{e} \pm 0.37$	$83.67^{e} \pm 1.38$	$3536.67^{d} \pm 67.44$	$13268.48^{e} \pm 905.77$	$48.94^{e} \pm 2.41$	$426.35^{d} \pm 39.42$
	6	$107.3^{b} \pm 6.51$	$47.3^{e} \pm 1.46$	$73.67^{c} \pm 5.97$	$33.0^{f} \pm 2.83$	$4830.0^{c} \pm 144.9$	$16317.57^{d} \pm 464.79$	$66.09^{c} \pm 5.04$	$513.91^{c} \pm 8.88$
	7	$66.79^{d} \pm 4.83$	$32.76^{e} \pm 0.42$	$25.0^{e} \pm 1.86$	$30.0^{f} \pm 1.51$	$4563.33^{c} \pm 117.1$	$9187.24^{e} \pm 708.95$	$34.96^{e} \pm 0.78$	$311.13^{e} \pm 22.55$
	8	$100.95^{b} \pm 2.29$	$69.33^{d} \pm 6.55$	$98.0^{b} \pm 6.24$	$42.0^{f} \pm 2.99$	$4286.67^{c} \pm 297.33$	$14839.71^{e} \pm 696.82$	$48.79^{e} \pm 4.15$	$425.34^{d} \pm 22.22$

Data = mean ± SD, Different letters indicate significant difference within each parameter ($p<0.05$)

Table 3: Total Arsenic in borewell water and soils from paddy fields of West Bengal and Uttar Pradesh and level of arsenic in different fractions extracted through sequential extraction procedure

District	*Sample*	*Total arsenic in water (ug l^{-1})*	*Total arsenic in soil (mg Kg^{-1})*	*Arsenic Fractionation*						
				Water soluble Arsenic (mg Kg^{-1})	*Exchangeable/ Surface-adsorbed Arsenic (mg Kg^{-1})*	*Specifically Sorbed Arsenic (mg Kg^{-1})*	*Amorphous Fe oxides Sorbed Arsenic (mg Kg^{-1})*	*Crystalline Fe oxides Arsenic (mg Kg^{-1})*	*Residual Arsenic (mg Kg^{-1})*	*Total (mg Kg^{-1})*
Nadia (West Bengal)	1	97.4 ± 1.4	9.81 ± 0.98	0.14	0.11	0.67	1.20	3.43	4.32	9.86
	2	157.56 ± 0.45	19.45 ± 1.5	1.01	0.19	1.44	2.80	5.45	7.59	18.48
	3	550.23 ± 2.4	33.4 ± 1.4	1.84	0.37	2.34	5.98	8.35	12.36	31.23
	4	445.13 ± 1.67	26.12 ± 1.7	1.36	0.34	1.85	5.09	6.01	9.93	24.58
	5	107.22 ± 1.1	11.23 ± 0.98	0.51	0.13	0.89	1.90	2.47	5.39	11.28
	6	356.2 ± 1.23	28.22 ± 1.23	1.47	0.31	2.00	5.91	7.34	10.72	27.76
	7	428.78 ± 1.89	31.32 ± 1.45	1.69	0.41	2.29	6.42	8.77	11.59	31.16
	8	402.89 ± 2.13	29.67 ± 1.23	1.31	0.36	2.14	5.76	7.71	11.57	28.84
	9	296.56 ± 2.45	27.56 ± 1.41	1.24	0.33	2.18	4.85	6.34	11.58	26.51
	10	558.34 ± 2.6	31.34 ± 2.11	1.47	0.38	2.57	5.52	10.03	9.09	29.05

North 24 parganas (West Bengal)	1	302.23 ± 1.3	24.65 ± 1.5	0.59	0.37	1.91	3.66	8.66	8.91	24.11
	2	289.34 ± 1.6	23.91 ± 1.87	1.08	0.55	1.78	3.76	5.54	10.60	23.33
	3	246.76 ± 0.98	18.24 ± 0.34	0.87	0.44	1.26	2.16	4.09	7.36	16.18
	4	318.24 ± 2.56	28.74 ± 1.56	1.56	0.77	2.12	5.36	6.78	12.08	28.67
	5	203.87 ± 2.87	14.93 ± 2.45	0.73	0.39	1.09	2.43	3.27	7.17	15.08
	6	228.45 ± 3.1	15.98 ± 1.43	0.85	0.40	1.19	2.39	3.05	7.70	15.58
Ballia (Uttar Pradesh)	1	5.27 ± 0.90	5.59 ± 2.10	0.13	0.21	0.68	0.68	1.96	1.48	5.13
	2	114.11 ± 0.01	18.32 ± 0.27	0.46	0.54	2.66	3.10	4.21	7.27	18.23
	3	119.45 ± 0.05	24.45 ± 0.43	0.46	0.70	2.70	4.27	5.86	9.14	23.14
	4	98.00 ± 0.22	12.05 ± 0.13	0.25	0.28	1.19	1.98	2.54	4.75	10.99
	5	230.12 ± 0.54	24.18 ± 1.21	0.68	0.88	3.50	5.01	5.29	9.06	24.42
	6	120.87 ± 0.25	21.75 ± 0.98	0.48	1.09	1.81	4.42	5.22	9.07	22.09
	7	117.65 ± 1.85	20.35 ± 1.05	0.49	0.45	2.70	3.75	5.68	6.70	19.77
	8	96.10 ± 0.33	17.86 ± 0.17	0.38	0.47	1.77	3.11	4.53	7.92	18.18
Prayagraj (Uttar Pradesh)	1	5.32 ± 0.34	7.25 ± 0.46	0.05	0.09	0.66	0.73	2.83	1.80	6.15
	2	82.99 ± 0.17	19.92 ± 0.53	0.33	0.88	1.66	2.19	5.83	6.23	17.13
	3	109.23 ± 0.18	21.68 ± 0.32	0.33	0.66	1.31	2.50	4.37	8.14	17.32
	4	108.65 ± 0.58	11.58 ± 0.24	0.26	0.57	1.82	2.02	3.63	7.30	15.60
	5	75.53 ± 0.14	14.31 ± 0.63	0.19	0.39	1.26	1.51	3.66	4.20	11.21
	6	110.12 ± 0.17	21.62 ± 0.17	0.45	0.51	1.97	3.39	4.72	9.20	20.25
	7	122.17 ± 0.19	24.67 ± 0.16	0.45	0.45	2.35	1.83	5.07	7.77	17.93
	8	312.67 ± 0.12	25.74 ± 0.09	0.33	0.73	2.19	2.45	4.38	7.94	18.03
Lakhimpur (Uttar Pradesh)	1	2.29 ± 0.07	5.15 ± 0.45	0.04	0.12	0.46	0.58	2.21	1.62	5.05
	2	51.26 ± 4.34	19.00 ± 0.63	0.25	0.48	1.90	2.95	6.27	6.59	18.43
	3	78.03 ± 1.95	21.45 ± 0.72	0.21	0.24	1.79	2.16	4.07	7.63	16.10
	4	62.48 ± 1.95	19.95 ± 0.56	0.20	0.47	1.97	2.48	4.13	8.49	17.73
	5	111.64 ± 6.90	20.74 ± 0.65	0.16	0.38	1.10	1.94	5.04	6.81	15.42
	6	60.10 ± 1.15	18.30 ± 0.38	0.37	0.42	3.94	5.73	6.97	12.44	29.87
	7	81.67 ± 2.85	20.66 ± 0.30	0.20	0.26	1.87	2.80	5.22	8.12	18.47
	8	110.28 ± 0.20	23.59 ± 0.60	0.35	0.57	3.07	4.10	5.66	9.53	23.28

Data = mean ± SD

soil As was positively correlated with the As concentration in borewell irrigation water, however, the retention of As in soil was significantly different as evident in the Fig.1. The soil As was strongly correlated with As concentration in water in paddy fields of Nadia, North 24 parganas and Lakhimpur, relatively less in Prayagraj and least in Ballia. The alkaline pH and high EC may have contributed to the sorption of As in the paddy soil of these districts. High EC indicates high level of ions (USDA, 2011) and at alkaline pH As mostly exist in oxyanion form. Thus, abundance of positive ions may cause precipitation and deposition of As in soil. Variable retention of As in soil is probably attributed to the soil physico-chemical properties. It was interesting to note that despite strong correlation of soil As to water As, the proportion of water As retained in soil was much lower in Nadia and North 24 Parganas than in district of Uttar Pradesh. Further, this proportion was significantly higher at low water As and reduced gradually at higher As concentration in water at all sites. The average proportion of water As retained in paddy soils of LGP was 8%, ranging from 5.6 to 12.3%, whereas, it was 37%, ranging from 8.3 to 225% in the paddy soils of MGP. The lower proportion of soil As in high As water irrigated fields show that accumulation of As in soil is a function of binding sites available on soil particles. This clearly indicates a high proportion of As added to the soil leached and/ washed off or percolated downwards.

Fractionation of As in paddy soil

From the above it is clear that part of total As added through irrigation water retained and accumulated in soil depending on soil properties. The total amount of As accumulated in soil might distribute in soil matrix and may incorporate in minerals. If As is incorporated in stable mineral such as scorodite, its mobility in field conditions might be insignificant (Meunier *et al*., 2010, Niazi *et al*., 2011). Thus, the overall content of arsenic in soils does not inherently reflect its biological availability or possible toxicity assessments. For toxicity assessment and environmental impact, consideration of bioavailable As is crucial which depends on the quantity of As, soil chemical composition, and nature of binding to soil particles. Therefore, in the current study soil was fractionated using a five step sequential extraction processes to release easily available water soluble (step 1), surface bound exchangeable (step 2), specifically sorbed (step 3), bound to amorphous Fe oxide (step 4) and As bound to crystalline Fe oxide (step 5). The remaining As obtained after complete acid digestion of residual soil was termed as As associated within the crystal lattice of primary and secondary minerals which is stable and may not be discharged in soil solution under natural field environments. Arsenic released from step 1 to step 4 are most mobile and available to plant absorption. The level of As in these fractions may differ depending on soil parameters, such as, pH, redox state, organic matter and elemental composition. Arsenic associated to crystalline Fe oxide is also supposed to less bioavailable to plant (Niazi et. al., 2011), therefore, it was combined with the residual As and it constituted 61-69% of the total soil As. The average level of water soluble As (Step 1) was higher in soils of LGP in comparison to MGP, while specifically sorbed As (Step 3) was significantly higher in MGP (Fig. 2). Arsenic

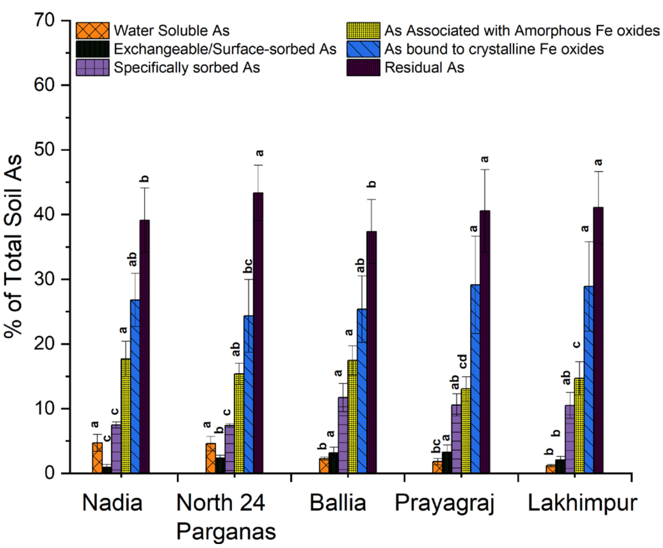

Fig. 2: Arsenic fractionation in paddy field soil of selected districts of Lower Ganga Plain (Nadia and North 24 Parganas districts of West Bengal) and Middle Ganga Plain (Ballia, Prayagraj and Lakhimpur districts of Uttar Pradesh). Means of each fraction are presented as percent (%) of the total soil arsenic concentration in the paddy field soil. Data is mean ± SD; different letters indicate significantly different values in each fraction from soil of various districts (P<0.05).

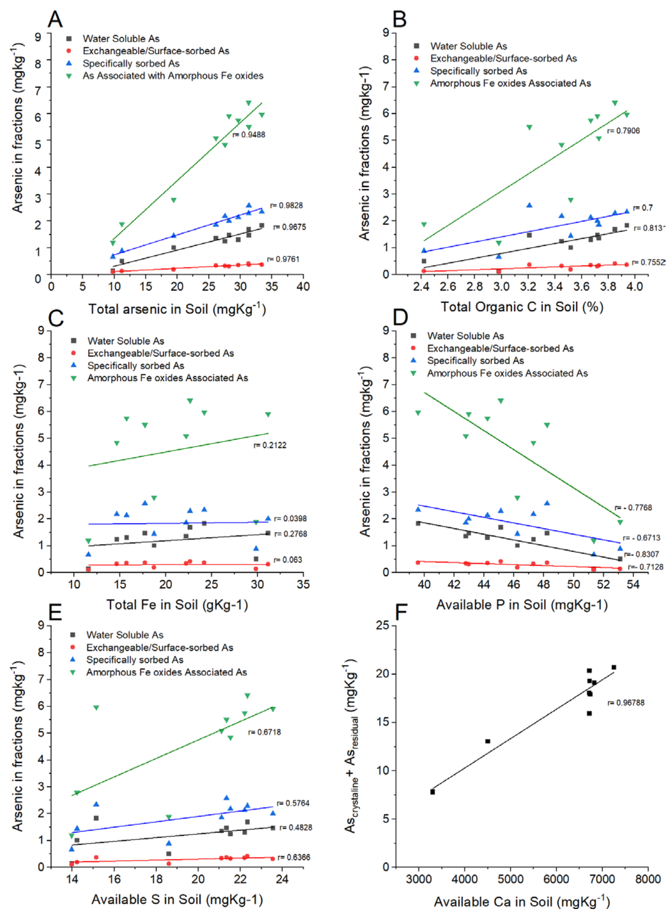

Fig. 3: Arsenic concentration in different fractions of paddy field soil of Nadia, West Bengal in relation to soil parameters; (A) Total soil arsenic, (B) Total organic carbon (TOC), (C) Total Fe, (D) Available P, (E) Available S, (F) available Ca.

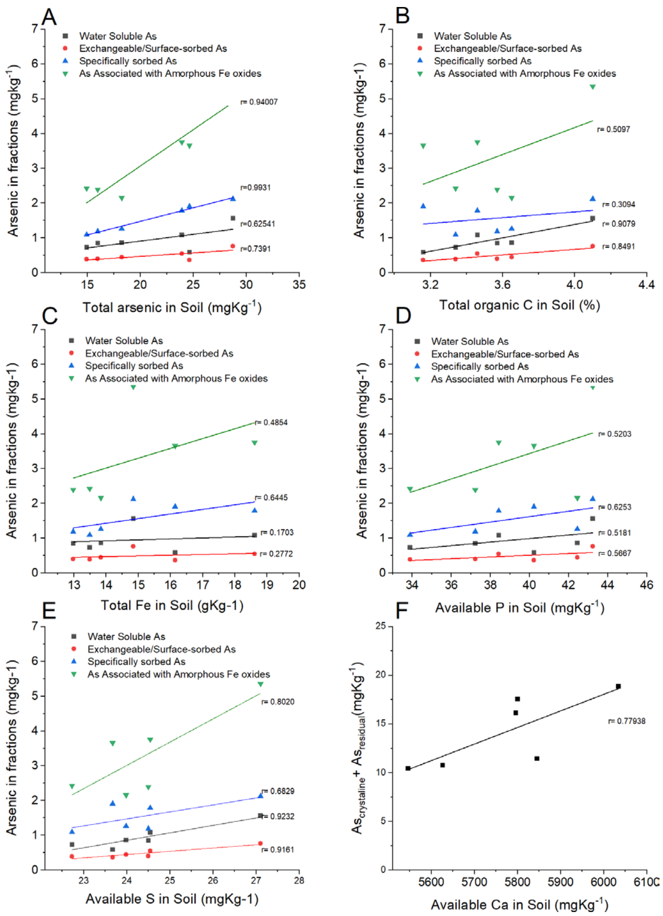

Fig. 4: Arsenic concentration in different fractions of paddy field soil of North 24 Parganas, West Bengal in relation to soil parameters; (A) Total soil arsenic, (B) Total organic carbon (TOC), (C) Total Fe, (D) Available P, (E) Available S, (F) available Ca.

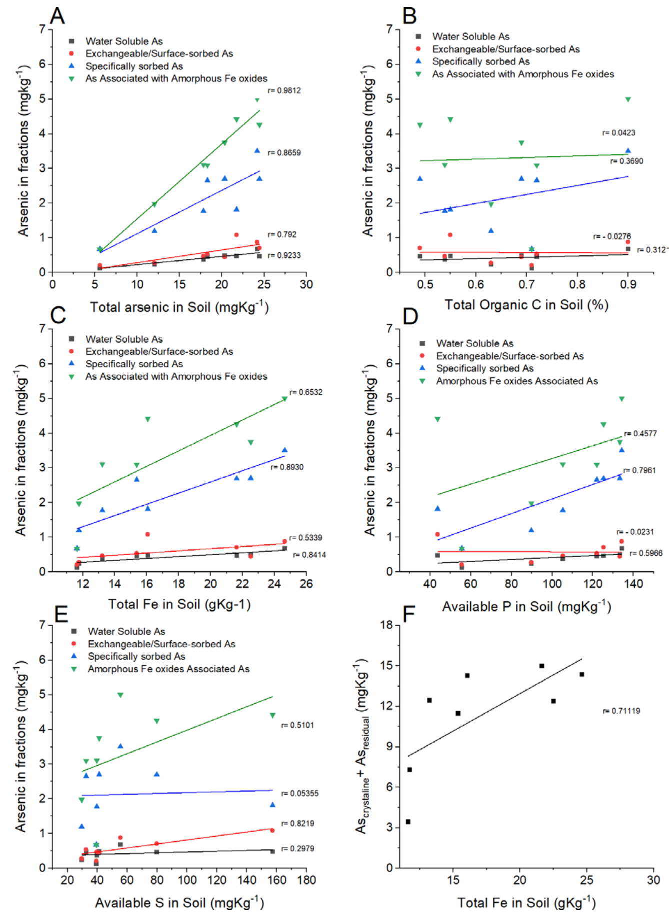

Fig. 5: Arsenic concentration in different fractions of paddy field soil of Ballia, Uttar Pradesh in relation to soil parameters; (A) Total soil arsenic, (B) Total organic carbon (TOC), (C) Total Fe, (D) Available P, (E) Available S, (F) Total Fe.

bound to amorphous Fe oxide (Step 4) was higher in soils of Ballia and Nadia districts in comparison to other studied districts of LGP and MGP. The water-soluble fraction in soils of LGP ranged 0.1 to 1.7% while in MGP 0.04 to 0.48% of total As. In contrast, the exchangeable As in soils of LGP ranged 0.02 to 0.8% while in MGP 0.09 to 1.1%. Among the mobile fractions of As, maximum was fractionated with amorphous Fe oxide (Step 4) in all the samples followed by specifically sorbed (Step 3) (Table 3). However, the level of As in amorphous Fe fraction in current study was much lower (11-21% of total soil As) than those reported by Niazi *et al.*, (2011) in soils from cattle dip site and railway corridors where As containing pesticides and herbicide were used in past, but it was higher than the mine soils (Anawar *et al.*, 2008). The high percentage of As in crystaline and residual fraction indicate that most of the As in the mineral matrix. Recently, Morosini *et al.*, (2023) also reported that residual fraction contained most of the As in agriculture soil industrial site.

The soil samples from Nadia showed a strong positive correlation between total soil As and the fractions from step 1 to 4 showing high mobility of As in paddy field of Nadia (Fig. 3A). Arsenic fractionation in relation to soil properties showed that the all four mobile fractions were positively correlated with TOC, with more strong correlation with water soluble fraction in Nadia (Fig. 3B). Available S was also positively correlated with all four mobile fractions with relatively stronger correlation with amorphous Fe oxide associated As (Fig. 3E). A weak positive correlation and negative correlation was observed with Fe and available P, respectively (Fig. 3 C-D). For soil of North 24 Parganas, the strong positive correlation with total As was found with specifically sorbed and amorphous Fe oxide associated As (Fig.4 A). The water soluble and surface sorbed As were also positively related. The water soluble and exchangeable fraction were positively correlated with TOC and available S while Fe and available S were relatively weakly correlated with all four mobile fractions in soil North 24 Parganas (Fig. 4 B-E). Arsenic associated to crystalline Fe oxide and residual fraction was positively correlated with available Ca in both Nadia and north 24 Parganas. In soil of Ballia, As associated to amorphous iron oxide was strongly correlated with total As followed by water soluble, specifically sorbed and exchangeable fractions. The water soluble and specifically sorbed fraction were also positively correlated with Fe and exchangeable fraction with S (Fig. 5 A-E). In soil sample of Prayagraj only water-soluble fraction showed strong correlation with total As. A positive correlation of As associated to amorphous iron oxide with Fe and exchangeable As with S was observed. In Ballia and Prayagraj As associated to

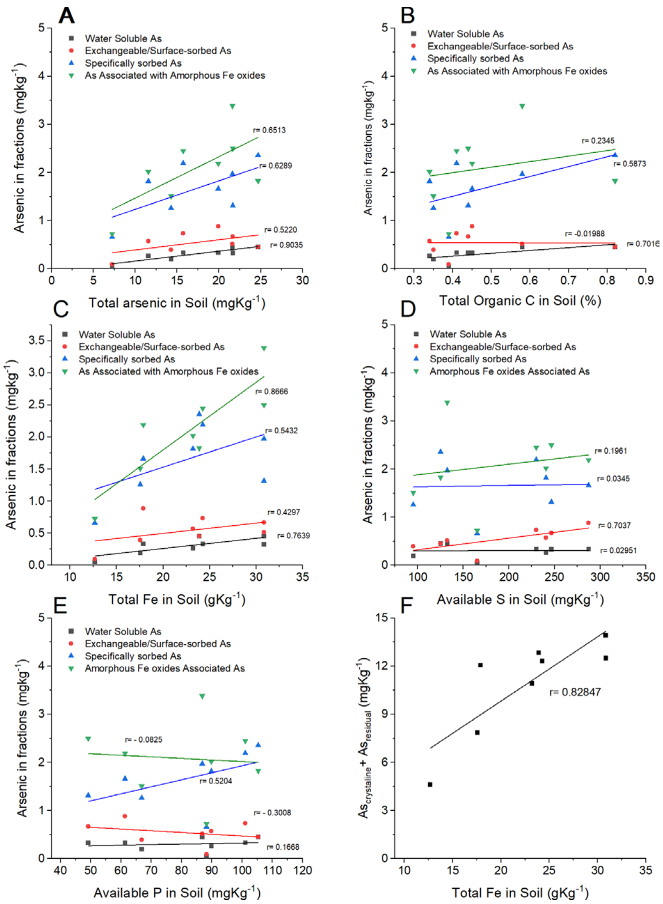

Fig. 6: Arsenic concentration in different fractions of paddy field soil of Prayagraj, Uttar Pradesh in relation to soil parameters; (A) Total soil arsenic, (B) Total organic carbon (TOC), (C) Total Fe, (D) Available P, (E) Available S, (F) Total Fe.

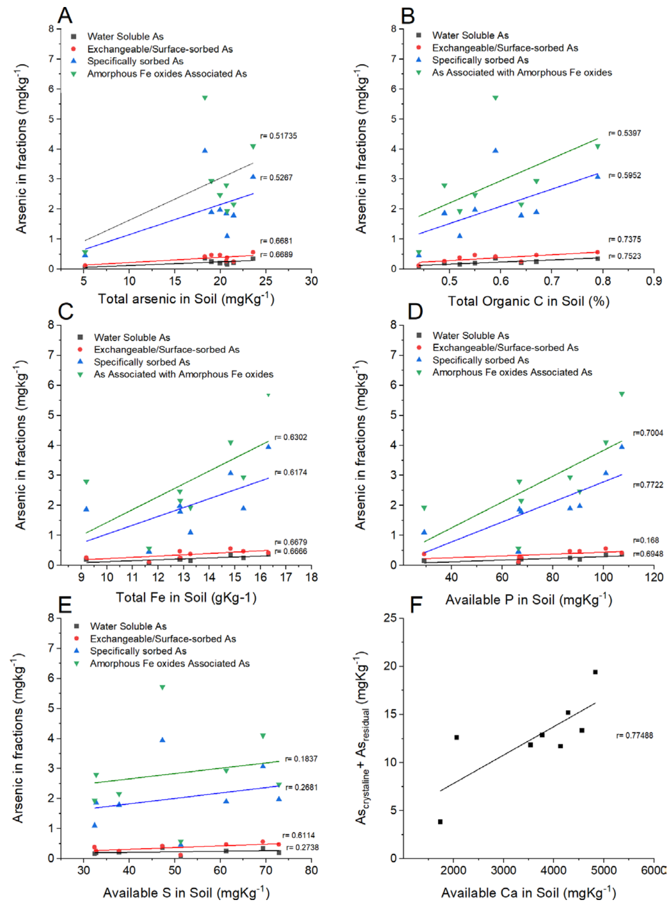

Fig. 7: Arsenic concentration in different fractions of paddy field soil of Lakhimpur, Uttar Pradesh in relation to soil parameters; (A) Total soil arsenic, (B) Total organic carbon (TOC), (C) Total Fe, (D) Available P, (E) Available S, (F) Available Ca.

crystalline iron oxide and residual fraction was strongly correlated with Fe (Fig 6). In Lakhimpur none of the soil parameters showed strong correlation with As fractions, however, water soluble and exchangeable fractions were positively correlated with TOC, specifically sorbed and As associated to amorphous iron oxide with P and As associated to crystalline iron oxide and residual fraction with available Ca (Fig. 7).

The soils of LGP were higher in Clay and TOC and poorer in available P and S. The high correlation of water soluble As with TOC may be associated to reductive dissolution of As. These results showed that in West Bengal soils high dissolution of As in water soluble and amorphous Fe oxide of seems related to high clay content and high TOC causing reducing condition resulting in reduction of Fe and release of As adsorbed to Fe. The reducing condition may release As adsorbed non specifically to soil surface in the water soluble fraction. In contrast the soils of Middle Ganga Plain were more sandy and poorer in TOC and OM, however, they were richer in available P and S. Thus, because of lower TOC relatively less As was released in water soluble and amorphous Fe oxide fraction in these soils. There was no clear trend of As release in different districts of MGP, however, higher release of As in exchangeable than water soluble fraction and relatively high As in specifically sorbed fraction than LGP might be related to high S and P in soils of MGP.

Further, strong correlation of As in amorphous Fe oxide with Fe content in the soil of Prayagraj may be due to more adsorption of As on Fe, because Prayagraj soil is rich in Fe and low in clay and TOC probably resulting in more Fe plaque formation on the surface of soil grains. As observed in Ballia where a positive correlation between As in specifically sorbed fraction and Fe content was observed. The As in crystalline and residual fraction showed interesting correlation pattern; in soil of Nadia, North 24 parganas and Lakhimpur it showed strong correlation with available Ca along with Fe probably due to formation stable calcium-Fe- arsenate (Anawar *et al*., 2008; Meunier *et al*., 2010). While in Ballia and Prayagraj the stronger correlation of crystalline and residual As was observed with Fe which may be associated to scorodite, geothite or ferrihydrite (Niazi *et al*., 2011). This observation could not be explained by the level of Fe or Ca in the soil because the Fe content was Prayagraj> Nadia> Ballia> north 24 Parganas> Lakhimpur and Ca was in Nadia> North 24 Parganas> Prayagraj> Ballia ≈ Lakhimpur. However, it was interesting that the ratio of Fe: Ca was about 3.5: 1 in Nadia, North 24 Parganas and Lakhimpur while it was about 5:1 in Ballia and Prayagraj. Thus, probably the stoichiometry of elements plays important role during the formation of stable crystals of As. However, a XANES spectroscopy with adequate reference material would give a clearer picture of the crystal composition.

The crystalline phase is considered stable (Zuhasz *et al*., 2007; 2009) and Ca – Fe arsenates demonstrate a significant capacity for arsenic retention in a broad range of soil pH (< 2 to > 9) (Zhang *et al*., 2024). Thus, under normal field condition it is supposed to be unavailable, however, it is more labile than arsenopyrite or scorodite (Meunier *et al*., 2010).

Conclusion

In conclusion, precipitation with Fe is the main process for As retention and accumulation in the soil. Most of the As was associated to crystalline Fe, and soils having a high Ca to Fe ratio, Ca was associated with the crystalline As probably in the form of Ca-Fe-arsenate. The mobile fraction of As was mostly associated with amorphous Fe oxide which was positively corelated with TOC. Thus, soils rich in Fe and low in TOC will have less dissolved As. TOC is the main factor effecting water soluble fraction of As as well, indicating high solubility of As under reducing conditions. High clay content, Fe and Ca and low P and S seems the main factors for accumulation of As in soil of West Bengal (LGP), whereas high TOC and EC, and alkaline pH may have facilitated the release of As. The soils of Uttar Pradesh (MGP) were low in TOC and high in Fe, available P and S. Thus, in these soils release of exchangeable and specifically sorbed As was significant. Application of P and S fertilizer would further increase the release of As through desorption of As from soil particles and amorphous Fe oxide. Managing soil properties like organic carbon, clay, phosphorus, sulfur, and iron oxides can effectively control arsenic mobility in paddy soils. Our findings underscore the importance of site-specific soil management strategies that align with sustainable agricultural practices and the UN Sustainable Development Goals (SDGs), particularly SDG 3 (Good Health and Well-Being) and SDG 6 (Clean Water and Sanitation) highlighting the levels of As contamination in groundwater used for drinking and irrigation.

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Author contribution

KS and PS, collection of samples, digestion and analysis; AT fractionation of As, participated in preparation of graphs; NM, assisted in data tabulation; GS assisted in data tabulation; SD, analysis and curation of data and final revision of MS; SM, conceptualise, made graphs, wrote and finalized the MS.

Conflict of Interest

Authors declare no conflict of interest.

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