Research Article

Bioavailability of arsenic in agricultural soils under the infuence of diferent soil properties

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Abstract

The major arsenic contamination in soil is resulting from the application of contaminated irrigation groundwater, which may further enter into the food chain via dietary intake. The severity of arsenic contamination in soil is regulated by the total arsenic content and its bioavailability. The bioavailable fraction of arsenic in soil is measured as the most considerable fraction, while assessing the latent risk arising from it. Various soil properties and their interactions with soil arsenic would give a better understanding of its availability in soil. The study was carried out to look into diferent bioavailable fractions of arsenic in soil and their relationships with diferent soil properties in the arsenic-prone areas of West Bengal, India. The results showed that the bioavailable soil arsenic fractions were in the order of water soluble < weakly adsorbed < specifcally adsorbed. The arsenic content in paddy soils was signifcantly (*p*<0.05) infuenced by bulk density, clay, pH, organic matter, available calcium, available phosphorus, and available sulfur contents in soil. Soil enzyme activities of dehydrogenase, hydrolase, and glucosidase were also positively regulating the soil arsenic content. The study provides a better understanding of the interaction between diferent soil properties and soil arsenic content for developing the site-specifc soil arsenic remediation strategies.

Keywords Contamination · Bioavailable fractions · Soil properties · Groundwater · Paddy · Arsenic

1 Introduction

Contamination of soils by arsenic is a major environmental concern. Arsenic (As) is considered as a toxic metalloid, a class-I carcinogen which is naturally distributed in water and soils in diferent parts of the world mostly in Southeast Asia [[20](#page-14-0), [32](#page-15-0)]. Soil contamination with As originates both geogenically and anthropogenically. Arsenic contamination of groundwater has been recognized in 105 countries with an estimate of 200 million humans exposed world-wide to arsenic toxicity [[24](#page-14-1), [25\]](#page-14-2).

Arsenic contamination is widespread in many countries, such as Argentina, Bangladesh, Cambodia, Chile, Taiwan, China, Thailand, the USA, and especially Bangladesh and West Bengal, India [[1,](#page-14-3) [3,](#page-14-4) [7](#page-14-5), [8](#page-14-6)]. The arsenic pollution occurs in the Ganga–Meghna–Brahmaputra (GMB) plains of India, and Bangladesh is the worst afected area among the world arsenic scenario. In GMB plain alone, currently, more than 100 million people are potentially at risk from groundwater arsenic contamination [[12\]](#page-14-7). Exposure from consumption of arsenic-contaminated drinking water and food crops has resulted in adverse health impacts on humans, such as stomach pain, circulatory problems, keratosis, cancer, and skin lesions. Arsenic contamination of groundwater in West Bengal was frst reported in the early 1980s. The permissible limits of arsenic in drinking water (10 μ g l^{−1}) and agricultural soil (20 mg kg⁻¹) have been given by the Agency for Toxic Substances and Disease Registry (ASTDR), 1985 [[15,](#page-14-8) [43\]](#page-15-1). Arsenic contamination in soil and water is a serious threat due to the transferring of

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arsenic through irrigation water to the soil–plant system. The arsenic contamination in soil is regulated by its content and availability in soil. The bioavailable fractions of arsenic are actually responsible for the toxicity compared to the total content. The bioavailable fraction is directly interacting with the living organism in soils. It is considered the most important fraction to assess the latent ecotoxicological threats. There is also a need to understand the important factors, which afect As availability, mobility, and chemistry in soils. These important factors are soil properties, solid composition, As-bearing phases, adsorption–desorption processes, biological transformations, and the volatilization of As in soil [[32](#page-15-0), [16](#page-14-9)]. Moreover, organic compounds and oxide/hydroxides of Fe, Zn, Al, and Mn also infuence the amount of bioavailable arsenic in soil [\[10,](#page-14-10) [32](#page-15-0)] by forming various compounds with diferent binding forces in the soil–water system. The total arsenic content in soil may be a good indicator to measure its degree of contamination, but insufficient for assessment of its environmental impact without considering the arsenic bioavailable fractions. Diferent fractions of arsenic in soil can provide useful information for the assessment of arsenic bioavailability and toxicity in soils [[23](#page-14-11)]. In order to devise remediation strategies, it is required to understand the relationship between arsenic (As) bioavailable fractions in soil and other soil properties, which may regulate the arsenic mobility in the contaminated soils. The objective of the study was to estimate bioavailable fractions of arsenic in soil in the arsenic-contaminated region. The interaction between the bioavailability of arsenic in soil and diferent soil properties was also assessed to fnd out the major soil parameters regulating the arsenic bioavailability in soil.

2 Materials and methods

2.1 Study site

Soil samples were collected from nine administrative blocks of fve districts in the state of West Bengal, India. These fve districts have been reported as arsenic-contaminated zone in the Lower Ganga plains, Bengal Basin of the Indo-Gangetic alluvium in South Asia [[9\]](#page-14-12). The fve districts were Hooghly (22°53'45" N and 88°22'07" E), Nadia (23°47'10" N, 88°55'65" E), Murshidabad (24°22'90" N, 88°24'61" E), Burdwan (23°23'24" N, 87°86'15" E), and North 24 Parganas (22°94′68″ N, 88°88′30″ E) (Fig. [1\)](#page-2-0). The climate of the study area is tropical to humid subtropical. The arsenic contamination in the study area is of geogenic origin and occurred through exploitation of groundwater for irrigation. None of any anthropogenic pollution sources were spotted in the study area.

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2.2 Sampling

Composite soil samples from agricultural fields were collected in two phases from arsenic-contaminated areas of five districts of West Bengal during May–July 2015 and July 2016. The soil was vertisols and clay–loam type. The field of soil sampling was being used for cultivating paddy in the region. Soil sampling was made to a soil depth of 5–15 cm from the surface. Thirty soil samples were collected in the Phase-I from ten different distantly located villages/sites of these five districts in West Bengal. Fifteen soil samples were further collected in the Phase-II from the 15 different distant sites (agriculture fields) at three villages, in which arsenic contents were found higher during the Phase-I. The Phase-II was conducted to augment the number of representative samples of these arsenic-contaminated sites of three villages of Phase-I. Samples were stored at low temperature for transportation to the laboratory and stored at 4 °C until further analysis. The samples were air-dried, crushed, and passed through a 2-mm sieve for determining all soil parameters, and moist samples were stored at 4 °C for soil enzyme analysis.

In the Phase-II, 15 groundwater samples (*n* = 3) were also collected from irrigation water sources in July 2016 from three villages. The water samples were collected in the sterilized polyethylene bottles fitted with a liquidtight stopper after running the tube well for 10 min. The water samples were then immediately acidified with 1% $HNO₃$ and analyzed for arsenic content within 7 days of sampling.

2.3 Soil physicochemical analysis

The physicochemical analysis of soil samples was carried out in triplicates. The pH and electrical conductivity (EC) of soils were measured by using the Orion meter in soil/ water a ratio of 1:2.5 (w/v). Soil water holding capacity (WHC) was measured gravimetrically according to Keen's box method by weighing water-saturated and ovendried samples (24 h at 105 °C) [[6](#page-14-13)]. The total organic carbon (TOC) was estimated by the method of Walkley and Black (1934). Organic matter (OM) values were obtained from the estimated organic carbon (OC) values using the following formula {OM = 1.724 (Van Bemelen factor) \times OC} [\[27](#page-14-14)]. The available nitrogen was determined by using the Kjeldahl method [[6\]](#page-14-13). The microbial biomass carbon (MBC) was determined by the chloroform–fumigation–extraction Vance method [[37–](#page-15-2)[39](#page-15-3)]. The available sodium (Na), potassium (K), and calcium (Ca) contents were measured by the extraction method by using flame

photometer (Systronix-128) (Jackson 1962). Available phosphorus (P) content was determined after the extraction of sample in 2% sodium bicarbonate solution [[26\]](#page-14-15).

Moisture content was estimated using the method of Bhattacharya et al. [\[4\]](#page-14-16). The bulk density (gravity bottles) was estimated according to the method as earlier described by Srivastava et al. [[37–](#page-15-2)[39\]](#page-15-3). The soil texture was estimated by the Bouyoucous hydrometer method. The soil available sulfur–sulfate was determined by the method of Tabatabai and Bremner [\[40](#page-15-4)]. Soil enzyme activities were done in moist soil samples for determining dehydrogenase (DHA), fluorescein diacetate hydrolase (FDA), arylsulfatase (ASA), alkaline phosphatase (APA) β-glucosidase (BG), cellulase (CeA), and protease (PA) using the standard methods of Dick et al. [[13](#page-14-17)] and Srivastava et al. [[37](#page-15-2)].

2.4 Total arsenic content

The digestion of air-dried soil samples (0.25 g) was made by using $HNO₃:H₂O₂$ (5:1). Cooled digested soil samples and acidifed water samples (5 ml) were fltered through Whatman syringe flter 0.2 µm, followed by a volume make up to 30 ml with deionized water. Total As content in water and soil samples was estimated by using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500 ce).

2.5 Soil bioavailable arsenic fractions

The fractionation of As in soil samples was performed using the sequential extraction procedure described by Wenzel et al. [\[42](#page-15-5)]. The bioavailable arsenic fractions were determined as water-soluble, weakly adsorbed extractable in 0.5 M NaHCO₃ and specifically adsorbed extractable in 0.05 M $NH_4H_2PO_4$. The aliquots were taken and centrifuged at 3000 rpm for 15 min at room temperature, fltered through Whatman flter paper no. 40. Extracted bioavailable arsenic fractions in soil samples were estimated using ICP-MS.

2.6 Quality control and quality assurance

Quality control measures for each batch including calibration with reference samples, blanks, and replicate analysis were followed throughout the analysis in order to ensure reliable analytical data. Sample digestion batches were accompanied by analytical blanks, rice flour certified reference material (CRM) (NIST 1568a) and blank spikes. The accuracy of the sequential extraction was also evaluated by analyzing the same CRM. Mean CRM and spike recoveries of total As were 90% (± 3.1; *n* = 5) and 85% (± 2.8; *n*=5), respectively. The method detection limit for As was 1 μg I^{-1} .

2.7 Statistical analysis

The data were subjected to statistical analysis using analysis of variance (ANOVA)—the general linear model (GLM) to study signifcant diferences at *p*<0.05 among the values of diferent parameters by using SPSS 10.0. Comparison of means and levels of signifcance were evaluated according to Duncan's multiple range test (DMRT).

Multivariate principal component analysis (PCA) was used to reduce a large number of variables to representative factors called "Principal Components." Principal components were computed by factors that are the eigenvectors of the correlation matrix of the original data. PCA as the multivariate analytical tool was used to reduce a set of original variables and to extract a small number of latent factors (principal components, PCs) for analyzing

SN Applied Sciences A SPRINGER NATURE journal relationships among the observed variables. The number of factors extracted from the variables was determined by a screen test according to Kaiser's rule. This criterion retained only factors with eigenvalues that exceed one. Varimax-rotated factor loadings greater than 0.50 were underlined to assist the interpretation of the meanings of the factors. In order to fnd possible tendencies in the samples and the discriminated power of the variables, PCA was applied. The components accounting for the maximum variance in the PCA output were chosen as signifcantly delineating the relationships between total soil arsenic content with bioavailable fractions of arsenic and diferent soil properties.

3 Results

In the study, 10 and 15 sites were surveyed during Phase-I and Phase-II, respectively. Physicochemical characteristics of paddy soil samples in ten villages were found signifcantly diferent (Tables [1](#page-4-0) and [2](#page-5-0)). The pH values of all the soil samples were alkaline in nature. The EC values of soils ranged between 0.145 and 0.344 dS m⁻¹ (Table [2](#page-5-0)). The soil was clay to clay loam. Clay contents ranged from 28 to 62% in all the sites covered in Phase-I and found correlated with arsenic content in soils (r^2 = 0.96; p < 0.05). The water holding capacity (WHC) ranged from 53 to 61%. The bulk density (BD) ranged between 1.27 and 1.46 gm cm⁻³ with a mean value of 1.32 gm cm⁻³ (Table [1\)](#page-4-0).

The contents of available phosphorus (36–58 mg kg⁻¹), available sulfur (8.86–30.41 mg kg^{-1}), and available K (71.27–133 mg kg^{-1}) in soils of ten sites are given in Table [2](#page-5-0). The soils were having high available Ca (3303–7245 mg kg^{-1}) and available Na (56.35–227.44 mg kg−1) contents (Table [2](#page-5-0)). The TOC, OM, and MBC were ranged normal to high as 2.32–5.64%, 3.99–9.70%, and 120.29–829.74 µg g^{-1} , respectively, at all sites (Table [2\)](#page-5-0).

Enzyme activities for PA, APA, and ASA found low in soil containing higher arsenic content, except DHA, FDA, BGA, and CeA (Table [3](#page-6-0)). The mean values for DHA, FDA, APA, and ASA ranged from 12.66–21.68, 13.30–20.20, 19.42–118, and 47.51–191.44 µg q^{-1} soil h⁻¹, respectively. Soil arsenic content was signifcantly (*p*<0.05) and negatively correlated with the enzyme activities. Highest values for DHA, FDA, BGA, and CeA in soil samples were recorded in Pipligram. The result showed DHA and FDA values were highest in highly contaminated sites.

In soil, the total arsenic content ranged from 6.64 to 31.11 mg kg⁻¹ (Table [4](#page-6-1)). The arsenic contents in soils of the studied area were found above (32–520%) the general naturally occurring soil arsenic content, i.e., 5 mg kg⁻¹ [[28](#page-14-18)]. However, arsenic levels in some of the villages were

Table 1 Soil physical properties of ten villages in

West Bengal

BD, bulk density; WHC, water holding capacity

The significant differences among the Mean \pm SE ($n=3$) values of a column are mentioned by different alphabets (in superscript) (*p*<0.05)

found above the threshold limit of 20 mg kg⁻¹ given for agricultural soils [[15\]](#page-14-8). Table [4](#page-6-1) shows the total arsenic contents and its sequential extracted bioavailable fractions in the soil samples. The results showed signifcant differences ($p < 0.05$) among all the bioavailable fractions at diferent sites. On average, the water-soluble fractions accounted for 3–5% of total As, whereas weakly adsorbed fraction accounted for 5–8%. The specifcally sorbed fraction comprised 7–12% of total As (Table [4\)](#page-6-1). Remaining As accounted for 75–85% of the total As would be bounded or residual fractions (Table [4](#page-6-1)). The results showed arsenic partitioning following a descending order: residual fractions (or well-crystallized hydrous oxides of Fe and Al, amorphous and poorly crystalline hydrous oxides of Fe and Al) \ge specifically sorbed $>$ weakly sorbed $>$ water soluble. The soil arsenic content found higher at Ghentughachi, Gotera, and Pipligram during the Phase-I. The results of the Phase-II for the arsenic contents in groundwater and soils of all 15 sites of these three villages are presented in Tables [5,](#page-7-0) [6](#page-7-1), [7](#page-8-0) and [8](#page-9-0).

In Phase-II, the total arsenic content ranged from 15.03 to 32.10 mg kg⁻¹ and 112.3 to 558.1 µg I^{-1} in soil and groundwater, respectively, among diferent sites of Ghentughachi, Gotera and Pipligram (Table [5](#page-7-0)). Among all the 15 diferent sites of Phase-II, bioavailable fractions were signifcantly varied (*p*<0.05) (Table [5\)](#page-7-0). The results showed that the water-soluble fractions ranged between 0.467 and 1.380 mg kg^{-1} of total As, weakly adsorbed fraction between 0.85 and 2.65 mg kg−1, and specifcally sorbed fraction between 1.308 and 3.360 mg kg⁻¹. The chemical properties of soils obtained in the Phase-II are given in Tables [6](#page-7-1) and [7.](#page-8-0) The enzyme activities were lower in higher arsenic-containing soils (Table [8](#page-9-0)). The relationships between total soil arsenic content with bioavailable fractions of arsenic and diferent soil properties were studied using PCA.

The PCA biplot of soil arsenic content of diferent sites of the Phase-I showed 98.74% of the total variance (Fig. [2](#page-9-1)). The PCA biplot of soil physical properties and soil arsenic content resulted in 83.39% of total variance (Fig. [3](#page-10-0)). Soil arsenic content was negatively correlated with the soil bulk density and positively correlated with soil moisture and water holding capacity at all the sites. The PCA biplot between soil arsenic and soil chemical properties resulted in 77.03% of the total variance, depicting that soil TOC, MBC, OM, and Ca contents were positively correlated with soil arsenic content (Fig. [4](#page-10-1)) at all the sites. Figure [5](#page-11-0) explains PCA biplot performed between soil enzyme activities and soil arsenic content accounted for 76.14% of the total variance, showing that DHA, FDA, CeA, and BGA soil enzyme activities were positively correlated with the soil arsenic contents, whereas the AP, PA, and ASA activities were negatively correlated at all the sites. The PCA biplot of total As content in the groundwater and soil samples of Phase-II resulted in 85.73% of total variance (Fig. [6\)](#page-11-1). Figures [7](#page-12-0), [8](#page-12-1), and [9](#page-13-0) show similar trend of the results between soil arsenic

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Table 3 Enzyme activities of soil of ten villages in West Bengal

DHA (dehydrogenase activity) as μg TPF g soil⁻¹24h⁻¹; FDA (fluorescein diacetate) as μg fluorescein g soil⁻¹ 2 h⁻¹; APA (alkaline phosphatase activity) as μg ρ-NP g soil⁻¹ h⁻¹; BG (β-glucosidase) as μg ρ-NP g soil⁻¹ h⁻¹; PA (protease activity) as μg Tyr g soil⁻¹ 2 h⁻¹; CeA (cellulase activity) as µg glucose g soil⁻¹24h⁻¹; ASA (arylsulfatase) as µg ρ-NP g soil⁻¹ h⁻¹

The significant differences among the Mean \pm SE ($n=3$) values of a column are mentioned by different alphabets (in superscript) (p < 0.05)

Table 4 Total and bioavailable fractions of soil arsenic (mg kg−1) of ten villages in West Bengal

TAs, total arsenic; BA/WS, bioavailable arsenic water soluble; BA/WA, bioavailable arsenic weakly adsorbed; BA/SA, bioavailable arsenic specifcally adsorbed; BA/RA, bioavailable arsenic residual

The significant differences among the Mean \pm SE ($n=3$) values of a column are mentioned by different alphabets (in superscript) (p <0.05)

Table 5 Arsenic content in soil and groundwater (GW) in 15 diferent sites of three villages in West Bengal

BA/WS, bioavailable arsenic water soluble; BA/WA, bioavailable arsenic weakly adsorbed; BA/SA, bioavailable arsenic specifcally adsorbed; BA/RA, bioavailable arsenic residual; GW, groundwater

The significant differences among the Mean \pm SE ($n=5$) values of a column are mentioned by different alphabets (in superscript) (p < 0.05)

properties of 15 diferent sites of three villages in West Bengal 15 sites of three villages in the Phase-II BD (gm cm⁻³) WHC (%) Moisture (%) Texture Ghetugachi, Chakdah, Nadia (SusBis) $1.4^d \pm 0.01$ $59.01^e \pm 0.02$ $27.9^e \pm 0.01$ Clay loam Ghetugachi, Chakdah, Nadia (DipGho) $1.3^{\circ} \pm 0.01$ $58.08^{\circ} \pm 0.02$ $28.0^{\circ} \pm 0.02$ Clay loam Ghetugachi, Chakdah, Nadia (HarCha) $1.3^c \pm 0.05$ 60.02^h \pm 0.08 27.3^{de} \pm 0.36 Clay loam Ghetugachi, Chakdah, Nadia (BikSar) $1.4^d \pm 0.08$ $57.94^{cd} \pm 0.28$ $27.0^d \pm 0.04$ Clay loam Ghetugachi, Chakdah, Nadia (PraBis) $1.4^d \pm 0.01$ 60.10^h \pm 0.08 27.1^d \pm 0.04 Clay loam Gotera, Nadia (SuvMon) $1.2^{bc} \pm 0.88$ $59.82^{9} \pm 0.01$ $24.6^{c} \pm 0.30$ Clay Gotera, Nadia (ChhMon) $1.1^{ab} \pm 0.07$ 60.21^h \pm 0.06 25.1^c \pm 0.02 Clay Gotera, Nadia (AnsMon) $1.2^{bc} \pm 0.01$ 59.33^f \pm 0.08 $23.8^b \pm 0.08$ Clay Gotera, Nadia (PraSan) $1.2^{bc} \pm 0.08$ $59.04^{e} \pm 0.02$ $21.9^{a} \pm 0.06$ Clay Gotera, Nadia (GanBar) $1.1^{ab} \pm 0.05$ $58.1^{d} \pm 0.05$ $25.2^{c} \pm 0.18$ Clay Pipli, N 24 Parganas (SubhRo) $1.3^c \pm 0.07$ $57.82^c \pm 0.01$ $32.8^g \pm 0.03$ Clay Pipli, N 24 Parganas (ShiRo) $1.3^c \pm 0.72$ $57.02^a \pm 0.15$ $33.1^g \pm 0.08$ Clay Pipli, N 24 Parganas (MadMon) $1.4^d \pm 0.06$ 57.63^b \pm 0.03 $31.9^{f} \pm 0.02$ Clay Pipli, N 24 Parganas (RaKrMo) $1.2^{bc} \pm 0.11$ $57.16^a \pm 0.02$ $33.7^h \pm 0.05$ Clay Pipli, N 24 Parganas (DebSar) $1.3^c \pm 0.05$ $57.97^{cd} \pm 0.01$ $34.0^h \pm 0.01$ Clay

BD, bulk density; WHC, water holding capacity

The significant differences among the Mean \pm SE ($n=5$) values of a column are mentioned by different alphabets (in superscript) (*p*<0.05)

Table 6 Soil physical

Table 8 Soil enzyme activities of 15 diferent sites of three villages in West Bengal

DHA (Dehydrogenase activity) as μg TPF g soil⁻¹24 h⁻¹; FDA (fluorescein diacetate) as μg Fluorescein g soil⁻¹ 2 h⁻¹; APA (alkaline phosphatase activity) as µg ρ-NP g soil⁻¹ h⁻¹; BG (β-glucosidase) as µg ρ-NP g soil⁻¹ h⁻¹; PA (protease activity) as µg Tyr g soil⁻¹ 2 h⁻¹; CeA (cellulase activity) as µg glucose g soil⁻¹24 h⁻¹; ⁷ASA (arylsulfatase) as µg ρ-NP g soil⁻¹ h⁻¹

The significant differences among the Mean \pm SE ($n=5$) values of a column are mentioned by different alphabets (in superscript) ($p < 0.05$)

Fig. 2 PCA biplot of soil arsenic content of ten villages in West Bengal. BA, bioavailable; WA, weakly adsorbed; SA, specifcally adsorbed; WS, water soluble; and RA, residual

Fig. 3 PCA biplot of soil arsenic and physical properties of ten villages in West Bengal. WHC, water holding capacity; BD and bulk density; moisture

Fig. 4 PCA biplot of soil arsenic and chemical properties of ten villages in West Bengal. MBC, microbial biomass carbon; Av-Na, available sodium; Av-Ca, available calcium; Av-K, available potassium; TOC, total organic carbon; EC, electrical conductivity; AP, available phosphorus; AS, available sulfate–sulfur; and OM, organic matter

Biplot (axes F1 and F2: 77.03 %)

content and diferent soil physicochemical properties and enzyme activities.

4 Discussion

Out of the total ten villages surveyed in fve diferent districts of West Bengal during the Phase-I, three villages (Ghentughachi, Gotera and Pipligram) exhibited higher arsenic contamination (ranged 24.7–31.1 mg kg^{-1}) in the paddy soils above the threshold limit (20 mg kg⁻¹) given by FAO. The arsenic content in groundwater ranged between 112.3 and 558.02 μ g l⁻¹, which also exhibited higher arsenic contamination in groundwater above the threshold limit of 50 μ g l⁻¹ given by the Indian Standards for Drinking Water, second revision of IS-10500, 2004. Several studies specify that irrigation with As-laden groundwater is building up the soil As levels [[17](#page-14-19), [31](#page-14-20)]. The study showed arsenic water soluble, weakly adsorbed fraction, specifcally sorbed, and the residual fraction in the range of 5–7%, 7–12%, 8–15%, and 75–85%, respectively, in the soil samples. The frst fraction represents water-soluble arsenic, which is the most mobile form of arsenic. The second fraction showed weakly exchangeable arsenic, **Fig. 5** PCA biplot of soil arsenic and enzyme activities of ten villages in West Bengal. FDA, fuorescein diacetate; APA, alkaline phosphatase; PA, protease; CeA, cellulase; BG, β-glucosidase; DHA, dehydrogenase; and ASA, arylsulfatase

Fig. 6 PCA biplot of soil and groundwater arsenic content of 15 diferent sites of three villages in West Bengal. BA, bioavailable; WA, weakly adsorbed; SA, specifcally adsorbed; WS, water soluble; RA, residual; and total As (GW), total arsenic groundwater

which binds to soil forming outer sphere complexes. This fraction can be released easily into soil water through ion exchange processes [[44](#page-15-6)]. The specifically sorbed fraction ranged from 8 to 15%, which represents the strongly bound inner-sphere surface complex between arsenic and metal oxide, which might be extracted into soil pore water by competitive ligand exchange [\[42\]](#page-15-5); Yolcubl et al. [[45](#page-15-7)]. The soil arsenic contents difered largely depending on the underlying site-specifc soil properties. Soil properties have a signifcant infuence on the speciation, bioavailability, and solubility of As (Bissen and Frimmel et al. [[5,](#page-14-21) [19](#page-14-22)]. In the study, key soil parameters that have been infuencing the bioavailability of soil arsenic were pH, phosphorus, sulfur, and organic carbon content. Arsenic mobility and bioavailability may vary within the pH range between 6.5 and 8.5 depending upon the oxidizing as well as reducing conditions in soil (Dzombak et al. [[14](#page-14-23)].

F1 (76.23 %)

The predominance of As fractions is observed in an order of residual > specifcally sorbed > weakly sorbed/ exchangeable > water soluble. The residual fraction of soil arsenic is based upon co-precipitation, adsorption, surface complex formation, ion exchange, and chemical bonding. Although As associated with Fe and Mn (hydro) oxides presents low mobility in a non-acidic oxidizing

Fig. 7 PCA biplot of soil arsenic and physical properties of 15 diferent sites of three villages in West Bengal. WHC, water holding capacity; BD, bulk density; moisture; and total As (GW), total arsenic groundwater

Fig. 8 PCA biplot of soil arsenic and chemical properties of 15 diferent sites of three villages in West Bengal. MBC, microbial biomass carbon; Av-Na, available sodium; Av-Ca, availcarbon; EC, electrical conduc-

able calcium; Av-K, available potassium; TOC, total organic $-2(30.44%$ tivity; AP, available phosphorus; AS, available sulfate–sulfur; OM, organic matter; and total As (GW), total arsenic groundwater

environments, there is a risk of its release, when soil redox potential or pH changes. Changes in the ionic composition or infuencing adsorption–desorption reactions could cause mobilization of As from this fraction. Signifcant correlations were obtained between the total soil As content and its specifcally sorbed, weakly sorbed or exchangeable, water soluble, and residual fractions. Total content of arsenic present in soils cannot provide a precise index for evaluating their toxicity to soil and crop cultivation in the contaminated soils. The water-soluble As was considered to be the most labile fraction and important for toxicity concern. The major amount of the As fraction holds up

 $\mathbf 1$

 $\overline{0}$

 -1

 -2

 -3 -4

A.Na Gotera (SuvMon)

Gotera (ChhMon)

 \cdot OM

 \bullet AN

Gotera (PraSan)

Gotera (AnsMon)

 -3

Gotera (GanBar)

 -2

 -1

 $\overline{0}$

 $\overline{1}$

F1 (56.02 %)

strongly or present in immobile residual forms binding to high clay matrices in the soil. Soil As content and its toxicity depend upon its various forms from easily leachable to recalcitrant ones due to its interactions with diferent soil components.

 \overline{a}

The TOC and OM content of soil found positively and signifcantly correlated with the bioavailability of arsenic in the soil. The correlation between As adsorption by humic acid is well known, although the accurate retention mechanisms remain contentious [[21](#page-14-24)], and some experiments indicate that the occurrence of organic matter causes the reverse efect, competing with As for adsorption sites on

 \cdot pH

 $• Av.S$

 $·$ MBC

• Pipligram (MadMon)
• Pipligram (ShiRo)
• Pipligram (SubhRo)

 $\overline{4}$

5

· Pipligram (DebSar) Pipligram (RaKrMo)

3

Fig. 9 PCA biplot of soil arsenic and enzyme activities of 15 diferent sites of three villages in West Bengal. FDA, fuorescein diacetate hydrolase; APA, alkaline phosphatase; PA, protease; CeA, cellulase; BG, β-glucosidase; DHA, dehydrogenase; ASA, arylsulfatase; and total As (GW), total arsenic groundwater

iron oxide surfaces [[30](#page-14-25)]. An increase in OM can augment desorption of As from solid phase [\[30,](#page-14-25) [41](#page-15-8)], because it can enhance microbial activity and decrease the soil redox potential, which favors the reductive dissolution of Fe-oxyhydroxide linked to OM. Additionally, dissolved OM leads to an augment As mobility, as it contains negative charges, which have a high potential to contend with As for sorption sites in soil [[22](#page-14-26)]. Higher arsenic-contaminated soil samples were rich in organic matter. Increases in organic matter may enhance the desorption of As from the solid phase by increasing microbial activity and reductive dissolution of Fe-oxyhydroxide. This process may lead to the sorption of humic anions on Fe oxides resulting in competition for sorption sites and preventing As sorption, or inducing As desorption and thus increase the mobility of As in the soil [[33\]](#page-15-9).

It is also found that higher calcium content may be attributed to the formation of stable Ca-arsenate precipitate [[29](#page-14-27)]. The increase in soil arsenic bioavailability was correlated with a decrease in the concentration of available phosphorus content in soil, because it competes with arsenic for sorption sites in soils [[35](#page-15-10)]. In Ghentughachi, Gotera, and Pipligram sites, a negative correlation was found between P and As because of the P-induced As mobilization and bioavailability by competitive displace-ment of AsO₄ by PO₄ at sorption sites [[36](#page-15-11)]. The negative correlation found between S and high As content in soil among all the study sites. S and As share similar chemical and biological redox transformation, and their biogeochemical cycles are often interconnected [[18\]](#page-14-28). Arsenic content and its build up in soils significantly hampered the soil enzyme activities. It has been reported that arsenite inactivates enzymes through reacting with –SH groups and formed As sulfide [\[11,](#page-14-29) [36](#page-15-11)]. Soil enzyme activity is a sensitive indicator of soil quality. The BG activity is reported to be significantly correlated with SOC (Bandick et al. [[2](#page-14-30)] of the study. The results also showed that DHA, FDA, CeA, and BG activities were increased in the highest arsenic-contaminated sites, which may be due to high OM content and corresponding increase in soil MBC content. This needs further investigation.

5 Conclusion

The study revealed that soil arsenic contents and its bioavailable fractions found strongly correlated with different enzymatic activities and physicochemical properties of soil. Soil As contamination in Gotera, Pipligram, and Ghentughachi observed as most alarming due to highest bioavailable As fractions reported compared to remaining other studied sites in West Bengal. Bioavailable soil arsenic content was in order of water soluble < weakly adsorbed < specifically adsorbed. The PCA results pointed out that OM, AP, AS, Ca, and pH are the most correlated soil properties to the different bioavailable soil As contents, while BD and AP negatively correlated and OM and Ca positively correlated with As content in soil controlling levels of bioavailable As contents. Further, arsenic speciation can be studied vis-à-vis bioavailability of arsenic in soils, which may confer more about toxicity of different bioavailable fractions in soil. These results may help to frame soil-based remediation strategies to reduce arsenic availability in contaminated soil.

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Author contributions Both the authors have made a joint contribution in all aspects to carry out and complete the study.

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Compliance with ethical standard

Conflict of interest The authors have no competing interests to declare.

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