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Safe limit of arsenic in soil in relation to dietary exposure of arsenicosis patients from Malda district, West Bengal- A case study

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ABSTRACT

Safe limit of arsenic in soil in relation to dietary exposure of arsenicosis patients was established in Malda district of West Bengal. Out of 182 participants examined, 80 (43.9%) participants showed clinical features of arsenicosis, characterized by arsenical skin lesion (pigmentation and keratosis), while 102 participants did not have any such lesion (control). Experimental results of the twenty eight soils (own field) of the participants showed the mean Olsen extractable and total arsenic concentration of 0.206 and 6.70 mg kg^{-1}, respectively. Arsenic concentration in rice grain ranged from 2.00 to 1260 µg kg^{-1} with the mean value of 146 µg kg^{-1}. The hazard quotient (HQ) for intake of As by human through consumption of rice varied from 0.03 to 3.52. HQ exceeds 1.0 for drinking water and rice grain grown in the study area in many cases. As high as 77.6% variation in As content in rice grain could be explained by the solubility-free ion activity model. Toxic limit of extractable As in soil for rice in relation to soil properties and human health hazard, associated with consumption of rice grain by human, was established. For example, the permissible limit of Olsen extractable As in soil would be 0.43 mg kg^{-1} for rice cultivation, if soil pH and organic carbon content were 7.5% and 0.50%, respectively. However, the critical limit of Olsen extractable As in soil would be 0.54 mg kg^{-1}, if soil pH and organic carbon were 8.5% and 0.75%, respectively. The conceptual framework of fixing the toxic limit of arsenic in soils with respect to soil properties and human health under modeling-framework was established.

1. Introduction

Arsenic (As) menace in drinking water has been reported from more than 20 countries (Sanyal et al., 2015). In this context, As-enriched groundwater of Bengal Delta Basin comprising Bangladesh and West Bengal (India), bound by the rivers Ganga and Padma, has a great significance, as it affects the health of millions of people adversely (Sanyal et al., 2015). In West Bengal, As-enriched groundwater has been detected in 111 blocks across twelve districts (Sanyal et al., 2015). Of these, severely affected districts are Murshidabad, Malda, Nadia, North and South 24 Parganas. In human, common symptoms of chronic As toxicity due to prolonged drinking of As contaminated water and food stuffs are pigmentation and keratosis. Apart from these symptoms, arsenicosis produces problems such as weakness, chronic respiratory disease, peripheral neuropathy, liver fibrosis, peripheral vascular disease, conjunctivitis, cardiovascular diseases, gangrene and skin cancer, pre-malignant skin lesions, bladder and lung cancer (Rahaman et al., 2013).

Although drinking water has been considered as the most important source for As exposure to human, other pathways like soil-crop-food transfer also contributes to As poisoning (Biswas et al., 2014). Accumulation of As in rice grain is considered as a calamity for South East Asia, where rice is a staple food (Meharg, 2004). Consumption of such As contaminated food materials, mainly rice grain, for prolonged period resulted into food-chain contamination, leading to arsenicosis. Several authors reported that content of As in rice grain and straw, grown on As affected region in Bangladesh, were 0.74 and 197 mg kg^{-1}, respectively, which was above the permissible limit of 1.0 mg kg^{-1}according to WHO permissible limit (Meharg and Rahman, 2003). Assessment of As contamination in drinking water and its effect on human health in

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West Bengal has been studied earlier (Guha Mazumder et al., 2013), but scanty information is available on assessment of soil contamination with As, followed by its transfer to plants and human food-chain.

Total As content ranging from 10 to 20 mg kg^{-1} in soil has been used as a simple index of As hazard in different countries (Rahaman et al., 2013). However, total As content in soil does not take into account how its availability is modified by important soil properties. For example, bioavailability of As in soils is governed by mainly pH, redox potential, organic matter content and presence of other ions in soil solution. Under acidic and aerobic conditions, the arsenate species (As-V) dominate over arsenite (As-III) which is chiefly present in soil under flooding condition in the neutral pH range of the affected belt of West Bengal, India and Bangladesh (Rattan et al., 2009). Native soil organic matter along with the incorporated organics decreases the extractable soil As, thereby reducing its plant availability, through organo-As chelation. So far no attempt has been made to prescribe a permissible limit of As in soil of West Bengal, based on (i) solubility of As in soil as affected by important soil properties, (ii) transfer of As to human food-chain, and (iii) health hazard associated with dietary intake of As by human. Few such studies with As and other pollutants were conducted elsewhere in South East Asia (Datta and Young, 2005; Meena et al., 2016). Besides, WHO has set standards for maximum permissible limit of As concentration in rice as 1 mg kg^{-1} (Das et al., 2004), while it is 0.15 and 0.5 mg kg^{-1}as prescribed by USDA and EU, respectively (Meharg and Zhao, 2012). However, such generalized permissible limit of As in rice and other food materials for human consumption does not have much practical relevance as amount of intake of particular food material varies from region to region. Prescribing permissible limit of extractable As in soil is of utmost importance for assessing suitability of arable land for crop production as well as management of As-polluted soil. The latter is, of course, a challenge since it is not possible to exclude large tracts of field soil in highly productive regions of the country (for instance, the Bengal delta), based on the use of very stringent permissible limit of As in soil, due to the ever increasing demand of food in our country. On the other hand, imposition of loose permissible limit will not be effective in protecting human or animal health from As hazard.

In West Bengal, epidemiological studies related to As poisoning of drinking water have been conducted in two districts, namely Nadia and South 24 Parganas (Guha Mazumder et al., 2010; Biswas et al., 2014). The findings of such epidemiological study in South 24 Parganas district of West Bengal revealed that 353 participants showed the prevalence of Arsenical skin lesion out of 7683 people examined in 57 As affected villages (Guha Mazumder et al., 1998). Again, the incidence of As related cancer was reported to be 5.1% among 4865 cases of arsenicosis examined during the period from 1983 to 2000 in West Bengal (Saha, 2003). However, the data of the former cross-sectional study represented information in the selected As affected region of one district of the state, while the latter data were compiled from the cases examined in a tertiary referral centre, as well as some scattered surveys, carried out by organizing various health camps and scattered examination of patients in different regions of the affected districts of the state. Seven blocks, namely Kaliachak I, II and III, English Bazar, Manikchak, Ratua-I & II are badly affected by As menace in Malda district in West Bengal (WHO, 2001). However, no information is available regarding the disease prevalence due to arsenicosis in these arsenic affected blocks of Malda. For this reason, a scientific epidemiological study was being carried out with the help of arsenic expert physicians, who have had many years of experience in diagnosing As-caused skin lesions in West Bengal by DNGM Research Foundation (DNGMRF), New Alipore, Kolkata, India. The Foundation had also been involved in creating awareness among the people about the As menace and the associated health hazard with the financial assistant from the UNICEF.

In summary, As-related epidemiological studies so far conducted laid major emphasis on chronic As toxicity of human through drinking water. Guha Mazumder et al. (2014) reported significant contribution of diet to As intake by human in As affected areas of West Bengal even if As level in drinking water was within the WHO-prescribed permissible limit. This underlies the importance of transfer of As from soil to edible portion of crop. Our hypothesis is that a link among As content in water, soil, edible plant part and arsenicosis in human of a particular area is prevailed whether that can be used in establishing permissible limit of As in soils. Keeping this in view, the status of As in soil, water and edible plant parts in As-contaminated block of Malda district was assessed in the present study. Relationships of occurrence of arsenicosis with As status in drinking water and dietary cereal like rice grain were worked through epidemiological survey. Permissible limit of extractable As in soil in relation to human health hazard, associated with dietary intake of As through rice grain, was also determined. We expect that this study will act as a model risk assessment protocol, which can further be extended to other parts of As-polluted areas of West Bengal. This would also help in management of As-polluted soil in a cost-effective manner.

2. Materials and methods

2.1. Study area and study population

The present investigation was carried out in Malda district (Total area 3733 km^2, with a population of 3997970) of West Bengal. Malda is situated 347 km north of Kolkata, the state capital, on the east of the confluence of the Mahananda and Kalindi rivers. Blocks, namely Kaliachak I, Kaliachak II, Kaliachak III and English Bazar were selected for the present investigation. Subjects of the present study have been selected randomly from a population identified based on a fully fledged epidemiological study which was being carried out by DNGM Research foundation, Kolkata with funding from UNICEF, with a view to assess the prevalence of arsenical disease manifestations in the district of Malda, West Bengal, taking into consideration the level of As in drinking water in the severe arsenic affected blocks. Further correlation of arsenical disease manifestations were done with various arsenic exposure data and different socio-economic class distribution of the population. For this study, 66 households were recruited from highly As-contaminated area of ten villages, namely Sahilapur, Sasani, Balukhara, Jot Domon, Jot Kagmari, Sovapur, Akandaberia Palpara, Akandaberia Mistripara, Sariadpur and Madanpur of the above mentioned four blocks of Malda District. The participants were interviewed face-to-face in the local language of Bengali, following a structured questionnaire, which included demographic information (e.g., age, sex, types of dwelling, level of education, occupation, annual income and sanitation status). Following the questionnaire survey, all patients were examined by one of the two physicians who have had many years of experience in diagnosing As-caused skin lesions in West Bengal. Among the 66 families (182 people) studied there were 80 cases that had typical arsenical skin lesions of pigmentation and/or keratosis (arsenicosis), while 102 subjects had no such skin lesions. A scoring system has been adopted to classify the degrees of severity of skin manifestations (Guha Mazumder et al., 2010). The criteria for classifying keratosis and pigmentation as As-caused skin lesions were as follows. Keratosis had to involve diffuse bilateral thickening of the palms and/or soles with or without nodules of various shapes and sizes. Hyperpigmentation was identified as areas of mottled dark brown pigmentation distributed bilaterally on the trunk. Hyperpigmentation was frequently present on the limbs and sometimes alongside spots of de-pigmentation, but these characteristics were not regarded as essential for the diagnosis. Approval of the study protocol was obtained from the Ethical Committee of the DNGM Research Foundation, fulfilling the Helsinki criteria and recommendation of the Indian Council of Medical Research, Government of India.

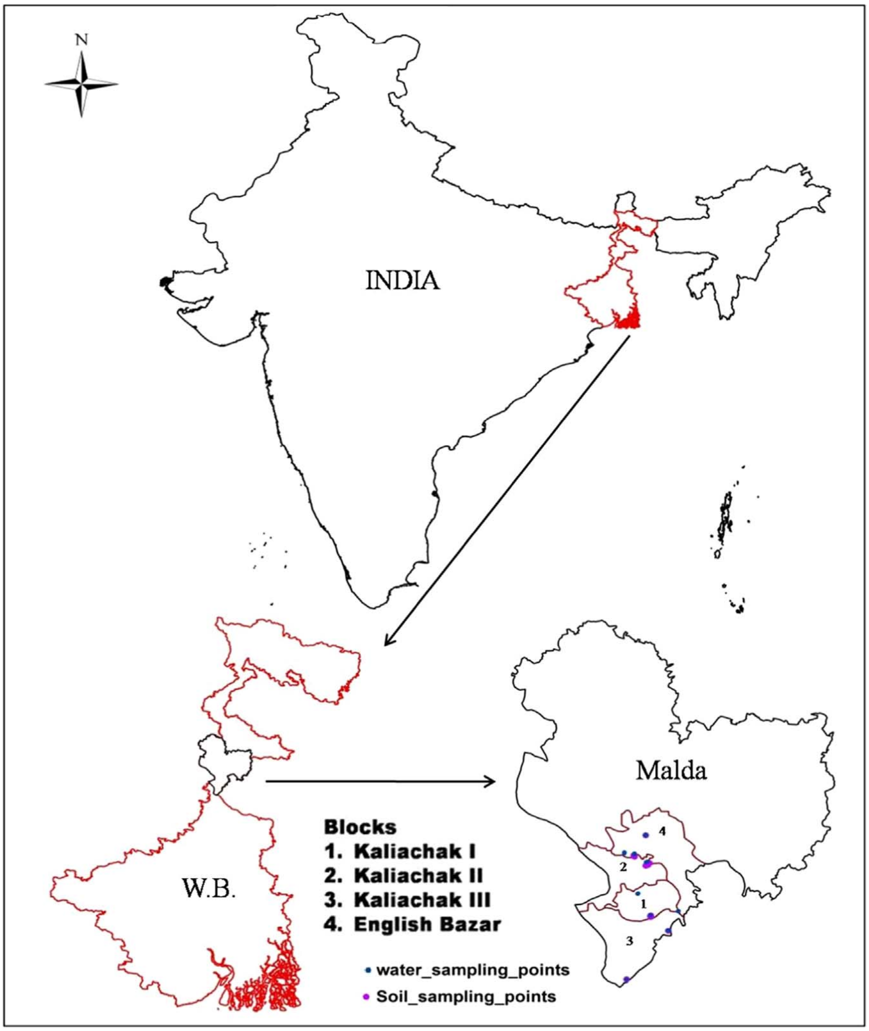

Fig. 1. Map showing drinking water and soil sampling points in the study area (Kaliachak I, II, III and English Bazar block of Malda district, West Bengal).

2.2. Sample collection

Sixty six water samples were collected from the existing drinking and cooking water sources of each family in certified metal-free container along with GPS coordinates (Fig. 1) and acidified *on-site* with 0.15 mL of concentrated HNO_3. In the field, eleven water samples were collected from the shallow and deep tube wells that were used for irrigation purpose in the participants' fields. Prior to sampling, the pumps were kept running for about 10–15 min in order to get a uniform rate of discharging water, and the samples were collected in certified metal-free container, followed by acidification with 0.15 mL of concentrated HNO_3. To assess the build-up of As in the soil, twenty eight bulk surface (0–15 cm) soil samples were collected from the patients' fields, irrigated with the As-contaminated water from Kaliachak II, Kaliachak III and English Bazar blocks in Malda district of West Bengal, India, along with GPS coordinates (Fig. 1). However, participants from Kaliachak I block do not practice rice cultivation in their own field and we have not collected any soil or irrigation samples from this block. To assess the transfer of As from soil to crops, 28 rice grain samples were collected from those family members who cultivated rice in their own fields. Rice grain was also collected from rest of the families (n = 38) who purchased raw rice from local market for their daily consumption. An attempt has been made in this study to present a human health risk assessment and an exposure to As via water and diet. Since such focused study to establish the link among water-soil-plant-human health was not conducted earlier, to start with, only 4 blocks having serious problem of As poisoning were selected. Possible maximum numbers of soil, water and rice grain samples were included in study. Number of soil samples collected does not match with the number of target family as all the families do not have their own farming.

2.3. Sample preparation

The drinking and irrigation water samples were filtered through Whatman No 42 filter paper, and samples were kept in polyethylene bottles at 4 °C for analysis in the laboratory. The soil samples were immediately air-dried, followed by grinding and passing through a 2.0-mm pore-sized sieve. The samples were stored in airtight polyethylene bags at room temperature.

2.4. Digestion of rice grain and As analysis

Grain samples were digested following the hot plate digestion procedure (Rahman et al., 2007). The total As of the samples was analysed with atomic absorption spectrophotometer (Model Analyst 200, Perkin Elmer, USA), coupled with hydride generator unit, after reducing with 2 mL10% KI (potassium iodide) solution and 2 mL 35% HCl (Hydrochloric acid), 0.2% $NaBH_4$ (Sodium borohydride) solution and 4 mol L^{-1} HCl solution, separately from three containers, and passing to a mixing manifold by a peristaltic pump. The As was atomized in a flame of air acetylene, and the As concentration in the sample was measured (Johnston and Barnard, 1979). The detection limits of atomic absorption spectrophotometer (Model Analyst 200, Perkin Elmer, USA) is 0.01 mg. L^{-1}. For quality control, standard reference material for drinking water (SRM1643e) from National Institute of Standards and Technology (NIST) was used during the analysis. The certified value of this standard material is 60.5 μg L^{-1}. Analysis of standard material was carried in triplicate and As content was recorded as 58.5 ± 0.45 μg L^{-1}. For rice grain, two reagent blank and one standard reference materials (SRM1568a), prepared by National Institute of Standards and Technology (NIST) were used in every batch of 30 samples to ensure accuracy of the analysis. The certified value of SRM1568a is 290 ± 30 μg kg^{-1}. Analysis of standard material was carried in triplicate and As content was recorded as 286 ± 10.3 μg kg^{-1}.

2.5. Arsenic, pH and organic carbon content in soil

For total and extractable As, soil was digested with aqua-regia (Quevauviller, 1998) and extracted with 0.5 *M* $NaHCO_3$, pH 8.5 (Olsen et al., 1954), respectively. The pH of soil was determined in 1:2 (soil: water) suspension using combined electrode (glass and calomel electrodes) by digital pH meter (Datta et al., 1997). Organic carbon content in soil was determined by wet oxidation method using $K_2Cr_2O_7$ as outlined (Walkley and Black, 1934).

2.6. Prediction of As content in rice grain

Arsenic content in rice grain was predicted by the integrated solubility-free ion activity model without actually measuring the free ion activity in soil solution (Hough et al., 2004; Datta and Young, 2005). Free ion activity model (FIAM) suggests that uptake may be controlled by metalloid ion activity in the soil pore water. Transfer factor is expressed as the quotient of metalloid concentration in the plant [M_{plant}] to metalloid ion activity in soil pore water (M^{n-}) as follows (Mirecki et al., 2015):

$$TF = \frac{[M_{Plant}]}{(M^{n-})} \quad (1)$$

Free ion activity of As was predicted by using the simple pH-dependent Freundlich equation (Jopony and Young, 1994; Datta and Young, 2005) as follows:

$$p(M^{n-}) = \{p[M_c] + k_1 + k_2pH\}/n_F \quad (2)$$

Where (M^{n-}) is the free metalloid ion (As) activity in soil solution; M_C is the labile pool of metalloid in soil, assumed to be exclusively adsorbed on the humus (mol kg^{-1} carbon); k_1 and k_2 are empirical, metalloid-specific constants; and n_F is the power term from the Freundlich equation. This model predicts the free ion activity of As in soil solution as a function of labile soil extractable metal and pH with the simplifying assumption that the whole amount of metalloid is adsorbed on humus. In the present study, 0.5 *M* $NaHCO_3$ (pH 8.5)-extractable As was used as the estimates of labile pool (Meena et al., 2016). In case of soil organic carbon, Walkley-Black organic carbon was used (Meena et al., 2016). The equation for prediction of As uptake by plant can be derived by combining Eqs. 1 and 2:

$$p[M_{Plant}] = C + \beta_1 p[M_C] + \beta_2 pH \quad (3)$$

Where, $C = \frac{k_1}{n_F} - logTF$, $\beta_1 = \frac{1}{n_F}$, and $\beta_1 = \frac{k_2}{n_F}$; C,β_1 and β_2 are empirical metalloid and plant-specific coefficient.

Eq. (3) was parameterized by non-linear error minimization using the "SOLVER" facilities in Microsoft Excel 2010. The error sum of squares was calculated for a numerical rather than logarithmic plant metalloid content data.

2.7. Risk assessment

Risk to human health for intake of As through consumption of rice grown on As contaminated soils was computed in terms of hazard quotient (HQ), following the US Environmental Protection Agency (USEPA) protocol (IRIS, 2017). Hazard quotient is the ratio of the average daily dose (ADD; mg. kg bodyweight^{-1}. day^{-1}) of metalloid to their reference dose (R_fD; mg. kg body weight^{-1}. day^{-1}), defined as the maximum tolerable daily intake of a specific metalloid from all the food items and drinking water that does not result in any deleterious health effect (mg As kg body wt^{-1} day^{-1}) (Pierzynski et al., 2000):

$$HQ = \frac{ADD}{RfD}$$

If HQ > 1, the ADD of a particular metalloid exceeds the R_fD, indicating that there is a potential risk associated with As intake. For As, 2.1 μg As kg body weight^{-1} day^{-1} was worked out as the PMTDI (WHO, 1996). Daily intake of rice grain was assumed to be 0.4 kg day^{-1}, respectively (Biswas et al., 2014). Average body weight for an adult was assumed to be 68 kg (Rahaman et al., 2013). Thus, the HQ for an adult was calculated as:

$$HQ = \frac{M_{Plant} \times W}{RfD \times 68}$$

Where M_{plant} is As content (mg kg^{-1}) in the grain of rice grown in As contaminated soils; W is the daily intake of grain of rice. Hazard quotient for intake of As through drinking water was computed as:

$$HQ = \frac{M_{Drinkingwater} \times W}{RfD \times 68}$$

Where $M_{Drinking\ water}$ is As content (mg L^{-1}) in the drinking water from the study area; W is the daily intake of drinking water. Daily intake of drinking water was assumed to be 3 L. day^{-1} (Guha Mazumder et al., 2014). Assessment of risk as computed here is not complete. Since As accumulation in the soil organisms and direct uptake by human from soil and animal are some of the other risks which have not been considered here.

For fixing the toxic limit of extractable As in soil at particular pH and organic carbon content, critical value of HQ was used as 0.5 under modeling framework. Hence, a ready reckoner was developed to compute the permissible limit of extractable As in soils, based on pH and organic carbon content. These permissible limits were based on the predicted HQ by solubility-FIAM.

2.8. Statistical analysis

Descriptive statistics for primary data were computed and simple correlation co-coefficients were worked out using the data analysis facilities in Microsoft Excel 2010.

3. Results

3.1. Status of As in the study area

3.1.1. Soil and irrigation water

Initial characterization of the collected soil samples indicate that pH was neutral to alkaline in nature in the study area with a mean value of 8.08 ± 0.31 (Table 1). Status of soil organic carbon was medium with a mean value of 0.66 ± 0.20%. Both shallow (40–80 feet depth) and deep tube wells (100–250 feet depth) have been used for irrigation purpose. The As contamination level in irrigation water was of the order of 0.57 mg L^{-1}(Kaliachak III, n = 4) > 0.48 mg L^{-1}(Kaliachak II, n = 5) > 0.18 mg L^{-1}(English Bazar, n = 2). The concentrations of As in the 28 agricultural soils, collected from the above mentioned three blocks, varied from 10.9 to 606 μg kg^{-1} with a mean value of 206 μg kg^{-1}. Mean Olsen extractable As content in soils followed the order as Kaliachak III (233 μg kg^{-1}) > Kaliachak II (213 μg kg^{-1}) > English Bazar (19.6 μg kg^{-1}). The total As concentration in soils ranged from 0.55 to 11.5 mg kg^{-1}, while few soils of Kaliachak III and Kaliachak II block of Malda district have As level above the global average of 10.0 mg. kg^{-1}(Das et al., 2002). The total As contamination in soils followed the order as Kaliachak III

Table 1
Initial properties of soils in the study area.

Location		pH	WBC (%)	Olsen extractable As (µg kg-1)	Total As (mg kg-1)
Kaliachak III (n = 9)	Minimum	7.58	0.26	16.8	0.84
	Maximum	8.69	0.67	606	11.4
	Mean	8.10	0.45	233	7.21
	SD	0.34	0.13	182	4.04
Kaliachak II (n = 17)	Minimum	7.63	0.47	25.0	1.25
	Maximum	8.91	1.05	540	11.5
	Mean	8.06	0.77	213	7.09
	SD	0.31	0.15	120	2.94
English Bazar (n = 2)	Minimum	8.00	0.56	10.9	0.55
	Maximum	8.23	0.65	28.3	1.42
	Mean	8.12	0.61	19.6	0.99
	SD	0.12	0.05	8.70	0.44
Overall (n = 28)	Minimum	7.58	0.26	10.9	0.55
	Maximum	8.91	1.05	606	11.5
	Mean	8.08	0.66	206	6.70
	SD	0.31	0.20	148	3.54

(7.22 mg kg^{-1}) > Kaliachak II (7.10 mg kg^{-1}) > English Bazar (0.99 mg kg^{-1}).

3.1.2. Drinking water and grain samples

In the study area, sources of drinking water include the Public Health Engineering Department (PHED) of the Government of West Bengal-supplied tap water, government-installed deep tube wells, and shallow private tube wells. The concentration of As in drinking water varied from 4.2 to 884 µg L^{-1} with the mean value of 271 µg L^{-1}. Arsenic content in rice grain varied from 2.00 to 1260 µg kg^{-1} with the mean value of 146 µg kg^{-1}. On an average, As content in rice grain (0.257 mg kg^{-1}) produced in participants' own field was higher than that in rice grain procured from local market (0.059 mg kg^{-1}).

3.2. Relationship of arsenicosis with As in water-soil-plant continuum and drinking water

3.2.1. Epidemiological study

Baseline information of the Head of the families in the study area is given in Table 2. A total number of 66 households of 10 villages in the 4 blocks were surveyed in the district of Malda. Majority of the population, living in the As affected villages, were of low socio-economic condition and education status, lived in *pucca* houses and were engaged in agricultural farming or as physical labour. Nearly 27.3% of the participants did not have access to sanitary latrine. Out of the 182 participants, 80 (43.9%) patients showed clinical features of arsenicosis (cases), characterized by arsenical skin lesion pigmentation and keratosis (Table 3) (see Plates I, II in Supplementary information). While 102 participants did not have any such lesion (control), indicating the occurrence of arsenicosis in 43.9% of the studied people. The incidence of such disease was found to be significantly high (70.0%) in males compared to females (30.0%). Out of the total number of cases having arsenical skin disease, 96.3% had pigmentation (mild-62.5%, moderate-30.0%, severe-3.75%), whereas 52.5% had only keratosis (mild-37.5%, moderate-12.5%, and severe-2.50%). Both pigmentation and keratosis were found in 47.5% of the patients, majority being males. In the study cases, pigmentation dominates over keratosis and most of the cases were mild. There were many systemic manifestations like cough, dyspnoea, weakness, diarrhea, limb pain, tingling sensation of limbs, and skin cancer and Bowens disease (Locally malignant skin lesion). Pigmentation and keratosis were rated as mild in 62.5% and 37.5% of the affected participants, respectively. People were *neither* aware *nor* serious about mild cases of arsenicosis, mainly because of poverty, lack of education and apathy.

Table 2
Characteristics of Head of the family (HOF) in the total household (66) studied in the district of Malda.

Characteristics	*(Cases)* (n=50)		*(Controls)* (n=16)	
	n	%	n	%
Age in years				
18- < 30	1	2.00	0	0.00
30- < 60				
> 60	28	56.0	8	50.0
	21	42.0	8	50.0
Sex				
Male	44	88.0	15	93.7
Female	6	12.0	1	6.25
Type of dwelling				
Kutcha	6	12.0	1	6.25
Kutcha-Pucca	18	36.0	6	37.5
Pucca	26	52.0	9	56.3
Education of family head				
Illiterate	22	44.0	4	25.0
Primary	15	30.0	5	31.2
Secondary	5	10.0	4	25.0
Graduate	8	16.0	2	12.5
School out	0	0.00	1	6.25
Occupation				
No earning	8	16.0	1	6.25
Farmer	9	18.0	2	12.5
Daily labour	16	32.0	6	37.5
Service	3	6.00	1	6.25
Petty business	11	22.0	4	25.0
Others	3	6.00	2	12.5
Annual income of family head				
BPL	8	16.0	3	18.8
< =50000	18	36.0	6	37.5
> =50001–100000	14	28.0	3	18.8
> =100001–200000				
> =200001–500000	7	14.0	3	18.8
> 500000	2	4.00	0	0.00
	1	2.00	1	6.25
Sanitation status				
Present	33	66.0	15	93.8
Absent	17	34.0	1	6.25

3.2.2. Drinking water and rice grain

On an average, duration of As exposure through drinking water was about 12 years in the study area. The concentration of As in drinking water, collected from arsenicosis patients' households, varied from 68.5 to 884 µg L^{-1}, with the mean value of 364 µg L^{-1} in the study area while mean level of As in drinking water, collected from non arsenicosis patients' households, was 24.5 µg L^{-1} indicating a positive relationship between As level in drinking water and the prevalence of pigmentation and keratosis in arsenicosis patients (Table 4).

Rice grain was found to contain 174 ± 217 µg As kg^{-1} in the samples collected from the patients' households (n = 50), while the value for the control (n = 16) was 50.0 ± 72.0 µg kg^{-1}. On an average, As content in rice grain, collected from patients' households, was significantly higher as compared to control households, which are free from As poisoning.

3.2.3. Irrigation water-soil and crop

In the study area, continuous application of contaminated groundwater from the shallow and deep tube wells as a source of irrigation, led to build-up of As in soil. Highest accumulation of Olsen extractable As in soil was noted in Kaliachak III (233 ± 181 µg kg^{-1}), followed by Kaliachak II (213 ± 19.0 µg kg^{-1}) and English Bazar (19.6 ± 8.70 µg kg^{-1}) (Table 1). Variation in available As in soil was also reflected in the corresponding variation in rice grain. Simple

Table 3
Characteristics of 182 participants studied in regard to their clinical features.

Characteristics	*Cases* n = 80		*Controls* n = 102	
Age	N	%	N	%
12- < 18	1	1.25	2	1.96
18- < 30				
30- < 60	11	13.7	27	26.5
> 60	46	57.5	53	52.0
	22	27.5	20	19.6
Sex				
Male	56	70.0	43	42.1
Female	24	30.0	59	57.8
Pigmentation				
+	50	62.5	-	-
+ +				
+ + +	24	30.0	-	-
	3	3.75	-	-
Keratosis				
+	30	37.5	-	-
+ +	10	12.5	-	-
+ + +	2	2.50	-	-
Cough	11	13.8	1	0.98
Dyspnoea	5	6.25	-	-
Solid Endema Limb	-	-	-	-
Weakness	23	28.8	-	-
Diarrhea	2	2.50	-	-
Limb Pain	11	13.8	-	-
Tinging	8	10.0	-	-
Liver Enlargement	-	-	-	-
Ascites	-	-	-	-
Pitting Limb Swelling	-	-	-	-
Gangrene	-	-	-	-
Conjestion of Eye/Location	-	-	-	-
Cancer	1	1.25	-	-
Bowens Disease	4	5.00	-	-

Table 4
Exposure of As through drinking water and raw rice (both from purchased and produced).

Exposure route	*Cases* (n = 50)	*Controls* (n = 16)
As concentration in drinking water (μg L^{-1}) (n = 66)		
Minimum	68.5	4.40
Maximum	884	69.6
Mean	364	24.5
SD	235	16.6
As concentration in raw rice grain (μg kg^{-1}) (n = 66)		
Minimum	2.00	4.25
Maximum	1260	293
Mean	174	50.0
SD	217	72.0

correlation coefficients (r) of As content in rice grain were 0.76 and 0.74 with extractable As content in soil and irrigation water, respectively.

3.3. Risk assessment and determination of toxic limit of extractable As in soil in relation to human health

Arsenic (metalloid) and crop specific parameters (*C, β_1 and β_2*) of solubility-free ion activity model (FIAM) along with prediction coefficient are presented in 1:1 line (Fig. 2). The values of *C*, β_1 and β_2 of solubility-FIAM were worked as −2.30, −0.03 and 0.80, respectively. Results indicate that as high as 77.6% variation in As content in rice grain could be explained by the solubility-FIAM model. Risk to human health for intake of As through intake of drinking water and rice was assessed in terms of hazard quotient (HQ). In case of drinking water, the HQ was 5.69 ± 5.13, which is far above the safe limit of HQ, i.e., 1. The HQ for As in case of rice, was 0.72 ± 0.72. An attempt has been made to compare the actual HQ with that computed based on the predicted As content in rice by solubility-free ion activity model (Fig. 3). Results indicate that by and large, the observed and the predicted values of HQ for As were in a reasonably close agreement. The toxic limits were also computed, based on the predicted HQ by solubility-FIAM for intake of As by human through consumption of rice grain (Fig. 4). Level of extractable As in soil was considered as permissible limit which would produce HQ as > 0.5 for intake of As through consumption of rice grain grown there on. For example, the permissible limit would be 0.43 mg kg^{-1} for rice, if soil pH and organic carbon content were 7.5% and 0.50%, respectively. However the critical limit of Olsen extractable

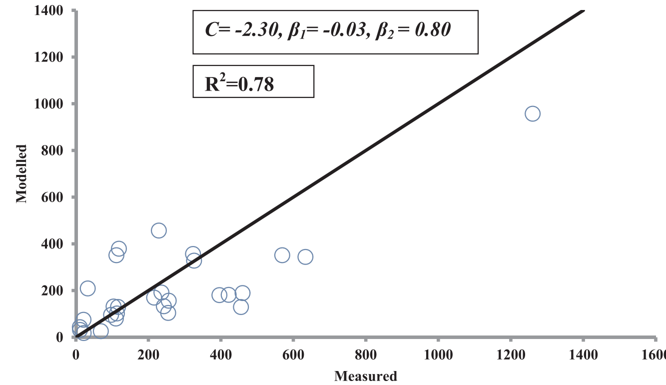

Fig. 2. Comparison of observed and predicted As content of rice grain on 1:1 line; As content in rice was predicted by solubility-free ion activity model based on pH M_c(EDTA extractable metal assumed to be adsorbed on Walkley and Black organic carbon.

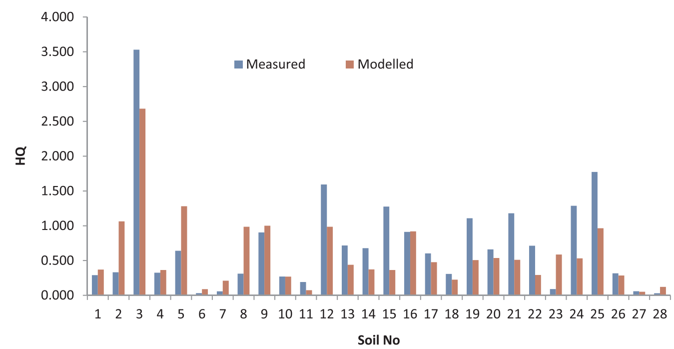

Fig. 3. Comparison of hazard quotient (HQ) values based on actual (measured) and modelled As content in rice grain; As content in plant was predicted by solubility-free ion activity based on EDTA extractable metal, Walkley-Black organic carbon and pH.

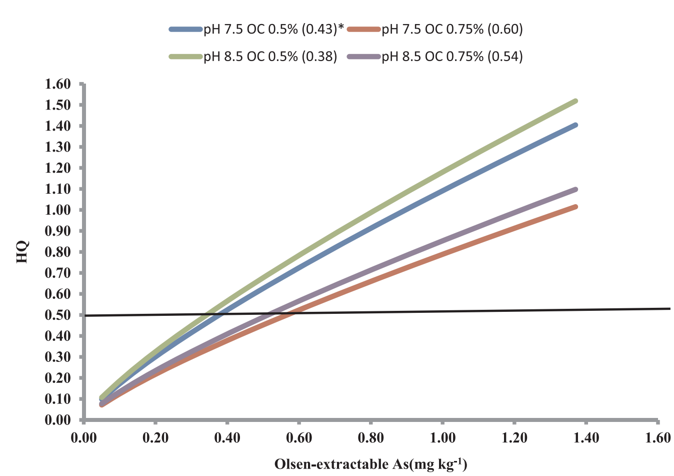

Fig. 4. Permissible limit of Olsen-extractable As in soils in relation to pH and organic carbon for intake of As through rice grain by human.* Values in parentheses indicate the toxic limit of extractable As in soil.

As, would be 0.54 mg kg^{-1}, if soil pH and organic carbon were 8.5% and 0.75%, respectively (Fig. 4).

4. Discussion

4.1. Status of As in the study area

To assess the status of As in the study area, soil samples from the participants' fields, along with the irrigation water samples were collected. It is worth noting that total As content is *not* a good index of As hazard in relation to food-chain contamination; in the present study, total As content in samples was within the maximum acceptable limit for agricultural soils, i.e., 20 mg kg^{-1}, as proposed by the European Union (Rahaman et al., 2013). As high as 28.5% soil samples exceeded the global average of 10 mg kg^{-1} total As. For extractable As in soil, neither the global average value nor the maximum allowable limit are available for comparison. Nevertheless, recently Meena et al. (2016) reported that extractable As in sewage irrigated soil was 50.6 ± 41.4 µg As kg^{-1} under rice crop, whereas the human intake of As through consumption of rice, grown thereon, was within the safe limit, as per the USEPA protocol. Soil reaction in the study area was neutral to alkaline in nature, which favors mobility and availability of As in soils. This is a matter of great concern as the As (III) is more prevalent in soils of West Bengal and Bangladesh owing to the neutral range of soil pH under flooded condition. Meharg and Zhao (2012) envisaged a dramatic mobilization of As, predominately as arsenite into the soil solution phase, once suboxic/anoxic conditions develop in the soils. Adverse effect of elevated level of As in soils of study area under flooded condition can be magnified due to such transformation and mobilization.

In the present study, the mean As concentration in irrigation water of the selected three blocks (Kaliachak II, Kaliachak III and English Bazar) ranged from 0.18 to 0.57 mg L^{-1}, which exceeded the FAO permissible limit of As for irrigation water (0.10 mg L^{-1}; FAO, 1985). As groundwater is extensively (more than 90%) used for crop irrigation in the Malda district, the possibility of a build-up of As concentration in soils and agricultural produce was expected. Purkait and Mukherjee (2006) envisaged that the high As concentrations are common in the alluvial aquifers of the Malda region (Bengal Basin), because of the Himalayan erosion, supplying immature sediments with low surface loadings of FeOOH on mineral, that may release As into water through changing redox state of aquifer during heavy pumping of groundwater for irrigation purposes. Groundwater contamination with As is also reflected in the drinking water in the study area. In 8 (12.1%) and 51 (77.3%) tube wells, the levels of As concentration were > 10–50 and > 50 µg L^{-1}, respectively. Out of the total surveyed drinking water sources (n = 66), only 7 (10.6%) sources are safe compared to the WHO provisional drinking water guideline of 10 µg L^{-1} (FAO, 1985). The PHED-supplied tap water and government-installed deep tube wells are safe, while privately owned household shallow tube wells are mostly contaminated with As. The survey data reveals that owing to the small number of drinking water sources with As concentration less than 10 µg L^{-1}, the majority of the participants collect drinking water from privately owned shallow tube well sources.

It is interesting to note that the As content was higher in rice grain that was produced in the participants' own fields, as compared to those which are procured from the local market. It is worthwhile to point out that in the Malda district, rice is mainly imported from Bardhhaman district (Rice Bowl) of West Bengal, while this district is relatively free from the As menace. The highest mean As content in rice grain, grown in participants' own fields, was 257 µg kg^{-1}. However, only one sample was found to exceed the WHO-recommended permissible limit of 1.0 mg kg^{-1}. On the contrary, 16 samples of rice grain were found to exceed the USDA recommended permissible limit of 0.15 mg kg^{-1}.

4.2. Relationship of arsenicosis with drinking water and As in water-soil-plant continuum

The present study highlighted the prevalence of arsenical skin lesion in a small subgroup of 182 people living in 10 villages situated in a scattered manner in four severely arsenic affected blocks of the district of Malda, West Bengal, taking into consideration exposure of arsenic through water and rice. The first report on scientific epidemiological survey was brought out in the South 24 Parganas district of West Bengal which highlighted that arsenic exposure causes skin lesion like pigmentation and keratosis in a dose response manner, showing that higher the dose of arsenic exposure higher is the prevalence of skin lesion, male members showing greater prevalence than female members (Guha Mazumder et al., 1998). Over and above pigmentation, and keratosis, arsenicosis was also found to produce protean manifestations like weakness, chronic respiratory disease, peripheral neuropathy, hepatomegaly and non-cirrhotic portal fibrosis, peripheral vascular disease, anemia, conjunctival congestion and non-pitting edema of hands and legs (Guha Mazumder, 2003). In the present study, also significant present of arsenic exposed people not only showed signs of skin lesion but also systemic manifestations like cough, breathing difficulty, weakness, limb pain, tinging and skin cancer. In this study higher numbers of patients were found to be males as compared to females. This is in concurrence with the finding of sex distribution of arsenicosis cases in Indo-Bangla sub-continent where males were found to be more affected (Guha Mazumder et al., 1998; Rahman et al., 2003). In the study group, pigmentation dominates over keratosis and most of the cases were mild. Thus, most of them could be relieved of their symptom if they use As-free water by using As-removing water filter. Most of the participants in the present investigation were daily labourers or farmer and belong to low socio-economic class. However, a significant number of people lived in *pucca* house and they have access to sanitary latrine because of some assistance provided by the Government scheme. Overall, insufficient education, poverty, lack of awareness and effective health-care support system are the major contributory factors to the malady of the severely As affected people.

Arsenic concentration in drinking water consumed by participants with skin lesions was 0.364 ± 0.235 mg L^{-1} while As concentration was 0.024 ± 0.016 mg L^{-1} in drinking water as consumed by participants without skin lesions. It is, therefore, an urgent need to make arrangement for safe water for As affected people in the given district. Most of them are not aware of contamination of their household tube wells with As. In this regard, DNGM Research Foundation with funding from the UNICEF has been carrying out awareness campaign and appraising the villagers about the need of drinking water without As contamination.

Along with drinking water, rice is considered as yet another major As exposure route in human being. Meharg and Rahman (2003) reported that more than 60% of dietary exposure was contributed by rice. In the present study, exposure of As to the people through rice grain was elaborately studied which indicated that As content (0.174 ± 0.217 mg kg^{-1}) in rice grain consumed by arsenicosis patient was higher as compared to non arsenicosis patient (0.050 ± 0.072 mg kg^{-1}). Arsenical skin lesion was recorded in male participants to greater extent (70%) as compared to that in female (30%). This may be attributed to higher intake of As-enriched rice grain by male as compared to that by female (Watanabe et al., 2004). This study clearly indicated that there is a strong link of occurrence of arsenicosis with abundance of As in soil and its transfer to rice grain as well as As content in drinking water. There was also a close positive relationship of As content in irrigation water and its build-up in soils of Kaliachak II, III and English Bazar blocks of Malda District.

4.3. Risk assessment and determination of toxic limit of extractable As in soil in relation to human health

Models, describing the transfer of As from soil to plants, express As bioavailability in terms of intensity and capacity (Sparks, 1985). Intensity may be defined as the activity of the particular species in soil solution, e.g., free As (ionic) activity, while the capacity is a metalloid reservoir in the soil, which re-supplies metalloid to the soil solution following its depletion. Metalloid supply capacity of soil is further controlled mainly by its pH and soil organic carbon (Datta and Young, 2005; Golui et al., 2014; Meena et al., 2016). In the present study, actual free ion activity of As in solution was not measured. Instead free ion activity of As in soil solution was predicted through the use of the solubility model. The variation in As uptake by rice grain could be explained by solubility-free ion activity model to the extent of 78% (Fig. 2). Such prediction should be considered very good for routine risk assessment of As-contaminated soil, based on easily measurable soil properties like extractable As, pH, and organic carbon. It can be inferred that parameterization of solubility, based on actual free As ion activity, would improve the predictability of the model (Datta and Young, 2005). The transfer of As from soil to rice grain is positively affected by pH as evident from model parameter (β_1). Further lability of As is decreased with increase in organic carbon in soil. Effect of soil pH on solubility and mobility of inorganic As is complex and sometimes difficult to predict. For example, Yamaguchi et al. (2011) reported that the distribution coefficient (solution phase concentration/solid phase concentration) for As (III) increases rapidly with increasing pH from 5.5 to 7.0, whereas for As (V), the increase is apparent only at pH > 7. This leads to increase in solubility and mobility of As in soil. In oxygen rich environment and well-drained soil, arsenate (AsO_4^{3-}) species dominant, whereas under reduced condition such as regularly flooded soil, arsenite (AsO_3^{3-}) is a stable species (Rattan et al., 2009). Solubility of As (V) was generally low except at high pH and E_h values. pH may decrease in alkaline soils after flooding and this could results in decreased As solubility in the case where E_h remained above the As (V)-As (III) boundary (Hamon et al., 2004). The overall effect generally is a drastic mobilization of As, predominately as As (III) into the soil solution phase once suboxic/anoxic condition developed in the soil (Meharg and Zhao, 2012). On the other hand, solubility of As is generally reduced with increase in organic matter content in soil through organo-arsenic chelation (Ghosh et al., 2012). Our findings open up an important area of remediation of As contaminated soil with addition of organic manure.

It is evident from the range of HQ values that HQ for rice grain, grown in the participants' fields exceeded 1.0 in seven cases. On an average, the value of HQ was unacceptable for drinking water indicating that by and large drinking water of the region was unfit for consumption. Hence, in prescribing toxic limit of extractable As in soil in relation to dietary intake of As by human through consumption of rice grain, As content in drinking water was assumed to be 10 ppb (safe limit). For 10 ppb As in drinking water, HQ would be 0.2. Permissible value of HQ was considered as 0.5 for rice grain thinking that value of HQ would be 0.2 for drinking water even if people of the region take safe water (10 ppb As). The remainder value of safe HQ, i.e., $1.0 - 0.5 - 0.2 = 0.3$ is kept for accounting for intake of As through food items other than rice grain. A ready reckoner was developed for computing permissible extractable limit of As in soil for rice crop in relation to human health (example Fig. 4). In the study area, permissible extractable limit of As in soil varied widely with change in organic matter content, while such variation was not evident with pH. This may be attributed to narrow range of soil pH values (in the alkaline range in the study area). Such findings further strengthen the argument as given in previous section that total As content is not a good index of As hazard in relation to human health. This shows the importance of fixing permissible limit of extractable As in soil taking into account of important soil properties. We should not put very stringent permissible limit, nor should we be very loose. Because we do not have luxury of arable land in our country for that matter in the entire South-East Asia and at the same time loose permissible limit would not help in protecting human health properly from As hazard.

5. Conclusions

From a public health perspective, our findings are particularly important given the fact that in near future, awareness generation and motivation of the people for testing their drinking water quality for As is going to be a key factor to prevent further exposure of As to these people. Further, As affected people with severe skin lesion suffer from unprecedented health hazard and misery. Supply of As-free drinking water, coupled with arrangement of free treatment of these patients in state referral hospital, could help considerably in alleviating the disease prevalence, in view of the fact the these affected people are very poor and live in distant villages.

The As-contaminated groundwater was the main source for irrigation, drinking and allied activities in the study area. Excessive use of As contaminated groundwater resulted into elevated level of As in soil-water-food-chain. This investigation not only describes effective protocol for prescribing toxic limit of extractable As in soil, but also suggests the way of reducing As hazard using organic manures. Novelty of the study is that an integrated approach by physicians and soil scientists was adopted to assess the As hazard in the study area.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2017.06.027.

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