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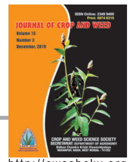

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Distribution and path analysis of arsenic in soil, water and rice in some affected blocks of lower Gangetic plain

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ABSTRACT

The present investigation was undertaken to study the distribution of arsenic in soil, in tube-well water used for irrigation, and in rice and the path analysis of available soil and rice grain arsenic in four arsenic affected blocks of Nadia district, West Bengal. About 51, 65.7, 59 and 70 per cent soil samples belonged to low (<5.0 mg kg^{-1})and 42, 29.3, 39 and 27 percent to medium (5.0-7.5 mgkg^{-1}) arsenic category in Chakdah, Ranaghat II, Shantipur and Haringhata block, respectively. The average arsenic content in soils ranged from 4.54 to 5.37 mg kg^{-1}, whereas that in tube-well water ranged from 151.43 to 213.71 µg L^{-1}. Available phosphorus had the highest positive, while iron oxide had the highest negative direct effect on soil arsenic content. Arsenic content in rice shoot had the highest positive and leaf had the highest negative direct effect on grain arsenic content due to re-translocation of accumulated arsenic from leaf to grain during grain filling.

Keywords: Arsenic, path analysis, rice, soil, tube-well water.

INTRODUCTION

A well circulated English daily newspaper 'The Times of India' on 24th Dec, 2017 reported that about 239 million people across 153 Districts in 21 States of India drink water that contains unacceptably high levels of arsenic (As). In Ganga-Meghna-Brahmaputra plain alone, currently more than 100 million people are potentially at the risk from groundwater As contamination because as small as 0.1g of As tri-oxide can prove lethal to humans (Jarup, 1992). The problem of groundwater contamination of As is further accentuated by the elevated As levels in the rice grain in regions of West Bengal and Bangladesh where rice fields are irrigated with As contaminated waters (Duxbury *et al*., 2003). Against global normal range of 0.08 to 0.2 mg As kg^{-1} (Zavala and Duxbury 2008), much higher value (1.8 mg As kg^{-1}) has been reported in rice grains (Meharg and Rahman, 2003) and in vegetables from Bangladesh (Das *et al*., 2004). Rice, one of the major crops of West Bengal, is cultivated both during *kharif* and *boro* season. The high buffering capacity though in some soils can act as a sink to As, application of contaminated ground water for irrigation increases the level of this pollutant in soil acting as a secondary source of As pollution. Rice crop assimilates both arsenate and arsenite efficiently and can accumulate 10 folds higher amount of As in grain than other cereal crops (Williams *et al.,* 2007). Rice being the staple food,the people of West Bengal consumed on an average 400 g rice per day, is a principal source of As entry into human system (Carbonell-Barrachina *et al.*, 2009). In case of arable crops, As is adsorbed by iron hydroxides and becomes largely unavailable to plants but under flooded anaerobic environment, where rice is normally grown, results in reductive dissolution of iron oxides and hydroxides (Sailo and Mahanta, 2014) leading to decreased adsorption of arsenite (As III) and its inadvertent uptake by rice plants.

In this backdrop, the present investigation was undertaken to study the distribution of As in soil, adjacent tube-well water and different parts of rice plant, as well as the path analysis of soil and grain As in some As affected blocks of lower Gangetic plain (Nadia district, West Bengal) of India.

MATERIALS AND METHODS

Study area

Total 51As affected Gram Panchayats comprising of 10 from Shantipur and Haringhata each, 14 from Ranaghat II and 17 from Chakdah block under Nadia district of West Bengal were selected for this study. From each gram panchayat10 geo-referenced surface (0-20 cm) soil samples, one plant sample from standing rice field and two water samples from the adjacent tube-well used for irrigating crops were collected in the month of April, 2017.

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Analysis of soil, water and plant samples

Soil sample: The soil samples after processing (< 2mm) were analyzed for relevant physical and chemical properties such as, mechanical analysis (Dewis and Freitas,1970), pH, electrical conductivity of saturation extract (EC_e) and organic carbon (Jackson,1973), available and total As (Schmidt *et al*., 2004), available P (Olsen *et al.,* 1954), iron and aluminium oxides (Mckeague and Day,1966) and AEC (Seifferlein *et al*., 2006) following standard methods.

Water sample: The collected samples were kept in 50 ml sized plastic container with 2-3 drops of diluted HCl to preserve it for delayed use. The samples were filtered through Whatman 1 filter paper and analyzed for total As content following the method of Schmidt *et al*. (2004).

Plant samples: The dry plant samples (60^{0}C) were separated into 4 parts *i.e.*,roots, shoots, leaves and grains. The grains were shelled by Indo-saw rice shelling machine and total As concentration in root, shoot, leaf, husk and grain samples were estimated following the method of Schmidt *et al*. (2004) after tri-acid digestion (Sparks *et al*.,2006).

Statistical analysis

Statistical analyses of soilparameters, As concentration in soil, water and plant parts were done for correlation coefficient and for path analysis of soil available As and grain As content using a PC with the help of SPSS software (SPSS 7.5, 1997).

Mapping: Using a PC with the help of ARC-MAP software (Arc-Map 10.1), all the geo referenced soil and water samples were spatially analyzed followed by preparation of spatial interpolation in ordinary kriging map.

RESULTS AND DISCUSSION

Physico-chemical properties

Except free Fe- and Al oxide and AEC there were little variation in other soil parameters among four blocks of Nadia district under consideration (Table 1). Most of the soils were agriculturally neutral in reaction (6.50 -7.50) and all soils under study were normal (EC_e< 2 dS m^{-1}) in salinity scale. The average clay contents were 23.99, 24.06, 24.11 and 23.84 per cent in soils of Chakdah, Ranaghat II, Shantipur and Haringhata block, respectively. The organic matter content varied from 4.70 to 8.10g kg^{-1}with a mean of 6.28 g kg^{-1}in soils of Chakdah block, 3.90 to 9.20 g kg^{-1} with a mean of 6.53 g kg^{-1} in Ranaghat II block, 4.10 to 7.40 g kg^{-1} with a mean of 6.15 g kg^{-1} in Shantipur block and 4.70 to 8.10 g kg^{-1} with a mean of 6.21 g kg^{-1} in Haringhata block. The average available phosphorus contents of soil were 6.51, 6.53, 6.33 and 6.28 mg kg^{-1} in Chakdah, Ranaghat II, Shantipur and Haringhata block, respectively. The total As content in soils ranged between 13.50 and 32.15 mg kg^{-1}with an average of 22.33 mg kg^{-1}, 14.70 and 27.33 mg kg^{-1} with an average of 20.34 mg kg^{-1},16.99 and 24.95 mg kg^{-1} with an average of 20.83 mg kg^{-1} and 11.82 and 27.46 mg kg^{-1} with an average of 19.99 mg kg^{-1} in Chakdah, Ranaghta II, Shantipur and Haringhata block, respectively.The free Fe oxide content varied from2.82 to 6.26 mg kg^{-1} with a mean of 4.23 mg kg^{-1} in Chakdah block, 2.82 to 6.51 mg kg^{-1} with a mean of 4.60 mg kg^{-1} in Ranaghat II block, 1.48 to 5.16 mg kg^{-1}with a mean of 3.66 mg kg^{-1} in Shantipur block, and 2.55 to 5.9 mg kg^{-1} with a mean of 4.54 mg kg^{-1} in Haringhata block. The free Al oxide content in soil varied between 0.52 and 3.60 mg kg^{-1} with a mean of 2.24 mg kg^{-1}, 2.17 and 5.83 mg kg^{-1}with a mean of 4.02mg kg^{-1}, 1.09 and 3.30 mg kg^{-1} with a mean of 2.39 mg kg^{-1}, and 0.50 and 3.80 mg kg^{-1}with a mean of 2.52 mg kg^{-1} in the above four blocks of Nadia district, respectively (Table 1). On the other hand, anion exchange capacity (AEC) of the soils ranged from 2.53 to 4.65 [cmol (e-) kg^{-1}] with an average of 3.41[cmol (e-) kg^{-1}], 4.66 to 7.26 [cmol (e-) kg^{-1}] with an average of 5.62[cmol (e-) kg^{-1}], 1.62 to 7.36 [cmol (e-) kg^{-1}] with an average of 5.80[cmol (e-) kg^{-1}], and 2.30 to 8.07 [cmol (e-) kg^{-1}] with an average of 4.42[cmol (e-) kg^{-1}] in Chakdah, Ranaghat II, Shantipur and Haringhata block, respectively.

As in soil, tube-well water and rice

The mean $NaHCO_3$ extractableAs content was the highest in the soils of Chakdah block (5.37 mg kg^{-1})followed by Ranaghat II (4.96 mg kg^{-1}), Shantipur (4.88 mg kg^{-1}) and Haringhata (4.54 mg kg^{-1}) the least (Table 2).Therefore, much lower values were found in contrast with the observation of Roychowdhury*et al.* (2002) who reported the 10.7 mgkg^{-1}as the mean As concentration in agricultural land of As contaminated blocks of West Bengal. Result of kriging map had been depicted through colour variation coded map; darker the colour higher was concentration of soil As. During preparation of map, As content of soils was divided into 5 classes*i.e.,*very low (<2.5 mg kg^{-1}), low (2.5-5.0 mg kg^{-1}), medium (5.0-7.5 mg kg^{-1}), high (7.5-10.0 mg kg^{-1}) and very high (> 10.0 mg kg^{-1}) (Figure 1). About 51 percent samples in Chakdah block were low, 42 percent medium, 3 percent high and 4 percent very high soil Asclass. In Ranaghat II block 65.7 per cent soil samples were tested as low, 29.3 per cent as medium, 2.1 per cent as high and 1.4 per cent in very high As category. In Shantipur block 59 per cent soil samples belonged to low, 39 per cent to medium and 2 per cent to high As status. On the other hand, block 70 per cent soil samples in Haringhata were in low, 27 per cent in

Table 1: Physico-chemical properties of soil samples of four blocks of Nadia district

Block		pH	EC_e (dS m^{-1})	AEC [cmol (e-) kg^{-1}]	Clay content (%)	OC (gkg^{-1})	Av-P (mg kg^{-1})	Free Fe Oxide (mg kg^{-1})	Free Al Oxide	Total As (mg kg^{-1}) (mg kg^{-1})
Chakdah	**Range**	6.30-7.74	0.001-0.797	2.53-4.65	21-86-27.13	4.70-8.10	3.75-9.55	2.82-6.26	0.52-3.60	13.50-32.15
	Mean	6.97	0.18	3.41	23.99	6.28	6.51	4.23	2.24	22.33
	S.D.	0.19	0.10	0.60	1.52	0.80	1.14	0.76	0.65	3.20
Ranaghat II	**Range**	6.59-7.41	0.09-0.959	4.66-7.26	20.21-27.43	3.90-9.20	4.08-10.46	2.82-6.51	2.17-5.83	14.70-27.33
	Mean	6.97	0.19	5.62	24.06	6.53	6.53	4.60	4.02	20.34
	S.D.	0.15	0.11	0.69	2.10	0.75	1.17	0.89	0.92	2.11
Shantipur	**Range**	6.54-7.20	0.109-0.998	1.62-7.36	21.33-26.08	4.10-7.40	3.58-9.68	1.48-5.16	1.09-3.30	16.99-24.95
	Mean	6.92	0.24	5.80	24.11	6.15	6.33	3.66	2.39	20.83
	S.D.	0.14	0.10	1.68	1.59	0.63	1.17	0.72	0.51	1.73
Haringhata	**Range**	6.48-7.53	0.018-0.365	2.30-8.07	21.84-27.73	4.70-8.10	3.10-9.04	2.55-5.99	0.50-3.80	11.82-27.46
	Mean	6.97	0.19	4.42	23.84	6.21	6.28	4.54	2.52	19.99
	S.D.	0.16	0.05	1.89	1.91	0.72	1.23	0.74	0.51	3.12

Table 2: Arsenic concentration in soil, tube well water and different parts of rice plant

Block		Soil (mg kg^{-1})	Tube well Water (µg L^{-1})	Root	Shoot	Leaf (mg kg^{-1})	Husk	Grain
Chakdah	**Range**	0.86-18.67	75.08-476.66	10.30-25.63	4.49-11.32	2.57-5.60	0.46-0.78	0.18-0.25
	Mean	5.37	213.71	16.95	8.62	4.24	0.59	0.22
	S.D.	2.08	108.35	10.30	4.49	2.57	0.46	0.18
Ranaghat II	**Range**	1.25-19.25	80.67-310.96	11.18-22.75	4.29-9.54	2.35-4.68	0.47-0.76	0.17-0.24
	Mean	4.96	185.53	17.35	6.68	3.38	0.59	0.20
	S.D.	1.75	49.12	4.18	1.41	0.59	0.09	0.02
Shantipur	**Range**	2.99-7.62	76.17-306.60	11.65-23.46	5.01-11.32	2.91-6.10	0.56-0.73	0.17-0.23
	Mean	4.88	171.57	17.11	7.32	4.20	0.63	0.20
	S.D.	0.92	65.31	3.25	1.87	0.99	0.06	0.02
Haringhata	**Range**	0.82-7.62	80.0 -308.37	13.27-20.78	5.46-10.13	3.17-4.60	0.41-0.68	0.16-0.23
	Mean	4.54	151.43	16.48	6.48	3.63	0.59	0.19
	S.D.	1.00	70.45	2.49	1.27	0.38	0.08	0.02

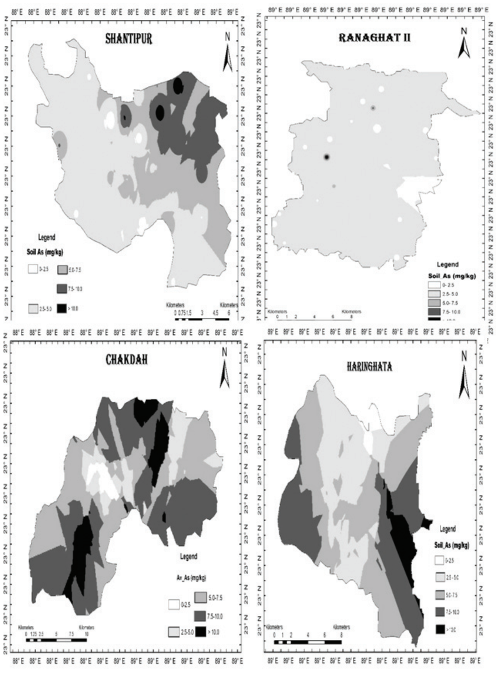

Fig. 1 : Kriging Maps of available soil As in four blocks of Nadia district

Table 3: Correlation coefficient (r) between different soil parameters, As content in tube well water and plant parts of rice in Nadia district

	pH	EC_e	Av-As	OC	Av-P	Free Fe-oxide	Free Aloxide	AEC	As in water	Root As	Shoot As	Leaf As	Husk As
EC_e	0.223*												
Av-As	-0.039	-0.209*											
OC	-0.132	-0.086	0.682**										
Av-P	-0.055	-0.044	0.486**	0.795**									
Free Feoxide	0.146	-0.046	-0.380**	-0.538**	-0.410**								
Free Aloxide	0.138	0.087	-0.517**	-0.447**	-0.446**	0.624**							
AEC	-0.009	0.300**	-0.149	0.080	-0.055	0.028	0.270**						
As in water	-0.056	-0.066	0.778**	0.818**	0.700**	-0.548**	-0.656**	-0.058					
Root As	-0.168	0.019	0.661**	0.647**	0.591**	-0.427**	-0.515**	0.097	0.825**				
Shoot As	-0.097	0.021	0.315**	0.258**	0.356**	-0.234*	-0.401**	-0.245*	0.389**	0.476**			
LeafAs	-.224*	0.002	.486**	.438**	.390**	-.373**	-.584**	-0.101	.598**	.617**	.794**		
HuskAs	-0.289**	0.057	0.335**	0.445**	0.367**	-0.132	-0.273**	0.174	0.486**	0.454**	0.098	.389**	
GrainAs	-0.094	0.012	0.175	0.118	0.208*	0.118	-0.096	-0.108	0.190	0.181	0.284**	.199*	0.477**

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).

medium and 2 per cent in very low and only 1 per cent in very high As class.

Similar sequence was observed in case of As content in the tube-well water, the ground water source for irrigating rice in four blocks of Nadia district under study. Basu *et al.* (2014) also reported that higher the ground water As concentration, higher was the As content of agricultural land due to use of contaminated ground water for irrigation purposes. The average soluble As content in tube-well water varied from 75.08 to 476.66 µg $l^{-1}$with a mean of 213.71 µg l^{-1}in Chakdah block, from 80.67 to 310.96 µg $l^{-1}$with a mean of 185.53µg l^{-1} in Ranaghat II block, from 76.17 to 306.60 µg $l^{-1}$with a mean of 171.57 µg l^{-1}inShantipur block and from 80.0 to 308.37 µg$L^{-1}$with a mean of 151.43µg l^{-1}in Haringhata block (Table 2). In general, the As content in the tube-well water under study area was found to be high. Basu *et al.*(2014) observed that As content of shallow ground water at Chakdah block was as high as 76.43 µg l^{-1} and the concentration of As even in the pond water was above the safety standard (32.63 ± 0.88 µg l^{-1}).

Similar to soil As map, darker colour in the kriging map of tube-well water depicted higher concentration of As. The tube-well water As content divisions were grouped into 4 classes: low (< 50.0 ppb), medium (50-150 ppb), high (150-300 ppb) and very high (> 300 ppb) (Fig. 2). About 35 per cent tube-well water samples in Chakdah block were rated as medium, 38 per cent as high and 26 per cent in very high As category. In Ranaghat II block 60.7 per cent samples were in medium, 28.5 per cent in high and 10.7 per cent in very high category. In both Shantipur and Haringhata blocks 60 per cent water samples belonged to high, 35 per cent to medium and 5 per cent to very high As category. Chakraborti *et al.* (2009) reported that As content in tube-well water of 24 per cent samples were above50 µg l^{-1} or 50 ppb.

The average As content in rice root, shoot, leaf, husk and grain in Chakdah block were16.95,8.62, 4.24, 0.59 and 0.22 mg kg^{-1}, respectively (Table 2). The same for Ranaghat II block were17.35,6.68, 3.38, 0.59 and 0.20 mg kg^{-1}, respectively.The mean As content of rice root, shoot, leaf, husk and grain in Shantipur block were 17.11, 7.32, 4.20, 0.63 and 0.20 mg kg^{-1} and in Haringhata block16.48, 6.48, 3.63, 0.59, 0.19 mg kg^{-1}, respectively. Except the As content in root, the highest As concentrations in different plant parts of rice were recorded from Chakdah block which also registered the highest soil As, while the least in Haringhata block. However, the uptake pattern of As followed the order: root>shoot>leaf>husk>economic produce (grain) in all the blocks. The results were corroborated well with the findings of Das *et al.* (2013).

Table 4: Path analysis for soil As of Nadia district

	pH	EC_e	OC	Av-P	Free Fe oxide	Free Al oxide	AEC
pH	**-0.051**	0.061	0.010	-0.084	0.019	-0.001	0.040
EC_e	-0.011	**0.280**	0.045	-0.049	0.011	0.000	0.024
OC	0.002	-0.058	**-0.216**	0.411	-0.145	0.003	-0.147
Av-P	0.007	-0.023	-0.147	**0.602**	-0.238	0.005	-0.127
Free Feoxide	0.003	-0.010	-0.105	0.479	**-0.299**	0.004	-0.126
Free Aloxide	-0.008	-0.013	0.082	-0.324	0.123	**-0.009**	0.177
AEC	-0.007	0.023	0.111	-0.269	0.133	-0.005	**0.283**

Residual Effect =0.7435

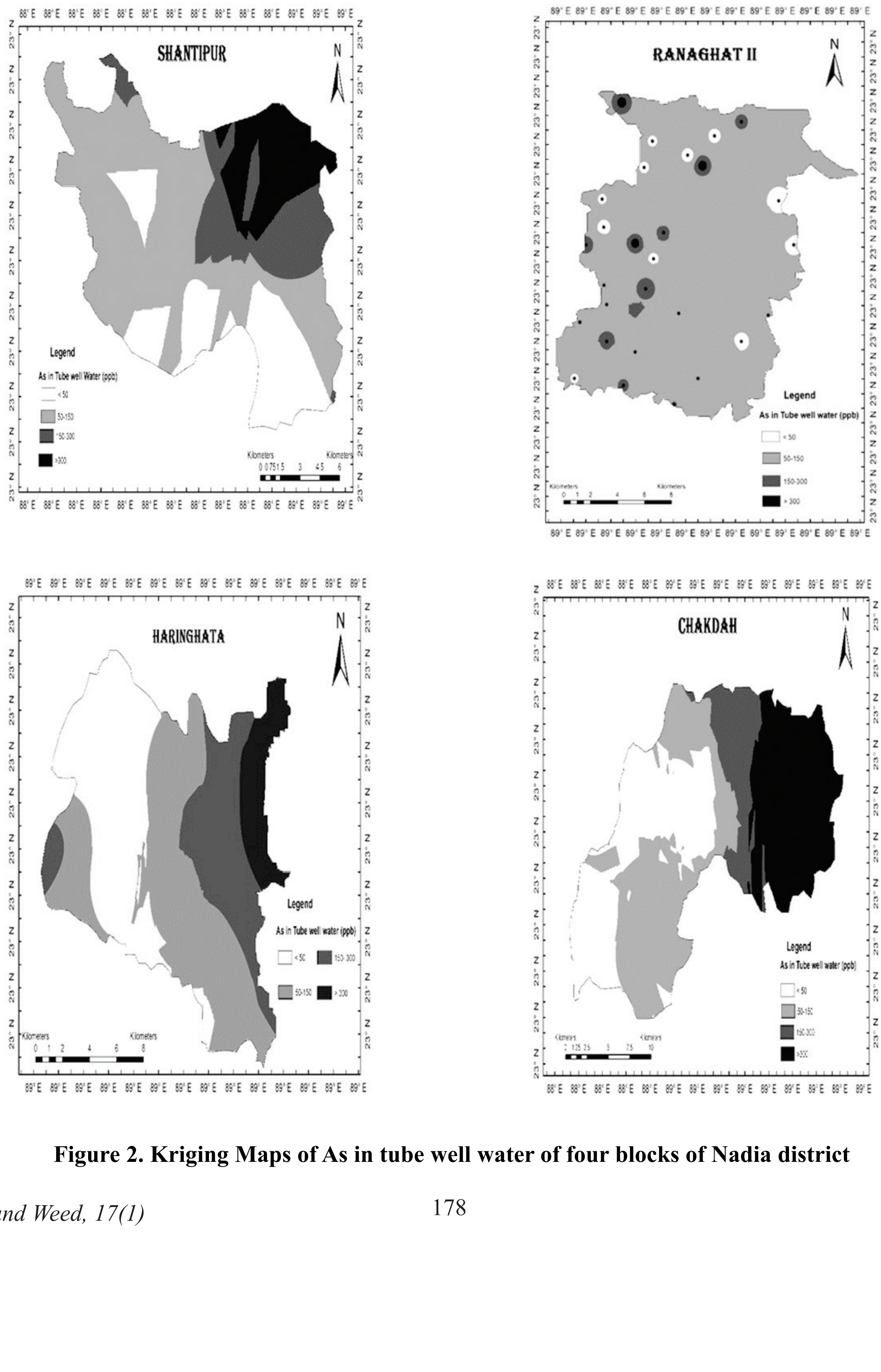

Figure 2. Kriging Maps of As in tube well water of four blocks of Nadia district

Table 5: Path analysis for Arsenic content in rice grain of Nadia district

	pH	EC_e	Av- As	OC	Av-P	Free Fe- oxide	Free Al oxide	AEC	As in water	Root As	Shoot As	Leaf As	Husk As
pH	**-0.031**	0.004	-0.008	0.031	-0.006	0.024	-0.004	0.000	-0.010	0.035	-0.065	0.126	-0.193
EC_e	-0.007	**0.017**	-0.035	0.018	-0.003	-0.008	-0.002	-0.011	-0.010	-0.006	0.022	-0.006	0.045
Av-As	0.001	-0.004	**0.170**	-0.149	0.044	-0.061	0.015	0.005	0.124	-0.132	0.209	-0.271	0.217
OC	0.004	-0.001	0.116	**-0.219**	0.072	-0.086	0.013	-0.003	0.130	-0.129	0.172	-0.245	0.287
Av-P	0.002	-0.001	0.083	-0.174	**0.091**	-0.065	0.013	0.002	0.111	-0.118	0.237	-0.218	0.237
Free Fe oxide	-0.005	-0.001	-0.065	0.118	-0.037	**0.159**	-0.018	-0.001	-0.087	0.085	-0.156	0.209	-0.084
Free Al oxide	-0.004	0.001	-0.088	0.098	-0.040	0.099	**-0.028**	-0.010	-0.104	0.103	-0.267	0.326	-0.177
AEC	0.000	0.005	-0.025	-0.017	-0.005	0.004	-0.008	**-0.035**	-0.009	-0.019	-0.163	0.057	0.113
As in water	0.002	-0.001	0.132	-0.179	0.064	-0.087	0.019	0.002	**0.159**	-0.164	0.258	-0.334	0.315
Root As	0.005	0.001	0.112	-0.142	0.054	-0.068	0.015	-0.003	0.131	**-0.199**	0.316	-0.344	0.294
Shoot As	0.003	0.001	0.054	-0.057	0.032	-0.037	0.011	0.009	0.062	-0.095	**0.665**	-0.444	0.062
LeafAs	0.007	0.000	0.083	-0.096	0.035	-0.060	0.017	0.004	0.095	-0.123	0.528	**-0.559**	0.252
HuskAs	0.009	0.001	0.057	-0.097	0.033	-0.021	0.008	-0.006	0.077	-0.090	0.063	-0.217	**0.650**

Residual effect = 0.5758

Relationships among soil properties

As content in the soil had significant positive relationship with organic carbon content (r = 0.682**), As content in nearby tube-well water (r = 0.778**) and As content in rice root (r = 0.661**), shoot (r = 0.315**) and husk (r = 0.335*) (Table 3).The result was in agreement with Cao *et al.* (2003), Clemente *et al.* (2015) and Waltham and Eick (2002). Competition between organic acids and As species might have influenced the mobility/solubility of As. Organic acid like HA and FA compete with arsenite (AsO_3^{-3}) and arsenate (AsO_4^{-3}) for active adsorption sites on mineral surfaces *i.e.,* Fe and Al oxides. Further, organic amendment increased available As content in soil possibly due to its role on reduction of As(V) to more mobile As(III) (For all the statements reference is required to support the statements). Further, organic amendment increased available As content in soil possibly due to its role on reduction of As(V) to more mobile As(III)(Wang and Mulligan, 2006). Significant positive correlation between tube-well water As concentration and soil available As content suggested that As loading in these soils was mostly occurred due to irrigating field with As contaminated ground water. The positive correlations between available As in soil and As content in plant parts suggested that As accumulation in different parts of rice plant was directly governed by the soil As loading. *Boro* (Summer) rice cultivation required approximately 1000 mm of irrigation water and added about 1µg As g^{-1} soil per season (Meharg and Rahman, 2003). Higher the As content in the ground water used for irrigating crops, higher was the As content in agricultural land (Basu *et al.*, 2014). While, As content in the soil had negative correlation with free Fe oxide (r = - 0.380*) and Al oxide (r = -0.517**) content, but a positive correlation with available soil P content (r = 0.486**). Hingston *et al.* (1972) also observed a positive relationship between phosphorus and As content in soil. In soil, phosphorus and As act as analogues, they both compete for the same sorption site on the soil particles. Thus, soil P content decreased As adsorption in soils and eventually increased available As in soil.

Free iron oxides had a significant positive relationship with free aluminium oxide (r= 624**) and negatively correlated with As content in tube-well water (r = -0.548**), rice root (r = -0.427*)and shoot (r = - 0.234*). Free aluminium oxide was also significantly negatively correlated with As content in tube-well water (r = -0.656**), rice root (r = -0.515**), riceshoot (r = - 0.401**) and rice husk (r = -0.273**). The results were in conformity with several workers (Goldberg and Jhons on, 2001; Lenoble *et al.,* 2002) who reported adsorption of As by oxides of Fe and Al in soil leading to its decreased availability to plant.

Organic carbon maintained a significant positive relationship with available phosphorus (r= 0.795**), but negative correlation with free iron oxides (r = 0.538**) and aluminium oxides (r = 0.447**). Availability of P in soil largely related to the desorption of P from solid to liquid phase and phosphate buffering capacity of the soil. Higher content of soil organic carbon enhances the P availability by reducing the strength of P adsorption and the maximum phosphate buffering capacity and increasing the desorption of P to some extent (Wang and Liang,2013. During formation of aggregates free iron and aluminium oxide strongly adsorb to organic matter and thereby prevent its accessibility to microorganisms and its degradation. Lalonde *et al.* (2012) also opined that iron oxides play an important role in protecting soil organic matter *via* adsorption and covering.

Available phosphorus had a highly significant positive correlation with As content in tube-well water (r = 0.700**) and negative significant correlation with free iron (r = -0.410*) and aluminium (r = -0.446**) oxides. Highly significant relationships were also observed between available phosphorus content and As content in rice root(r = 0.591**), shoot (r = 0.356**) and husk (r = 0.367**). Significant positive correlation between As content in tube-well water with As content in rice root (r = 0.825**), shoot (r = 0.389**) and husk (r = 0.486**) indicated the pathway of As from soil to plant system.

Path analysis of available soil As

Soil available phosphorus (0.602) had the highest positive direct effect followed by AEC (0.283) and EC_e (0.280), whereas free oxide (-0.299) had the highest negative direct effect on soil As content followed by the organic carbon (- 0.216) (Table 4). Positive effect of available phosphorus on available soil As content was attributed to the competition between these two anions for the same sorption sites in soil. Detailed spectroscopic studies showed that both As(V) andAs(III) sorbed to Fe and Al oxides via inner sphere surfaces complexation (Arai *et al.,*2001). Decreased availability of As in soil was probably the reflection of negative direct effect of Fe and Al oxides content in soil. Moreno-Jimenez *et al.* (2013) and Bolan *et al.* (2013) were in agreement with this observation. Available soil phosphorus had positive indirect effect on soil As content through soil pH and negative indirect effect through free iron oxide content. AEC had shown the positive indirect effect on soil As content through free iron oxide content and negative indirect effect *via* available P content. The bio-availability and behavior of As in natural system is strongly influenced by sorption on solid surfaces such as oxides of Mn, Al and Fe (Jones *et al.,* 2000). Free iron oxide had the highest positive indirect effect through available phosphorus and negative effect *via* AEC on soil As content.The high residual effect (0.744) indicated that other factors substantially contributed to availableAs content in these soils.

Path analysis of grain As

The As content in rice shoot (0.665) had the highest positive direct effect on As content in rice grain followed by the As content in rice husk (0.650) and available soil As content (0.170) (Table 5). On the other hand, leaf As had the highest negative direct effect (-0.559) followed by organic carbon content of soil (-0.219) and root As content (-0.199). Translocation of As from leaf to grain occurring in the later part of life cycle might be the cause behind this effect. Zheng *et al.* (2011) reported that the concentration of dimethylarsinic acid (DMA) decreased during grain fill, suggesting that its accumulation in grain occurred via the re-translocation of DMA accumulated in the plant before flowering. Punshon *et al*. (2018) also reported that As exposure later in grain development caused higher grain As concentrations due to increased efficiency of As transporters during grain fill. The As content in rice shoot had shown the positive indirect effect on grain As content *via* As concentration in tube-well water and husk As content, while negative indirect effect *via* As content in leave and root. The rice husk showed the positive indirect effect on grain As content *via* As concentration in tube-well water and As content in rice shoot and negative indirect effect via As content in rice leaf and organic carbon content in soil.

Leaf As content had shown the positive indirect effect *via* As content in rice shoot and husk and negative indirect effect *via* As content in rice root and organic carbon content in soil.

The residual effect (0.576) indicated that the 13 parameters included in this study explained only 42.4 per cent variation in grain arsenic content in these soils.

Availability of As content in soil was positively influenced by available soil phosphorus content, and negatively by free iron oxide content.On the other hand, As concentration in rice grain was positively regulated by As content in rice husk and available soil As content, but negatively by leaf As content.

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