
ARSENIC IN GROUNDWATER, SOIL AND RICE GRAIN OF NEPAL

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ABSTRACT

Arsenic (*As*) contamination in groundwater is a serious issue of South Asian countries. *As* can also contaminate soil and crops growing in that area. To evaluate the level of *As* contamination in water, soil and crops (rice grain), sites were selected from highly *As* affected southern district of Nepal, Nawalparasi. The *As* level in water was above the national (0.05 mg L^{-1}) and WHO standards (0.01 mg L^{-1}). However, soil and rice grain showed *As* contamination in the safe level. The average ratios of *As* concentration of soil to water, rice grain to water and rice grain to soil samples was found to be 6.2, 2 and 1.5, respectively. Furthermore, positive correlation of *As* in water with soil and negative correlation of *As* in water with rice grain indicates that soil gets contaminated first with *As* followed by rice grain. Hydride generation atomic absorption spectrophotometer was used for *As* analysis.

Keywords: Arsenic (*As*), groundwater, soil, rice grain, HGAAS

Introduction

Arsenic is a significant contaminant and pollutant of groundwater and soil in many regions of the world. Higher concentration of arsenic in drinking water have been reported in several countries including Argentina, Bangladesh, China, India, Nepal, USA, Japan etc (Thakur et al., 2011). The most severe problem of arsenic contamination in groundwater is in Bangladesh and West Bengal State of India (Sijapati et al., 2004). In 1999, *As* presence in groundwater in the Terai districts of Nepal was brought to light for the first time during the survey conducted by WHO (WHO, 2001). Importantly, *As* containing water can contaminate soil and also crops growing in that soil.

Specifically, available documents indicate that Nepal's 24 districts, including all 20 Terai districts and four hilly districts have shown arsenic contamination (FAO, 2004). The studies (Panthi et al., 2006; Maharjan et al., 2006 and Thakur et al., 2011) revealed that arsenic contamination was found to be severe in districts of Terai namely Nawalparasi, Bara, Parsa,

Rautahat, Rupandehi, and Kapilvastu. In these districts, arsenic contamination in tubewells varied from 2.1% of 2043 tubewells examined in Rupandehi district to 25.7% of 3211 tubewells examined in Nawalparasi district (Maharjan et al., 2006). Also, the highest arsenic concentration, above 0.05 mg L⁻¹, was reported in Nawalparasi district and minimum arsenic concentration was reported in Palpa, Ilam and Chitwan districts (Thakur et al., 2011). Of the total studied population of six districts (N = 18,288), 400 were identified as cases of arsenicosis. The occurrence of arsenicosis was on average 2.2% (400/18288) and varied from 0.7% (11/1666) in Kapilvastu district to 3.6% (109/3011) in Nawalparasi district. The highest prevalence (18.6% = 97/521) of arsenicosis was reported in Patkhouli village of Nawalparasi, where 95.8% of tubewells were contaminated with arsenic (Maharjan et al., 2006). The toxicity of As to human health ranges from skin lesions (melanosis and keratosis) to cancer of the brain, lungs, kidney and stomach (Thakur et al., 2011).

Nepal is agricultural country and rice is the staple food of the country. The rice cultivation mainly depends on the underground water. Terai, a plain southern part of Nepal is very rich in groundwater and thus have been the primary source for drinking water and irrigation purposes (FAO, 2004). Over 90 % of Terai population draws groundwater from tubewells for drinking and irrigation (Gurung et al., 2005). Generally As is available in much higher concentration in groundwater compared to surface water (Sijapati et al., 2004). Also, arsenic concentration in groundwater varies seasonally. Groundwater has higher As-concentration in pre-monsoon season and the dilution of the underground water causes the lowering of As concentration in post-monsoon season (Shrestha et al., 2014). Arsenic mobilization in the water residing in aquifers may have been caused by over withdrawal of groundwater during cultivation. The widespread use of arsenic contaminated groundwater in irrigation for a prolonged period of time could elevate its concentration in surface soil and eventually into vegetations for example, rice plants and rice grain. The arsenic content in tissues of rice plant is in the order: straw > husk > rice grain (Rahman et al., 2007).

World Health Organization (WHO) has set 0.01 mg L⁻¹ As concentration as the limit value in the drinking water. Many countries, particularly developing one like Nepal, including India and Bangladesh, have adopted the limit of 0.05 mg L⁻¹ As concentration as their national standard because of lack of adequate tests and also removal and mitigation facilities to lower the level of arsenic concentration (Thakur et al., 2011). The lowest standard currently set for acceptable As concentration in drinking water is implemented by Australia, which has a national standard of 0.007 mg L⁻¹ (ADWG, 2004). However, limited literatures are available on As accumulation in rice varieties and soil. Unfortunately, there is no upper standard limit of arsenic in food grain for South and East Asian countries, United Kingdom and Australia has set the food hygiene standard

level of As as 1.0 mg kg^{-1} (Warren et al., 2003). European Union recommends $20 \text{ mg of As kg}^{-1}$ soil as the maximum limit of As in agricultural soil for crops (Kabata-Pendias and Pendias, 1992).

As contamination in groundwater and food grain is a major health issues in Terai region of Nepal, where the population density is very high. The long term use of As contaminated groundwater for irrigation results the elevated As contamination in agricultural land followed by food grain. Previous studies clearly indicated that the Terai region as a whole has been in deteriorating condition due to As contamination and also, more importantly, there are reports of As contamination in food grain in Bangladesh and West Bengal of India. There is no any scientific investigation in this issue in case of Nepal. In this regard, prediction of actual concentration of As dissolved in water and food grain will allow to make a clear picture of total dose taken by the people from drinking water and food materials so that Nepal Government can make a proper plan accordingly for providing pure water. Therefore, this study has been conducted to find the As concentration in groundwater, soil and rice grain of Nawalparasi district. This study also indicates the flow of As from groundwater to soil and then, from both groundwater and soil to rice grain.

Methodology

Sampling sites

Nawalparasi is one of six districts of Lumbini zone in Nepal's Western Development Region. Area inside the dashed line in Fig. (1) shows the google map of Nawalparasi district. It is one of the 20 Terai districts of Nepal and bordered by Chitwan and Tanahu districts in the east; Rupandehi and Palpa in the west; Palpa and Tanahu in the north and Uttar Pradesh state of India in the south. Nawalparasi has 74 VDCs and one municipality. The head quarter of the district is Parasi bazaar. The district lies between 91 and 1,936 meters above sea level. It occupies the area between $27^{\circ} 21'$ and $27^{\circ} 47'$ latitudes, and $83^{\circ} 36'$ and $84^{\circ} 25'$ longitudes (New ERA, 2000).



Fig. 1: Google map of Nawalparasi district (Source: Shrestha et al., 2014)

Devgaun and Manari are two Village Development Committees (VDCs) of Nawalparasi district. Of many villages, Pathkauli village of Devgaun VDC and Mahuwa village of Manari VDC were selected as the project site.

Sample collection and arsenic analysis

The sampling of groundwater (taken from hand pumps, 40-100 feet deep) and soil was conducted at post-monsoon season from 1st to 3rd October 2012. Similarly, sampling of rice grain samples was done on 18th October, which is nearly the time of rice harvesting. Groundwater (N = 46), soil (N = 10) and rice grain (N = 7) samples were collected for As analysis. Rice grain samples were collected at the rice field and soil samples were also collected from the rice field at a depth of 0-15 cm.

Analysis was performed by two different techniques. For qualitative analysis, a HACH As-test kit was used and for quantitative analysis, hydride generation atomic absorption spectrophotometer (HGAAS) (Thermo Electron Corporation) was used.

Presence of As in the tubewell water was confirmed by HACH As-test kits at the site, which gives rough range of As concentration on the basis of color change. Briefly, the As-test kit contains mercuric bromide ($HgCl_2$) coated film with which arsine gas (AsH_3) reacts due to which color of the film changes. Arsine gas (AsH_3) is produced from the reaction between As^{3+} and hydrogen ions (H^+). As^{3+} is formed from the reduction of As^{5+} by the addition of potassium iodide (KI) and stannous chloride ($SnCl_2$) in an acidic medium and hydrogen ions (H^+) are formed by the reaction of HCl and zinc granules. This stain is then compared against a colour coded chart indicating the As concentration from zero to 0.5 mg L^{-1} (Nepal, 2011).

After confirmation of presence of As in a particular tubewell by testing with HACH As-test kit during the blanket testing in field visit, two sets of samples were prepared in polyethylene vials for laboratory analysis (note that, the plastic bottles were previously washed by distilled water and dried in oven). In one set of vials, groundwater samples were collected without preservative for the analysis of Physio-chemical parameters: pH, conductivity and total dissolved solids (TDS) and kept in ice box. The Physio-chemical parameters were measured in the laboratory of Kathmandu University and the findings were reported in our previous article (Shrestha et al., 2014). While for quantitative analysis of arsenic, five ml concentrated HCl per liter was added to vials containing water and transferred to Aquatic Ecology Center (AEC) at Kathmandu University in Dhulikhel for further analysis by HG-AAS for the more accurate result.

Digestion of soil and rice grain samples

The rice grain and soil samples were digested in the laboratory before quantitative analysis of As. The digestion method was followed as reported by Rahman et. al (2007) and is briefly described below.

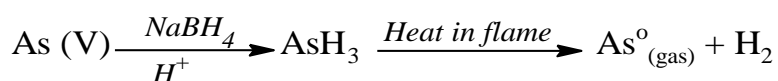
The collected samples (rice grain and soil) from each spot were tagged properly and sun dried for 3 days putting the samples on a wooden table. The sun dried samples were stored in a drying cabinet at 45°C . Again, taking the final weight, all samples were oven dried at 65°C for 72 hours. Then, the samples were ground and sieved. About 0.5 g of the sample was taken into a dry clean digestion tubes and 5 ml of concentrated nitric acid was added in it. The mixture was allowed to stand overnight under fume hood. In the following day, the digestion tubes were placed on a heating block and heated at 60°C for 2 hours. Then, the tubes were allowed to cool at room temperature. About 2 ml of concentrated perchloric acid was added to the rice grain samples. For the soil samples (initial soil), 3 ml sulfuric acid was added in addition to 2 ml perchloric acid.

Again, the tubes were heated at 160°C for about 4–5 hours. Heating was stopped when the dense white fume of perchloric acid occurred. The digest was cooled, diluted to 25 ml by distilled DI water and filtered through filter paper (Whatman: No.1) and stored in 30-ml polythene bottles previously washed by distilled DI water and dried. Then, the extracts of the digested samples were transported to Aquatic Ecology Centre (AEC) at Kathmandu University in Dhulikhel for further analysis by HGAAS.

Method for Arsenic (As) analysis by HGAAS

The compounds of arsenic are converted to their volatile hydrides by the use of sodium borohydride ($NaBH_4$) as reducing agent in acidic medium created by HCl . Then, the hydride is dissociated into an atomic vapour by the relatively moderate temperature of an air-acetylene flame (Mendham et al., 2002).

The reaction sequence for arsenic analysis by HG-AAS may be represented by



Results and discussion

As-concentration in underground water, soil and rice grain samples

During post-monsoon season from 1st to 3rd October 2012, groundwater (N = 46), soil (N = 10) and rice grain samples (N = 7) were collected and analyzed for As concentration using HGAAS. Figures (2) & (3) and Table (1) respectively show the concentration of As in groundwater, soil and rice grain samples.

This study shows that the level of As concentration in groundwater was found above the Nepal's national (0.05 mg L⁻¹) & WHO standards (0.01 mg L⁻¹) in all analyzed samples ranging from 0.121 mg L⁻¹ to 1.103 mg L⁻¹ with the average of 0.59 mg L⁻¹. Similarly, Bhattacharya et al. (2009) revealed that the level of arsenic concentration in irrigation water in the range of 0.11±0.012 to 0.76±0.014 mg L⁻¹ in the study of the arsenic affected 17 villages of Nadia district, West Bengal, India. A survey study conducted on arsenic concentration of tube-well water of 41 districts from the total 64 districts of Bangladesh by the British Geological Survey (2000) showed that 51% samples were above 0.01 mg L⁻¹ (WHO standard), 35% samples were above 0.05 mg L⁻¹ (national standard), 25% were above 0.10 mg L⁻¹, 8.4% were above 0.30 mg L⁻¹ and 0.1% were above 1.0 mg L⁻¹ (Abedin and Meharg, 2002).

Some soil and rice grain samples, collected from arsenic affected area where the arsenic contaminated tubewell water was used for irrigation, showed arsenic contamination. This study shows that As concentration in all soil samples are in the range of 0.35 to 9.55 mg kg⁻¹ with average of 3.14 mg kg⁻¹ which is below than 20 mg of As kg⁻¹ soil as the maximum limit of arsenic in agricultural soil for crops. Similarly Bhattacharya et al. (2009) revealed that the total soil arsenic concentration ranged from 1.38±0.108 to 12.27±0.094 mg kg⁻¹ dry weight of arsenic in the study of the arsenic affected 17 villages of Nadia district, West Bengal, India. In the next study by Meharg and Rahman (2003), the arsenic level in the 0 - 15 cm surface paddy soil in 27 administrative districts of Bangladesh varied between 3.1 to 42.5 mg kg⁻¹.

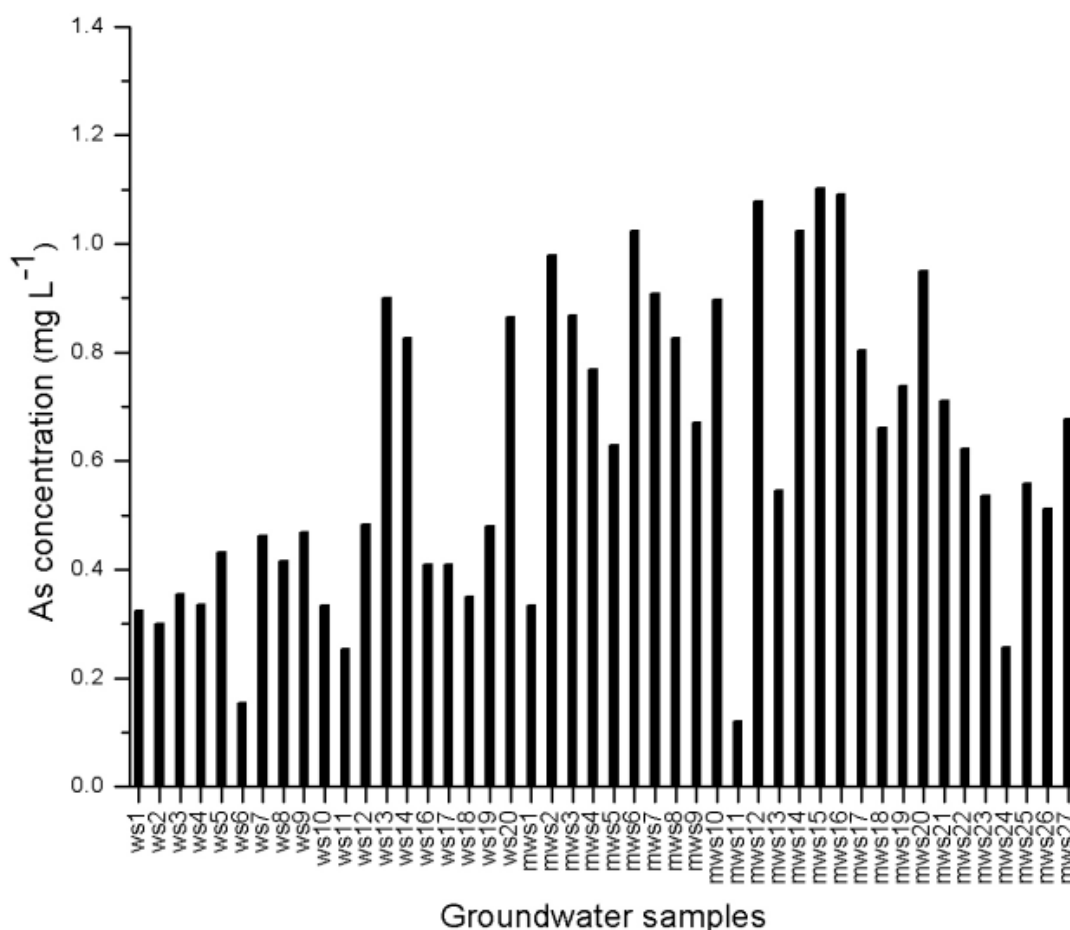


Figure 2: As concentration in groundwater samples

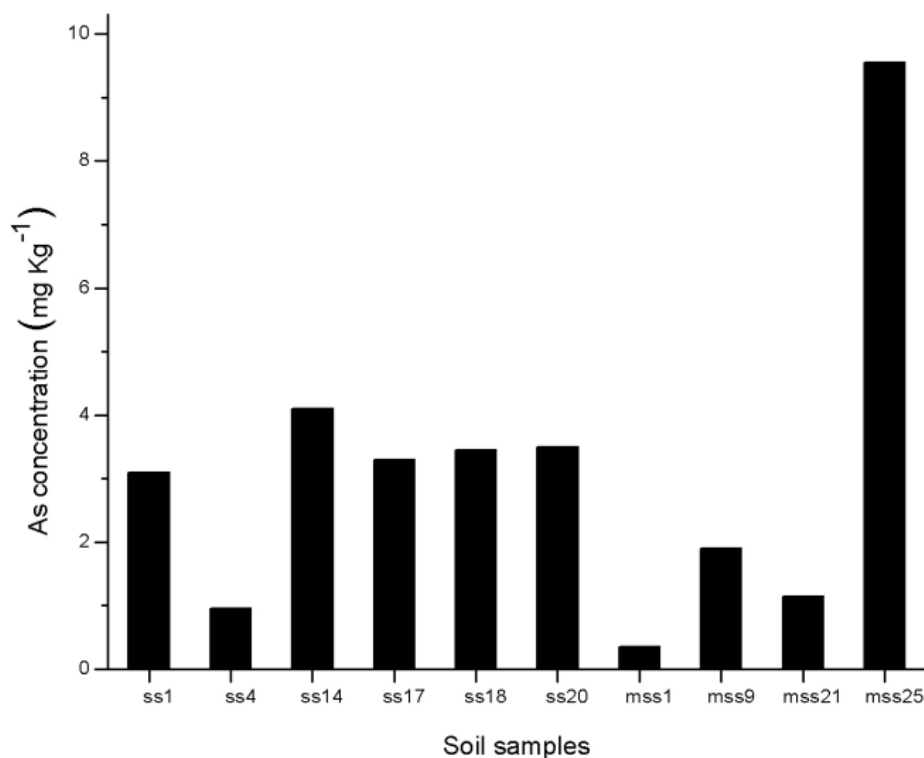


Figure 3: As concentration in soil samples

In all rice grain samples analyzed, this study shows that the average As concentration was about 0.74 mg kg^{-1} which is below the food hygiene standard level of As (1.0 mg kg^{-1}) in United Kingdom and Australia. Specifically, three samples showed As level below detection limit (0.005 mg kg^{-1}) reported as ND (not determined) in the table (1) and other four samples demonstrated in the range 0.35 mg kg^{-1} to 1.9 mg kg^{-1} . Similarly, in the study of the arsenic affected 17 villages of Nadia district (West Bengal, India) by Bhattacharya et al. (2009), the results showed that the level of arsenic in the rice grain ranging from 0.25 ± 0.014 to $0.73 \pm 0.009 \text{ mg kg}^{-1}$. In the next study by Meharg and Rahman (2003), the arsenic level in rice grain varieties collected from different western Bangladesh districts ranged from 0.058 to 1.83 mg kg^{-1} . In another study, As level in rice grain ranged from 0.03 to 0.11 mg kg^{-1} in North American cooked rice (N=18) (Tao and Bolger, 1998) and on raw rice grain, this range was $0.2 - 0.46 \text{ mg kg}^{-1}$ with a mean of 0.303 mg kg^{-1} wet weight (N=4) (Schoof et al., 1999). For Taiwan, values ranged between 0.063 mg kg^{-1} and 0.2 mg kg^{-1} dry weight (N=4) (Schoof et al., 1998).

Table 1: As concentration in rice grain samples

S.N.	Rice grain samples	As concentration in rice grain (mg kg^{-1}) samples
1	rs ₁	ND(<0.005)
2	rs ₄	0.35
3	rs ₁₄	ND(<0.005)
4	rs ₁₇	ND(<0.005)
5	rs ₁₈	0.35
6	rs ₂₀	0.35
7	mrs ₁	1.9

Table 2: Ratios of As concentration in rice grain to soil samples

S.N.	Ratios of As concentration in rice grain to soil sample	Ratios of As concentration (ppm) in rice grain to soil sample	Average of ratios of As concentration (ppm) in rice grain to soil sample
1	rs_4/ss_4	$0.35/0.95 = 0.37$	
2	rs_{18}/ss_{18}	$0.35/3.45 = 0.101$	
3	rs_{20}/ss_{20}	$0.35/3.5 = 0.1$	1.5
4	mrs_1/mss_1	$1.9/0.35 = 5.43$	

Table 3: Ratios of As concentration in rice grain to water sample

S.N.	Ratios of As concentration in rice grain to water sample	Ratios of As concentration (ppm) in rice grain to water sample	Average of ratios of As concentration(ppm) in rice grain to water sample
1	rs_4/ws_4	$0.35/0.335 = 1.05$	
2	rs_{18}/ws_{18}	$0.35/0.35 = 1$	
3	rs_{20}/ws_{20}	$0.35/0.865 = 0.405$	2.03
4	mrs_1/mws_1	$1.9/0.334 = 5.69$	

Table 4: Ratios of As concentration in soil to water sample

S.N.	Ratios of As concentration in soil to water sample	Ratios of As concentration (ppm) in soil to water sample	Average of ratios of As concentration (ppm) in soil to water sample
1	ss_1/ws_1	$3.1/0.325 = 9.54$	
2	ss_4/ws_4	$0.95/0.335 = 2.84$	
3	ss_{14}/ws_{14}	$4.1/0.827 = 4.96$	
4	ss_{17}/ws_{17}	$3.3/0.41 = 8.05$	
5	ss_{18}/ws_{18}	$3.45/0.35 = 9.86$	
6	ss_{20}/ws_{20}	$3.5/0.865 = 4.05$	6.2
7	mss_1/mws_1	$0.35/0.334 = 1.05$	
8	mss_9/mws_9	$1.9/0.671 = 2.83$	
9	mss_{21}/mws_{21}	$1.15/0.712 = 1.62$	
10	mss_{25}/mws_{25}	$9.55/0.559 = 17.08$	

Table 5: The correlation coefficient value (r) between As concentration in groundwater, soil and rice grain samples

	As in groundwater	As in soil	As in rice grain
As in groundwater		0.19	
As in soil			-0.772
As in rice grain	-0.279		

Also, the ratios of arsenic concentration in rice grain to soil, rice grain to water and soil to water samples were calculated and shown in Table (2), (3) and (4). The average ratios of As concentration of soil to water samples, rice grain samples to water and rice grain to soil samples were found to be 6.2, 2 and 1.5, respectively. The correlation coefficient value (r) between As concentration in groundwater, soil and rice grain samples were also calculated with the help of Microsoft Office Excel 2007 and shown in the Table (5). The correlation coefficient between As concentration in groundwater and soil samples shows positive relation and equal to 0.19. Negative correlation of As concentration in groundwater with rice grain (- 0.279) and As concentration in soil with rice grain (- 0.772) were observed. The results indicate that the agricultural soil gets contaminated with As due to the irrigation by As contaminated groundwater. The irrigation by As contaminated groundwater may increase the As concentration in the agricultural soil and eventually leading to more accumulation in rice plants, one of the major food crops in many countries like Nepal. Thus, As is transferred from groundwater to soil and then, from both contaminated irrigation water and agricultural soil to rice plants.

Conclusion

This study shows that the level of As concentration in groundwater in the study area was found well above the Nepal's national (0.05 mg L⁻¹) & WHO standards (0.01 mg L⁻¹). The soil and rice grain samples also show the As contamination. None of soil samples show the As contamination greater than permissible limit of 20 mg of As kg⁻¹ soil. The average As concentration in rice grain samples is found below food hygiene standard level of As (1.0 mg kg⁻¹). The study indicates that As contaminated groundwater and soil are highly responsible for the transfer of As in rice plants and rice grain. Thus the people living in the study area are in high risk of As

exposure to human bodies through As contaminated groundwater by drinking and cooking purposes and through As contaminated rice grain.

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