RECENT STATUS OF ARSENIC CONTAMINATION IN GROUNDWATER OF NEPAL – A REVIEW

Sudan Raj Panthi¹, Subodh Sharma², Abadh Kishore Mishra¹

¹Department of Water Supply and Sewerage, Kathmandu, Nepal. ² Aquatic Ecology Centre (AEC) P.O. Box: 6250 Kathmandu University, Dhulikhel, Nepal.

Corresponding author e-mail: kuhimal@ku.edu.np

ABSTRACT

Arsenic in ground water is becoming an emerging issue in the water supply and health sectors of Nepal. Considerably high percentages of people live in rural Terai region and most of them are dependent on hand tube wells for drinking water consumption in Nepal. The ground water in the past was considered to be safe for drinking purpose but now it came to be known that many shallow tube wells contain arsenic at concentrations higher than the safe limit set for drinking purpose by WHO 1993. This paper reviews the recent status of arsenic in ground water of Nepal and recommends proper research methods to be adopted in mitigating the effects of it to human health.

Keywords: Arsenic, Arsenic in ground water, contaminated tube wells, drinking water in Nepal

INTRODUCTION

Arsenic occurs widely in nature and is best known for its toxic properties. Arsenic can occur in the environment in four different oxidation states $(-3, 0, +3, -1)$ but in natural waters is mostly found in inorganic form as oxyanions of trivalent arsenite, As (+3) or pentavalent arsenate, As $(+5)$. In the natural waters of pH ranging from 5 to 9, the predominant species of arsenic are H₂AsO₄ - (lower pH) and HAsO₄ - 2 (higher pH) in $+5$ (Arsenate) state, which is more common in aerobic surface water and H_3AsO_3 in $+3$ (Arsenite) state, which can be found in anaerobic groundwater. It readily participates in oxidation, reduction, methylation, demethylation and acid-base reaction. Arsenite is more mobile and more stable than arsenate in aqueous solution especially at pH greater than 7. Hence it is difficult to remove, arsenite compared to arsenate due to higher stability in solubility in natural waters by simple adsorption and precipitation process. The major issue of arsenic contaminated water is to find out the level of contamination of arsenic and it is not so easy because of no color, no odor and no taste even in the highly contaminated water. Arsenite is more toxic (about ten times) than the arsenate due to former ability to react with sulfhydryl groups there by increasing the residence time (Nagarnaik *et al.*, 2002) Although there is no widely accepted mechanism of the release of arsenic in ground water, but it has been accepted that most of all including in Nepal is of natural, geological origin. The arsenic is thought to be closely associated with oxidation-reduction process of iron oxides and pyrite. Evidence exists to support oxidizing/reducing desorption of iron oxides and pyrite oxidation theories of releasing arsenic. In the context of strongly reducing environment ($Eh - 110$ to -200 mV) of ground water in Nepal (Bhattacharya *et al*., 2003), reductive desorption theory is the most likely explanatory in which arsenic rich iron oxides break down and get dissolved into water.

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Toxicity and health effects of arsenic

The United States Environment Protection Agency (USEPA) and International Agency for Research on Cancer (IARC) have specified arsenic as known human carcinogen. According to EPA weight of evidence classification for carcinogens, arsenic is categorized as Group A Carcinogen. Its classification indicates that there is sufficient evidence from epidemiological studies to support a case–effects relationship between the substance and cancer. As is virulent poison on acute ingestion, 76 mg As (3+) is considered to be lethal to adults and extremely toxic on long-term exposure to a very low concentration (Azcue and Narjagu, 1994 in Sharma 1999). Extremely toxic arsenicoxide former use as a poison for vermin has been vastly reduced on account of concerns over its accumulation in the food chain. Arsenic enters the human body through ingestion, inhalation, or skin absorption. Significant route of As ingestion is drinking water. There may be some degree of skin absorption in contact of trivalent oxide, because of its rapid solubility. Most ingested and inhaled arsenic is well absorbed through the gastrointestinal tract and lungs into blood stream. It is distributed in large number of organs including the liver, lung, kidney and skin. About 70 % of the arsenic is excreted mainly through the urine. Most arsenic absorbed into the body is converted by liver to less toxic methylated arsenic then efficiently excreted in the urine (Saha, 1999, in Nagarnaik 2002). In the initial stage of chronic exposure of arsenic for more than five years, skin colour becomes black (melanosis), rough and tough (keratosis), eyes become red (conjunctivitis). Also in some cases there will be pain in inhaling (Bronchitis) and Vomiting and Diarrhea (Gastroenteritis). The manifestations of arsenicosis are clearer in the second stage with black and white spots on the skin (leukomelanosite), palms and soles are affected by hard nodules (Hyperkeratosis), swelling of legs, Peripheral Neuropathy and complications of kidney and liver. Finally it also turns to cancer in skin, lungs, kidneys, liver and other organs.

Guideline value for arsenic in drinking water

The first version of International standards for drinking water included arsenic in the category of toxic substances and established 200 ppb as the allowable concentration in drinking water (WHO, 1958). In updated standards of 1963, WHO lowered the allowable concentration to 50 ppb (WHO, 1963). The WHO continued its review work to lower the guideline value for arsenic in drinking water by establishing a guideline value (provisional) of 10 ppb in 1993 (WHO 1993). This provisional Guideline Value (GV) of 10 ppb has been adopted as the national standards for drinking water by a number of countries. However many developing countries have retained the previous WHO GV of 50 ppb as their national standards.

Table 1. Currently accepted national standards for arsenic in drinking water in some selected countries.

Testing for arsenic

Field methods

The most important characteristic of the field-testing method is that the testing can be carried out in field, where the sample is taken. In this method relatively very simple testing field-kits are used. Although the test resulting from field kits are not precise, field-testing is considered best option for Nepal, where there are only a few laboratories with competent personnel and equipments. When any metal arsenide reacts with strong acids, arsine gas is formed. Most arsenic test kits rely on the reduction of inorganic arsenic to arsine gas (AsH3) using zinc metal and hydrochloric acid. This gas is allowed to pass through the mercury bromide (HgBr2) indicator paper and the intensity of colour indicates the concentration of arsenic. Many field kits, including two Nepali kits are available in Nepal listed as follows;

- AAN Kit (Japan)
- E-Merck Kit (Germany)
- NIPSOM Kit (Bangladesh)
- AIIHPH Kit (India)
- ENPHO Kit (Nepal)
- Modified AAN Kit (Nepal)
- Hach EZ (USA)
- Wagtech Arsenator (UK)

Analytical Methods

Numerous methods are described in the literature, for the analysis of total arsenic in water but limited equipments are available in Nepal. Many analytical methods essentially employ the same principles, but apply different reagents or concentrations.

The possibilities for total arsenic determination include:

- 1. Atomic absorption spectrometry (AAS)
	- a. Hydride Generation System (AAS-HG)
	- b. Graphite furnace (AAS-GF) for atomization,
- 2. Inductively coupled plasma a. With atomic emission spectrometry (ICP-AES) b. With mass spectrometry (ICP-MS)
- 3. Atomic fluorescence spectrometry (AFS)
- 4. Anodic stripping voltammetry (ASV) or
- 5. Spectrophotometry.

Both atomic absorption spectrometry and atomic fluorescence spectrometry, a relatively new and sensitive technique, are single element specific techniques with known and controllable interferences. The inductively coupled plasma techniques offer the possibility of examining a number of contaminants, as they are multi-element techniques, again with known and controllable interferences. Anodic stripping voltammetry is a useful technique for samples containing only free dissolved arsenic, while the spectrophotometric method, which is also a single element technique, has the advantage of being relatively inexpensive in terms of equipment. The mostly used in Nepali laboratories, AAS-HG technique is based on the atomic absorption measurement of arsenic generated by thermal decomposition of arsenic $(3+)$ hydride. As $(3+)$ is reduced to arsine gas by reaction with sodium tetrahydroborate in a hydrochloric acid medium (ISO 11969:1996; SM 3114:1999). Arsenate and Arsenite have different sensitivities using this technique so any arsenate must be reduced to trivalent arsenic prior to the determination and done by using a solution of hydrochloric acid, potassium iodide and ascorbic acid.

In Nepal the silver diethyldithiocarbamate spectrometric method (SDDC) and spectrophotometry have been also used as alternate to AAS-HG. The key points of each of the above techniques are summarized below in Table 2.

Method	Detection limit (ppb)	Sample size (ml)	Equipment cost (USS in (000)	Daily Throughput	Remarks	Selected References
AAS-HG	0.05	50	20-100	30-60	Single element	ISO 11969 (1996) : SM 3114 (1999)
$AAS-GF$	$1 - 5$	$1 - 2$	40-100	50-100	Single element	ISO/CD 15586 (2000); SM3113 (1999)
ICP-AES	35-50	$10 - 20$	60-100	50-100	Multi element	ISO/CD 11885 (1996); SM3120 (1999)
ICP-MS	$0.02 - 1$	$10 - 20$	150-400	20-100	Multi element	SM 3125 (1999)
HGAFS	0.01	40-50	$20 - 25$	30-60	Single element Only free	CEN/TC/230/WG1 /TG, 12 N 3 (1999)
ASV	0.1	25-50	10-20	25-50	dissolved	USEPA 7063
SDDC	$1 - 10$	100	$2 - 10$	$20 - 30$	arsenic Limited to water samples	SM 3500 (1999) ISO 6595 (1982)

Table 2. Summary of analytical methods for Arsenic test

Global situation of arsenic in groundwater

Active groundwater contributes about 0.274 percent of total water budget and is the major source as fresh water for drinking water proposes. Arsenic contamination in groundwater has been reported in 20 different countries of the world. Four major calamities in order of magnitude are in Asia and these are Bangladesh, India (West-Bengal), China (including Inner Mongolia) and Taiwan. In terms of population exposed, arsenic problems in ground water from the alluvial deltaic aquifers of Bangladesh and West Bengal represent the most serious occurrences identified globally. The southwest coastal zone of Taiwan was perhaps the first area to be identified as a problem area for health effects arising from chronic arsenic exposure. Awareness of the arsenic problem began during the 1960s (Smedly *et al*., 2003) and arsenic–related health problems were documented. Well-known black-foot dieses in Taiwan had been identified science then. The Chaco-Pampeon Plain of central Argentina perhaps is the largest region of high-arsenic groundwaters known, covering around one million km2.

S.No.	Country/Region	Population exposed	Area	Max Conc. Range (ppb)
		(Million)	(Km ²)	
	Bangladesh	30	150000	2500
2	India/W.Bengal	6	23000	3200
3	China	5.6	NА	NА
4	Argentina	2	1000000	5300 (7800 in some porewaters)
5	Nepal	$0.46 - 0.75$	30000	600 (2620 in one case)
6	Chile (North)	0.5	125000	1000
	Mexico	0.4	32000	620
8	USA (South West)	0.35	206300	2600
9	Taiwan	0.1	4000	
10	Mongolia (Huhhot Basin)	0.1	4300	2400

Table 3. Naturally-occurring As problems in world groundwaters: (In Smedley et al., 2003 except Nepal)

Arsenic in nepal

Safe drinking water is still an important issue in Nepal. Until 1970s most rural people of Terai region of Nepal obtained and consumed water from dug-wells, rivers, canals or ponds. These contaminated waters were consumed directly without any treatment. Epidemics of cholera, diarrhoea, typhoid and other water-borne diseases were very common in this region. Thousands of people particularly the infants died only because of drinking these unsafe waters. From 1980s an idea of tapping ground water came as the most popular program for controlling many waterborne dieses by providing clean and pathogen free drinking water. Agencies and individuals installed a considerable number of shallow tube wells. Although emerging number of tube wells succeeded in reducing the number of death from waterborne dieses but unfortunately it is now established that many of tube wells water contain As at concentration higher than the safe limit for drinking purpose.

When an unexpected issue came to be known as arsenic contamination in groundwater of Bengal Delta Plain (BDP) in neighboring Indian State of West Bengal and Bangladesh, the Department of Water Supply and Sewerage (DWSS), with assistance from WHO, Nepal, conducted for the first time a systematic research study on possible As contamination in groundwater of Jhapa, Morang and Sunsari districts of the Eastern Terai of Nepal bordering to Indian State of West Bengal in 1999. The result of the study showed that out of 268 water samples tested for arsenic, 24 samples exceeded WHO Guideline Value (10 ppb) with even 2 of them showing a concentration level higher than 50 ppb that is the interim national drinking water standard for arsenic in Nepal and national standard for arsenic in India and Bangladesh (Sharma, 1999).

S.No.	District	Total no. of tests	Samples with Arsenic Concentrations			Max. conc ⁿ .	
			$<$ 10 ppb	10 ppb to 50 ppb	> 50 ppb	detected.	
1	Jhapa	571	493	77	1	79	
2	Morang	341	264	72	5	70	
3	Sunsari	675	566	105	4	75	
4	Saptari	772	669	94	9	98	
5	Siraha	289	191	70	28	90	
6	Dhanusha	331	267	55	9	140	
7	Mahottari	202	177	21	4	80	
8	Sarlahi	532	402	114	16	98	
9	Rautahat	2485	740	1520	225	324	
10	Bara	2124	1783	291	50	254	
11	Parsa	2207	1895	253	59	456	
12	Chitwan	219	219	$\overline{0}$	0	8	
13	Nawalparasi	3833	1385	1340	1108	571	
14	Rupandehi	2725	2191	410	124	2620	
15	Kapilbastu	4099	3471	466	162	589	
16	Dang	667	639	25	3	81	
17	Banke	1835	1316	486	33	270	
18	Bardiya	652	472	160	20	181	
19	Kailali	299	149	106	44	213	
20	Kanchanpur		167	21	12	221	
	Total Samples Tested	25058	17456	5686	1966	2620	
Percentage of Total Tested		100%	69%	23%	8%		

Table 4. Summary of known As concentration in Nepal (Source NASC, July 2003)

The exact number of tube wells in Nepal is still unknown. But a very rough estimation shows that there are more than 400,000 tube wells. The actual scenario of the arsenic contamination in Nepal will not be reflected unless most of all tube wells are tested for arsenic. So far only 25058 tube wells have been tested and the Department of Water Supply and Sewerage/UNICEF had plan of testing about 200,000 tube wells in the most effected ten *Terai* districts. The summary of known arsenic concentration (district-wise) is presented in the table 3 and bar chart (Fig. 1) and concentration in Nepal is shown by Pi-Chart (Fig. 2). In the table it is shown that out of total 25,058 tube wells, 1,916 tube wells, that is about 8% of total tested tube wells have arsenic concentration more than 50 ppb; and 5,686 tube wells (23%) are contaminated with concentration more than 10 ppb, that is the WHO guideline value. The first manifestation shows that Nawalparasi is the most affected district in Nepal. Rautahat, Kailali, and Siraha are other seriously affected districts.

In Nawalparasi, the most affected district, there are about 31,875 tube wells (WSSDO, Nawalparasi 2003) and total 3,833 tube wells have been tested so far. The district comprises 72 village development committees (VDCs) and one municipality. Among those 72 VDCs, 19 VDCs are such that they do not have any tube wells. Ramgram Municipality and Panchnagar VDC have been identified as the most As-affected (about 63% of tube wells have

As concentration more than 50 ppb) when all tube wells in 10 VDCs and one municipality have been tested. The summary of the test result from Ramgram Municipality and other most affected VDCs having As concentration more than 50 ppb in at least 20 % tube wells is presented in table 5.

VDC/	Total tests	Conc. _{10ppb}		Conc. 10-50ppb		$Conc. > 50$ ppb	
Municipality		Numbers	%	Numbers	$\frac{9}{6}$	Number	0/6
Ramgram	729	98	13.4%	270	37.0%	459	63.0%
Panchnagar	70	6	8.6%	26	37.1%	44	62.9%
Manari	139	17	12.2%	64	46.0%	75	54.0%
Tilakpur	164	49	29.9%	105	64.0%	59	36.0%
Ramnagar	213	42	19.7%	155	72.8%	58	27.2%
Swathi	322	97	30.1%	248	77.0%	74	23.0%

Table 5. Summary of As concentration in the six most affected VDCs/ Municipality of Nawalparasi District.

Exposed population & health effect of arsenic in nepal

According to the population census data 2001, the total population of Nepal is 23.4 million. Out of this about 10.4 million people (45% of total) live in 20 Terai-districts of Nepal, where about 8 % of total tube wells were found contaminated, in average. Since ninety percent of the Terai population (9.4 million) is supposed to use tube wells for their drinking and others purpose, eight percent of its population is estimated as the exposed population. If the estimation is made according to individual district-population and its exposed-population, this total exposed-population lowers to 0.46 million. In case of the affected area one can estimate the total Terai area, which is 30000 km2, as the arsenic-affected area. So far total four studies about prevalence of arsenicosis were done in Nepal. Two studies were done in the most effected district, Nawalparasi by Department of Water Supply and Sewerage (DWSS) and Nepal Red-Cross Society (NRCS) and remaining two in Parsa and Bara districts by NRCS. From the studies it is estimated that about 2.6 % of the total population, exposed to arsenic contaminated water with a concentration more than 50 ppb, have a prevalence of arsenicosis. The summary of the study is given in table 5.

Study conducted		District	Population	Prevalence of Arsenicosis		
Вy	In		Surveyed	Nos	%	
DWSS/ UNICEF	2002	Nawalparasi	961	49	5.1	
NRCS	2001	Nawalparasi	855	27	3.2	
NRCS	2001	Parsa	2732	50	1.8	
NRCS	2002	Bara	667	9	1.3	
Total		5215	135	2.6		

Table 5. Prevalence of Arsenicosis (Dermatosis) in Nepal

Conclusion and recommendations

- Blanket testing is the first and most essential step to deal with the arsenic problems. The number of 25,000 as tested tube wells is very low out of total estimated tube wells of 400,000 tube wells in Nepal.
- According to health survey conducted so far, a very rough estimation of about 20,000 Nepalese people may have arsenicosis. Further health survey should be conducted with the initiation from the Ministry of Health in all hotspot areas and a separate recording system should be developed in all health institutions for identification, treatment and monitoring of *Arsenicosis* patients.
- Regarding the pattern of the arsenic contaminated tube wells in Nepal, switching of the contaminated tube well is the best option for mitigation measures. Three-*gagree* and Biosand Filter (BSF) can be used as the As removal technology at household level.
- Many options for mitigation developed in other countries may not fit in Nepalese context. Research on removal options should be carried out in local environment.
- It is necessary to seal the highly contaminated tube wells to protect the noncontaminated aquifers.
- A tube well designated, as safe upon one time testing in an affected area cannot be presumed permanently safe. Hence, to determine the cause of changing arsenic concentration with respect to time it needs further investigation in hydrogeology, geochemistry, and geohydrodynamics of the groundwater of the hotspot areas.
- Every field kits should be checked for their performances. For this purpose establishment of a reference laboratory is urgent.
- Every new tube well should be constructed only after the test for arsenic.

REFERENCES

- 1. CEN/TC/230/WG1/TG 12 N 3:1999, Water quality Determination of arsenic in drinking, surface, ground, saline and industrial and domestic waste waters.
- 2. ISO 11885, 1996, Water quality Determination of 33 elements by inductively coupled plasma atomic emission spectrometry
- 3. ISO 11969, 1996, Water quality Determination of arsenic Atom absorption spectrometric method (hydride technique)
- 4. ISO 6595:1982, Water quality Determination of total arsenic silver diethyldithiocarbamate spectrophotometric method
- 5. ISO/CD 15586, 2000, Water quality Determination of trace elements by atomic absorption spectrometry with graphite furnace
- 6. Nagarnaik P. B. , Bhole A.G. and Natarajan G.S. (2002), " Arseni removal of ground water – a state of art", Water Resources Journal, December 2002, pp 51-66.
- 7. NASC July 2003, Updated data from National Arsenic Steering committee, DWSS, Nepal
- 8. P. Bhattacharya, N. tandukar, A. Neku, A.A. Valero, A.B. Mukherjee and G. Jacks (2003) "Geogenic arsenic in groundwaters from Terai Alluvial Plain of Nepal"- Journal Phys. IV France 107. pp 173-176.
- 9. Saha J.C., Dixit A.K., Bandyopadhyay M., Saha K.C. (1999), " A review of arsenic poisoning and its effects on human health", Critical reviews in Environmental Science and Technology, Vol. 29, No3, pp. 281-313.
- 10. Sharma, R.M. (1999). Research study on possible contamination of groundwater with Arsenic in Jhapa, Morang, and Sunsari districts of Eastern Terai of Nepal. Report of the WHO Project, DWSS, Govt of Nepal.
- 11. SM 3113:1999, Standard Methods for the Examination of Water and Wastewater. Metals by electrothermal atomic absorption spectrometry.
- 12. SM 3114:1999, Standard Methods for the Examination of Water and Wastewater.Arsenic and selenium by hydride generation/atomic absorption spectrometry.
- 13. SM 3120:1999, Standard Methods for the Examination of Water and Wastewater. Metals by plasma emission spectrometry.
- 14. SM 3125:1999, Standard Methods for the Examination of Water and Wastewater. Metals by inductively coupled plasma/mass spectrometry.
- 15. M 3500-As B, 1999, Standard Methods for the Examination of Water and Wastewater, Silver Diethyldithiocarbamate method.
- 16. Smedley P.L. and David G K. 2003, Source and behaviour of arsenic in natural waters, chapter 1, Arsenic report, WHO.
- 17. USEPA 7063:1996, Arsenic in aqueous samples and extracts by anodic stripping voltammetry (AVS), method 7063. U.S. Environmental Protection Agency.
- 18. WHO, 1958. International Standards for Drinking-water
- 19. WHO, 1963. International Standards for Drinking-water, Second edition, vol. 3
- 20. WHO, 1993. Guidelines for drinking-water quality, second edition, vol. 1.
- 21. WSSDO Nawalparasi, 2003, "Tube wells Data collection report, Nawalparasi 2003".