

International Journal of Applied Sciences and Biotechnology

A Rapid Publishing Journal

ISSN 2091-2609



Available online at:

<http://www.ijasbt.org>

&

<http://www.nepjol.info/index.php/IJASBT/index>

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Research Article

SEASONAL VARIATION OF ARSENIC CONCENTRATION IN GROUND WATER
OF NAWALPARASI DISTRICT OF NEPAL

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Abstract

Ground water of southern part of Nepal, also known as Terai region where population density is relatively very high, has been contaminated with poisonous element arsenic (As). This study has been carried out to determine the variability of the level of arsenic contamination in groundwater with seasons at Pathkhauli village of Devgaun VDC and Mahuwa village of Manari VDC in Nawalparasi district, the western Terai district. Hydride Generation Atomic Absorption Spectrophotometer (HG-AAS) and UV-visible Spectrophotometer were used for analysis. Total 55 groundwater samples in post-monsoon season and 45 groundwater samples in pre-monsoon season were collected. The level of arsenic contamination in groundwater was found above the Nepal interim standard of 50 ppb. Of the total 42 water samples from each pre- and post- monsoon seasons analyzed, 28 water samples (66.67%) showed higher As-concentration in pre-monsoon season.

Keywords: arsenic; arsenic contamination; groundwater; seasonal variation; HG-AAS; UV-VIS spectroscopy

Introduction

Arsenic (As), a naturally occurring element with atomic number 33 and metalloid properties, is hazardous to both the human health and ecosystem. International Agency for Research on Cancer (IARC) had identified it as one element causing cancer. It often presents in environmental samples (for eg. soil, sediment, water, aerosol, rain, aquatics, vegetation, milk, etc) (Craig 1986; Abernathy *et al.*, 1997; WHO, 1999). In nature, as a heavy metal, it exists in the form of both organic and inorganic compounds in four oxidation states: -III (arsine), 0 (arsenic), +III (arsenite) and +V (arsenate) (Ng *et al.*, 2005; Thakur *et al.*, 2011). Compared with arsenic in the form of As (+V), As (+III) is reported to be more mobile and more toxic (about ten times) (Panthi *et al.*, 2006). Due to being readily soluble in water at pH 8 and above, it enters the human and animals mainly by consumption of contaminated water and also food.

Arsenic mobilization in the water residing in aquifers may have been caused by over withdrawal of groundwater during cultivation. Generally, arsenic is available in much higher concentration in groundwater compared to surface water. The widespread use of arsenic contaminated groundwater in irrigation for a prolong period of time could elevate its concentrations in surface soil and eventually into vegetations for example, rice plants and rice grains (Rahman *et al.*, 2007).

World Health Organization (WHO) has set 0.01 milligram per liter (10 parts per billion) as the limit for the safety of water for drinking purposes. Nepal, including India and Bangladesh, has adopted the limit of 50 ppb. Lack of expertise and knowledge of the implementation, economic consideration and technical ability to measure arsenic concentration below 50 ppb in the field are main reasons behind the national standard. The lowest standard currently set for acceptable arsenic concentration in drinking water is implemented by Australia, which has a national standard of 7 ppb (Thakur *et al.*, 2011). The drinking water standard for arsenic is likely to be lowered in the coming year(s) because of threat to human health. The major issue of arsenic contaminated water (and also food grains) 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.

World's highest concentration of arsenic is presently observed to be located in Bangladesh and West Bengal State of India. It is reported that about 46 million people of Bangladesh are believed to be victims of this problem among which 0.2 to 0.27 million people may die due to the same reason. Similarly 4 million people in India are also suffering from the same problem (Chakrabarti *et al.*, 2000). It has also been a measure problem in Terain region of Nepal.

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). 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). Available documents indicate that Nepal's 24 districts, including all 20 Terai districts and four hill districts have shown arsenic contamination (FAO, 2004). Among the 29,953 tube wells tested, 32 % have arsenic level above the WHO standards (10 ppb) and 7 % have arsenic level above Nepal Interim Standard (50 ppb). Note that in Terai region projected tubewells to be around 737000 (Thakur *et al.*, 2011)). That is the tested tubewells cover only less than four percent. This situation is highly alarming also because earlier international studies have shown that even with the threshold level of 10 ppb, 4 people out of 10,000 have chances of getting cancer (Adamsen *et al.*, 2002). The later study was based on a mathematical model for risk analysis and predicted that 20-40 thousands cancer incidents per year in the near future because of arsenic contamination. The studies (Panthi *et al.*, 2006; Maharjan *et al.*, 2006; Thakur *et al.*, 2011) reveal that arsenic contamination was found to be higher in districts of Terai namely Nawalparasi, Bara, Parsa, Rautahat, Rupandehi, and Kapilavastu. In these districts, arsenic contamination in tubewells varied from 2.1% in Rupandehi district to 25.7% in Nawalparasi district (Maharjan, *et al.*, 2006). Moreover, the later study also showed that the occurrence of arsenicosis was, on average, 2.2% and varied from 0.7% in Kapilavastu district to 3.6% in Nawalparasi district. The highest prevalence (18.6%) of arsenicosis was reported in Patkhouli village of Nawalparasi, where 95.8% of tube wells were contaminated with arsenic (Maharjan, *et al.*, 2006). The contamination caused the common symptoms of arsenicosis of skin manifestations, such as melanosis and keratosis. Most patients were identified in the early or mild stage of the disease and it was recommended that they are expected to recover if further exposure to arsenic could be avoided by providing arsenic-safe drinking-water through intervention measures. Also, the highest arsenic concentration, above 50 ppb, was reported at Nawalparasi district and minimum arsenic concentration was reported at Palpa, Ilam and Chitwan districts (Thakur *et al.*, 2011). Therefore, there is a need to understand and systematically explore the extent of arsenic threat in light of policies and strategies adopted by Nepal Government (NG).

As mentioned above, in Nawalparasi district, among all the communities, Pathkauli village of Devgaun VDC and also Mahuwa village of Manari VDC contain the maximum concentration of arsenic, in particular. For this reason, investigation of variation of As as a function of seasons would help people to take precaution and tackle the problem with appropriate technology. Therefore, we have selected these two villages for our study.

In this article, variation of arsenic concentration in the water sample from ground water (tube wells) in pre- and post-monsoon season has been presented.

Rationale of the Study

Access to quality water, grain and vegetable supply is one of the fundamental requirements for sustaining human life. Without safe, good quality water, people are susceptible to various water related diseases. Therefore, the concern of the government and the people has to be not only the accessibility of adequate water supplies, but also the availability of good quality water supplies. The impact of contamination of water with this heavy metal has not been assessed extensive manner yet. Previous studies clearly indicated that the Terai region as a whole has been in deteriorating condition due to arsenic contamination and also, more importantly, there have been report of As contamination in food grain in Bangladesh and West Bengal. There is no any scientific investigation in this issue in case of Nepal, however. In this regard, prediction of actual concentration of arsenic (As) dissolved in water and food grains 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 plan accordingly for providing pure water.

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. It is bordered by Chitwan and Tanahu districts in the east; Rupandehi and Palpa in the west; Palpa and Tanahu in the north; and the 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° 21' and 27° 47' latitudes, and 83° 36' and 84° 25' longitudes (New ERA, 2000).

Devgaun and Manari are two of the village development committees (VDC) of Nawalparasi. Of many villages, Pathkauli village of Devagaun VDC and Mahuwa village of Manari VDC were selected for the project site. The sampling of ground water (taken from hand pumps, 40-100 feet deep) was conducted two times, at pre- and post-monsoon seasons. Post monsoon sampling was conducted from 1st to 3rd October 2012, while sampling on pre-monsoon was carried out from 5th to 8th April, 2013. A total of 55 water samples (post monsoon season) and 45 water samples (pre monsoon season) were collected for analysis.

Analysis Techniques

Analysis was performed by three different techniques: For qualitative analysis, a HACK As-test kit was used and for

quantitative analysis, Hydride Generation Atomic Absorption Spectrophotometer (GENESYS 10uv, Thermo Electron Corporation) and UV-Visible spectrophotometer (uv-1700 pharmspec, uv-spectrophotometer SHIMADZU) were used. For measurement with later technique with a higher accuracy, Molybdenum Blue method was used.



Fig. 1: Google Map of Nawalparasi district

Presence of arsenic (As) in the tube well water was confirmed by HACK 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 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. 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 are formed by the reaction of HCl and zinc granules. This stain is then compared against a colour coded chart indicating the As concentration in ppb from zero to 500 ppb (Nepal, G.D.,2011).

After confirmation of presence of As of a particular tube well by testing with As - test kit, 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, water samples were collected without preservatives for the analysis of *Physio-Chemical parameters*: pH, conductivity and total dissolved solids (TDS) and kept in ice box. The pH, conductivity and TDS were measured in our lab using the pH meter, conductivity meter and TDS meter. The instruments were calibrated before measurements.

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.

Results and Discussion

Variation of Arsenic concentration in water samples at pre- and post- monsoon seasons

Total of 55 water samples from the hand-pumps of Mahuwa and Pathkouli villages of Nawalparasi district were collected for analysis in post-monsoon season. While, in pre-monsoon only 42 samples were collected from the same tubewells from where samples in post-monsoon were taken. The analysis of the samples were performed by HG-AAS. Fig. (2) shows the comparison of arsenic concentration, measured with HG-AAS technique, in pre- and post-monsoon season. The results were further confirmed by UV-Vis spectroscopy as well (discussed in the next paragraph). Data represented by open squares and solid diamond represent As concentration in pre- and post-monsoon seasons, respectively. The mean temperature of the samples was $24.8^\circ C$, the TDS was $304.42 mg/l$, the conductivity was $547.67 \mu s/cm$ and pH was 7.33. All the samples showed the level of arsenic concentration above 0.05ppm, ranging from 0.1 ppm to 1.8 ppm, but only one sample was with 0.009 ppm. The average value of the As concentration of all the data analyzed in pre- and post-monsoon were, respectively, 0.73 ppm and 0.59 ppm. More importantly, As demonstrated in the Fig. 2, among 42 samples from each season, 28 water samples (66.67%) showed higher As concentration in pre-monsoon season than that of post-monsoon. Fourteen samples showed lower concentration than in post- monsoon season. It is, most likely, because of lowering of water table in pre-monsoon than that in post-monsoon season (lowering of water table may cause to increment of As concentration). On the other hand, as sampling in the post monsoon season was carried out immediately after the summer, maximum level of dilution of the underground water can be expected.

For checking the reproducibility of our analysis, we also carried out the measurement of As with UV-Visible spectroscopy. For this technique, molybdenum blue method was adopted for As analysis (Mendham *et al.*, 2002). Briefly, In molybdenum blue method, an acidified solution of $As (+III)$ was oxidized to $As (+V)$ with the help of potassium permanganate. Thus formed $As (+V)$ was treated with ammonium molybdate which gives colorless molybdoarsenic heteropoly acid. After its reduction with hydrazine hydrate, blue colored complex was formed. The intensity of the color is directly proportional to the concentration of arsenic and its absorbance was measured by UV-Visible spectrophotometer at 840 nm, which is λ_{max} for the arsenomolybdenum blue complex (Shrestha, 2010).

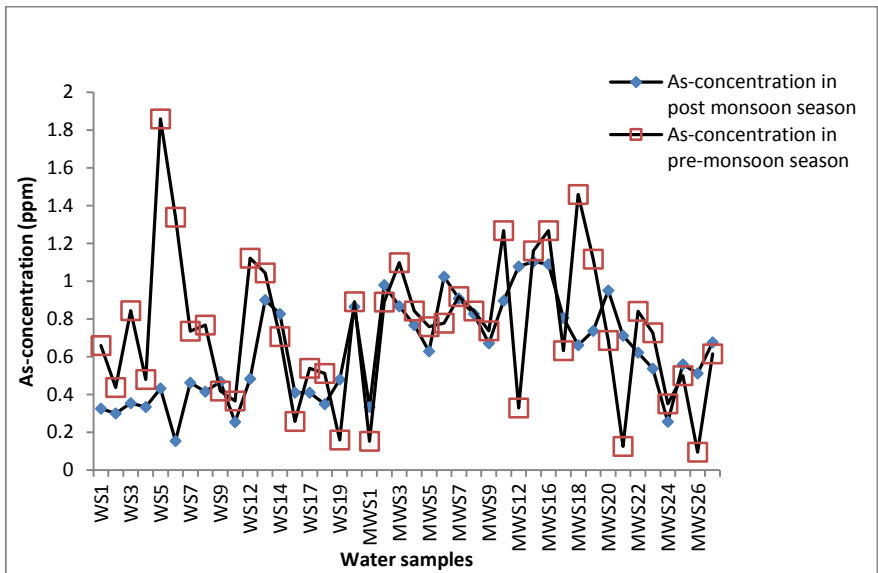


Fig . 2. Seasonal variation of As concentration measured by HG-AAS. Data represented by open squares and solid diamonds represent As concentration in pre-and post-monsoon seasons, respectively.

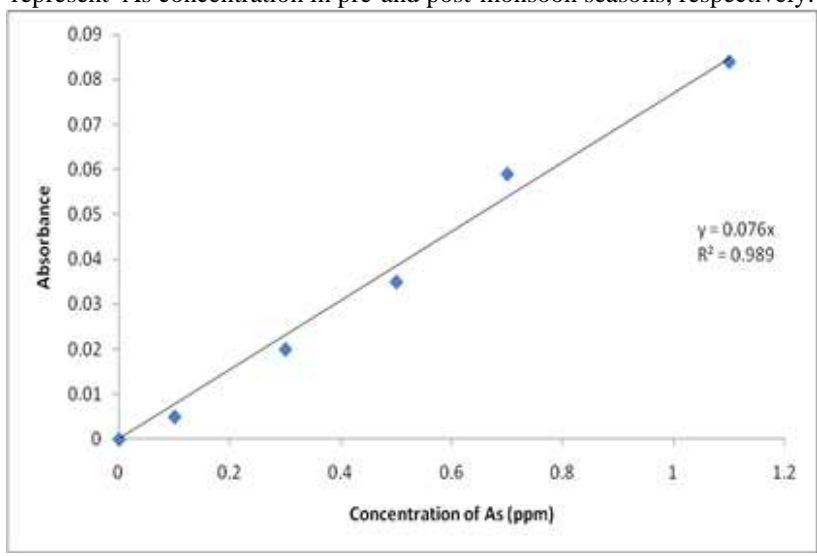


Fig. 3: Calibration curve for arsenic analysis by UV-Visible spectrophotometric technique

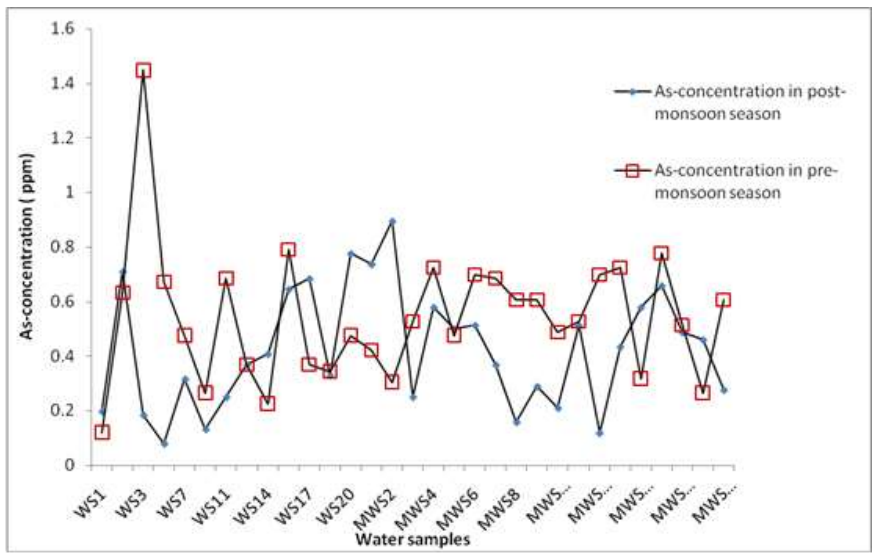


Fig. 4: Seasonal variation of arsenic concentration measured by UV-Visible spectrophotometry. Data represented by open squares and solid diamonds represent As concentration in pre-and post-monsoon seasons, respectively..

Calibration curve was constructed at λ_{\max} by varying the concentrations of the arsenic standards. As shown in the (Fig. 3), obtained calibration curve is linear and obeyed Beer–Lambert’s law. For highly concentrated samples (samples which show out of range of calibration curve), dilution of the samples were performed. With the help of (Fig. 3), we have evaluated the concentration of As of all the samples and reported in the (Fig. 4).

Fig. 4 also shows the comparison of arsenic concentration in pre- and post- monsoon seasons measured with UV-Visible spectrophotometer (same samples presented in Fig. 2). Around 64.5 % of the total samples showed higher value in pre-monsoon than post-monsoon, demonstrating an excellent agreement with the analysis with HG-AAS technique. In particular, among 31 samples analyzed, 20 samples taken in pre- monsoon showed higher concentration than that in post-monsoon. One sample showed equal concentration and ten samples showed lower concentration than that of samples taken in post- monsoon season.

Conclusion

On the basis of the present study, Pathkauli village of Devgaun VDC and Mahuwa village of Manari VDC of Nawalparasi District were found to be highly affected by arsenic contamination in groundwater. In agreement with previous studies, we also have found that the level of arsenic contamination in groundwater is well above than the WHO guideline (ca.70 times higher in average). More importantly, this study shows that the arsenic concentration in groundwater varies seasonally, significantly. The arsenic concentration in most of groundwater samples was found high in pre-monsoon season than that in the post-monsoon season.

Besides, from our recent investigation in the same location, it was also found that soil and rice grains samples were also severely contaminated.

Acknowledgement

This research project was supported by University Grant Commission (UGC), Nepal. The authors are thankful to the Aquatic Ecology Centre (AEC) at Kathmandu University in Dhulikhel, for providing research facilities. The authors also would like to thank Dr. Prem Chapagain of Florida Int. Univ., USA for his valuable suggestions and discussions.

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