



# "ADVANCED PERSPECTIVES ON TEMPORAL AND SEASONAL VARIATIONS OF ARSENIC IN GROUNDWATER: INTEGRATING HYDROCHEMICAL ANALYSIS FOR SUSTAINABLE POLLUTION MITIGATION"

<sup>1</sup>Dr. Akbare Azam

<sup>2</sup>Dr. Awanish Kumar Pandey

<sup>3</sup>Manisha

<sup>4</sup>Hemant Kumar Nirala

<sup>5</sup>Najam Ul Rafi

<sup>6</sup>Sankatha Prasad Sonkar

<sup>1</sup> Assistant Professor, Department of Chemistry,

<sup>2</sup> Assistant Professor Department of Chemistry,

<sup>3</sup> Assistant Professor, Department of Home Science,

<sup>4</sup> Assistant Professor, Department of Chemistry

<sup>5</sup> Assistant Professor, Department of Chemistry

<sup>6</sup> Assistant Professor, Department of Chemistry

<sup>1</sup> Govt. Girls' P. G. College Ghazipur U. P. India

## Abstract

Arsenic contamination in groundwater poses a significant threat to human health and ecosystems globally. Arsenic, a naturally occurring element, exhibits spatial and temporal dynamics influenced by geological, hydrological, and anthropogenic factors. Understanding these variations is crucial for developing effective mitigation strategies.

In this paper we are going to discuss hydrochemistry of Arsenic and process of contamination in groundwater of Ganga Brahmaputra river basin of India. Arsenic mostly exists in two types of oxidation states which are arsenate ( $As^{5+}$ ) and arsenite ( $As^{3+}$ ). These two oxidation states are interconvertible by oxidation of  $As^{3+}$  into  $As^{5+}$  and reduction of  $As^{5+}$  into  $As^{3+}$ . Arsenic also exists in another form, i.e., organic form and it is formed by biomethylation of Arsenic. It was reported a clear temporal and seasonal variability of As concentrations in different water samples of Ballia & Ghazipur districts of eastern U. P. During post monsoon season As concentration decreases in Samples. A definite relationship exists between the behavior of arsenic and rainfall intensity. With increasing rainfall intensity rate of dilution increases which minimizes the arsenic concentration in the groundwater. During monsoon period there is considerable decrease in the arsenic concentration. Groundwater stream design is influenced by water level surface and subsurface redox potential because of seasonal rainfall. During monsoon seasons groundwater level is increased due to its low-land shallow basin and flooding condition also help in rising its groundwater level. For an extensive stretch of the year, the land remains water-logged and this prompts low groundwater flushing rates. The review then delves into advanced hydrochemical analysis techniques, including isotopic tracing, speciation studies, and high-resolution monitoring approaches.

**Keywords:** *Hydrochemistry of Arsenic, Temporal and seasonal variability, pre and post monsoon, Arsenic acid, Ganga Brahmaputra river.*

## INTRODUCTION

Arsenic is a naturally occurring element found in the Earth's crust and ranks as the 20th most abundant element. Its presence in soil and groundwater is widespread and results from various sources, including industrial activities and natural processes such as rock weathering, volcanic eruptions, and the transportation of particles through water or air. Once introduced into the atmosphere, arsenic circulates throughout the entire ecosystem [1].

In groundwater, arsenic primarily exists in two oxidation states: arsenate ( $\text{As}^{5+}$ ) and arsenite ( $\text{As}^{3+}$ ). These states are interconvertible through the oxidation of  $\text{As}^{3+}$  into  $\text{As}^{5+}$  and the reduction of  $\text{As}^{5+}$  into  $\text{As}^{3+}$ . Arsenic also takes on an organic form through biomethylation, a process in which living organisms such as plants, aquatic animals like fish and crabs, and the human body contain organoarsenic compounds. Microorganisms, such as bacteria or fungi lacking chlorophyll, undergo a biological conversion of inorganic arsenic into organic arsenic through a process known as biomethylation [2,3].

High concentrations of arsenic are found in sulphide ores and metal oxides like iron oxide. Previous studies indicated that arsenic-contaminated groundwater was primarily confined to the Ganga basin, originating from sulphide-rich mineralized areas in Bihar and surrounding basins. However, recent findings reveal elevated arsenic concentrations extending from the Indo-Gangetic alluvium to the west and Brahmaputra alluvium. During the deposition of Holocene segment sediments, hydroxides precipitate, and arsenic released from the weathering of sulphide minerals is adsorbed. Subsequently, through redox processes, iron oxides dissolve, releasing arsenic into aquifers via biogeochemical processes. In the late Quaternary and Holocene age sediments deposited in rivers, arsenic is carried in the aqueous phase within the Ganga-Brahmaputra river basin. Currently, most arsenic-contaminated water results from the mobilization of arsenic through various biogeochemical processes [4,5,6,7,8].

## TEMPORAL AND SEASONAL VARIABILITY OF ARSENIC IN GROUNDWATER

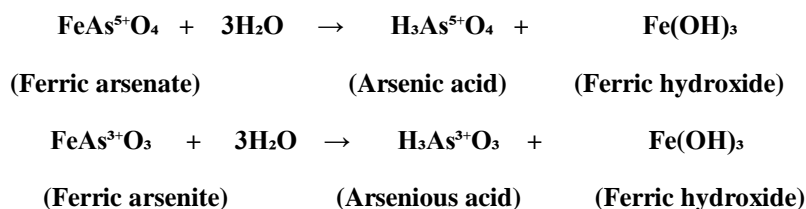
A pronounced temporal and seasonal variation in arsenic (As) concentrations across diverse samples has been documented. Specifically, during the post-monsoon season, there is a notable decrease in arsenic concentration in the samples. This observed variability in arsenic concentrations is likely linked to the seasonal fluctuations in groundwater recharge and the influences of irrigation drawdown, as noted by MacArthur et al. The disparity in arsenic concentration between pre and post-monsoon seasons is directly correlated to its concentration levels. A discernible association exists between arsenic behavior and rainfall intensity. As rainfall intensity increases, there is a corresponding rise in the rate of dilution, leading to a reduction in arsenic concentration in groundwater, as highlighted by Farooq et al. (2010). The monsoon period particularly witnesses a significant decrease in arsenic concentration. Consequently, a robust correlation is evident between rainfall conditions, dilution effects, and arsenic concentration. In contrast, the winter season and pre-monsoon periods exhibit an increase in arsenic concentration, attributed to a reduction in the dilution effect [9,10,11].

The Oxidation of Arsenic-Rich Sulfide Minerals is a common occurrence in geological deposits housing sulfide minerals with high arsenic content, including arsenopyrite ( $\text{FeAsS}$ ), realgar ( $\text{As}_4\text{S}_4$ ), and orpiment ( $\text{As}_2\text{S}_3$ ). These minerals exhibit stability at significant depths beneath the Earth's surface, shielded from oxygen and water. However, exposure to atmospheric conditions through natural weathering or human activities like mining can trigger oxidation [12,13,14].

Upon contact with molecular oxygen ( $\text{O}_2$ ) from the atmosphere and water ( $\text{H}_2\text{O}$ ), arsenopyrite undergoes oxidative degradation. In this process, arsenic in its sulfide form transforms into highly water-soluble arsenate ( $\text{AsO}_4^{3-}$ ). This transformation is especially notable in bedrock aquifers experiencing a shift to oxidizing conditions during dry seasons, leading to a decrease in groundwater levels. The resulting  $\text{Fe}^{2+}$  is released into groundwater, and simultaneously, sulfur oxidation in sulfide minerals produces  $\text{SO}_4^{2-}$  ions. Both arsenate and sulfate ions, being soluble, have the potential to leach into surrounding soil, groundwater, and surface water.

Studies reveal that the primary source of these sulfide minerals in fluvial silt within the Ganga, Brahmaputra, and Meghna river systems is the metamorphic and granitic Himalayan parent rocks. Surprisingly, the low correlation between arsenic and bicarbonate ( $\text{HCO}_3^-$ ) suggests that competitive adsorption by bicarbonate may not be the primary mechanism for arsenic mobilization in the Ganga and Ghagra River basins. Fluvial geomorphology in Bihar may influence arsenic dispersal, with concentrations being highest near the Ganges River. The presence of reduced levels of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ions, along with their limited correlation with arsenic, indicates that redox processes significantly impact arsenic mobilization [15,16,17].

Scorolite [ $\text{FeAs}_4$ ,  $2\text{H}_2\text{O}$ ] and Arsenopyrite, originating from iron arsenite  $\text{FeAsO}_4$ , serve as significant sources of arsenic in groundwater. The oxidation states of arsenic ( $\text{As}^{3+}$  and  $\text{As}^{5+}$ ) coexist as ferric arsenite and ferric arsenate. Upon hydrolysis under conditions of low pH and high Eh, ferric arsenate transforms into arsenic acid ( $\text{H}_3\text{AsO}_4$ ) and ferric hydroxide, while ferric arsenite transforms into arsenious acid ( $\text{H}_3\text{AsO}_3$ ) and ferric hydroxide.



In an acidic environment,  $\text{Fe}(\text{OH})_3$  is soluble; however, as acidity decreases, it undergoes precipitation. Both  $\text{As}^{3+}$  and  $\text{As}^{5+}$  ions adsorb onto the surface of the precipitated  $\text{Fe}(\text{OH})_3$  colloidal particles. The differential solubility of  $\text{As}^{3+}$  and  $\text{As}^{5+}$  ions leads to greater solubility of  $\text{As}^{5+}$  compared to  $\text{As}^{3+}$  ions.

Therefore, the  $\text{As}^{3+}$  ion concentration in water surpasses that of  $\text{As}^{5+}$  ion. The pertinent chemical reactions are as follows:

1.  $\text{FeAs}^{3+}\text{O}^4 + (2\text{H}_2\text{O}+\text{O}) \rightarrow \text{HAsO}_4^{2-} + \text{Fe}(\text{OH})_3$
2.  $\text{FeAs}^{3+}\text{O}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{As}^{3+}\text{O}_3 + \text{Fe}(\text{OH})_3$

Under mild alkaline conditions,  $\text{FeAs}^{5+}\text{O}_4$  undergoes hydrolysis, leading to the formation of Arsenic acid ( $\text{H}_3\text{AsO}_4$ ) and Ferric hydroxide. In the biomethylation process, the initial sediment undergoes hydrolysis, yielding Arsenic acid ( $\text{H}_3\text{AsO}_4$ ), which is then reduced to arsenite ( $\text{As}^{3+}\text{O}(\text{OH})$ ) by bacteria. This biomethylation process contributes to an elevation in toxic arsenic concentrations. Bacteria further methylate arsenite into various soluble and highly toxic compounds, such as methyl Arsenic acid ( $\text{CH}_3\text{As}^{5+}\text{O}(\text{OH})_2$ ), dimethyl arsenic acid or cacodylic acid ( $(\text{CH}_3)_2\text{As}^{5+}\text{O}(\text{OH})$ ), and trimethyl arsine ( $(\text{CH}_3)_3\text{As}^{3+}$ ). During agricultural activities, groundwater containing arsenic is extracted and subsequently absorbed by plants, animals, and humans from the surface soil and water. Consequently, the concentration of arsenic rises in both soil and water.

### ARSENIC DISTRIBUTION IN BALLIA DISTRICT

The design of groundwater flow is scientifically influenced by the water level of both surface and subsurface regions, primarily dictated by seasonal rainfall patterns. In the context of the monsoon seasons in Ballia, the groundwater level experiences a notable rise owing to its low-lying shallow basin. The flooding conditions further contribute to the elevation of the groundwater level. Consequently, for a significant duration of the year, the land remains waterlogged, leading to low rates of groundwater flushing. This observed phenomenon results in variations in mean concentrations of arsenic during the monsoon season compared to the pre-monsoon season.

**Table 1.1 Distribution of Arsenic during Post monsoon& Pre monsoon in Blocks of Ballia district**

Blocks in Ballia district	As in ppb	
	Post monsoon	Pre monsoon
Belhari	542	731
Bansdeeh	545	690
Sikandarpur	129	180

During the investigation period, a noteworthy correlation between sedimentary rocks and water was observed, arising from the prolonged contact facilitated by the slow flow of water currents and conducive reducing conditions. This phenomenon contributed to elevated concentrations of arsenic (As) in groundwater. In the monsoon season, arsenic infiltrates the groundwater through the disintegration of Fe(III)-oxyhydroxides, while in the pre-monsoon period, arsenic adsorbs reversibly onto Fe(III)-oxyhydroxides. These dual processes exert control over arsenic concentrations in groundwater during the pre-monsoon and post-monsoon periods. Sampling sites in Ballia district, namely Belhari, Bansdeeh, and Sikandarpur, were selected for detailed analysis [18,19].

### ARSENIC DISTRIBUTION IN GHAZIPUR DISTRICT

Comparatively, arsenic concentrations were found to be lower in the groundwater of Ghazipur district as opposed to Ballia district [20]. The spatial distribution of Oxidation-Reduction Potential (ORP) in groundwater indicated predominantly lower values in most wells. Elemental concentration variations were predominantly influenced by clay content in both the marginal and central areas. The sediments exhibited a progressive increase in finer particles and trace elements towards the central region, attributed to decreasing grain size. The concentration of metals in sediments tended to escalate in fine-grained sediments. The region experiences prolonged waterlogging throughout much of the year, resulting in low groundwater flushing rates. Consequently, observed variations in mean arsenic concentrations during the monsoon season differed from those in the pre-monsoon season, as detailed in Table 1.2. Sampling sites in Ghazipur district included Bhavarkole, Reotipur, and Karanda blocks.

**Table 1.2 Distribution of Arsenic during Post monsoon& Pre monsoon in Blocks of Ghazipur district**

Blocks in Ghazipur district	As in ppb	
	Post monsoon	Pre monsoon
Bhavarkole	15	22
Reotipur	17	27
Karanda	45	52

In the Ganga–Meghna–Brahmaputra region, around 3000 communities exhibit arsenic concentrations surpassing 50 parts per million (ppm), posing a significant threat to the well-being of approximately 6 million individuals. Prolonged exposure to arsenic leads to severe health consequences, including skin lesions, premature hair depigmentation, accelerated aging, and the development of cancer.

It has been observed that in West Bengal, India, sedimentary soil comprises pyrite, magnetite, hematite, quartz, and calcite minerals, releasing arsenic through mineral dissolution mechanisms. Bihar's fluvial geomorphology may influence arsenic dissemination, resulting in lower levels of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  and a limited association with arsenic. Pre-Cenozoic metamorphics and Riverian alluvial deposits release arsenic into the groundwater of Jharkhand, a process further intensified in the presence of organic carbon [21,22].

Each sample shows variation in As concentrations due to seasonal variation. There is decrease in As concentration from pre monsoon to post monsoon season. The cause of variation is change in groundwater level during rainy season and also consumption of groundwater in irrigation process. Arsenic concentration fluctuation during pre and post monsoon seasons is correlated in terms of its concentration. A direct relationship exists between As concentration and average amount of rainfall in rainy season. As concentration decreases with increase in amount of rainfall as it increases rate of dilution of As in water. To address arsenic contamination in India's groundwater, active community involvement is crucial. Arsenic mobility and removal factors pose challenges, and various removal technologies are assessed for efficacy, affordability, and scalability. Non-governmental organizations employ sustainable techniques, including affordable household filters. Community water purifiers and arsenic removal plants have successfully reduced arsenic concentrations by up to 90%. Additionally, rainwater collection contributes to improving water quality. The significant health risks associated with arsenic exposure underscore the urgency of comprehensively addressing this issue. Strategies and interventions must be tailored to the unique challenges and geological conditions of each affected area [23,24,25].

The study recommends establishing a regular national monitoring system using GIS to identify arsenic hotspots. Collaborative efforts involving policymakers, researchers, and local communities are deemed essential to mitigate the adverse effects of arsenic contamination and ensure access to safe drinking water for affected populations.

#### FUTURE SCOPE

1. The complex task of selectively extracting arsenic (As) from aqueous solutions is influenced by various geochemical factors. In natural waters or wastewater, numerous common anions coexist, often at significantly elevated concentrations, creating a competitive environment for As adsorption processes. Consequently, finding effective techniques for separating arsenic remains a prominent area of research.
2. The focus of research efforts will be on developing targeted therapies to alleviate the toxic effects of arsenic, addressing both acute and chronic exposure. Nanotechnology is poised to play a pivotal role in crafting drug delivery systems that specifically target tissues affected by arsenic, thereby minimizing damage to healthy cells.
3. Additionally, advancements in personalized medicine may give rise to tailored treatment approaches based on individual susceptibility and genetic factors. The integration of artificial intelligence into diagnostic processes has the potential to enhance accuracy and efficiency in identifying cases of arsenic poisoning.

#### ACKNOWLEDGEMENT

The researchers wish to extend their appreciation to the World Health Organization (WHO) and the Bureau of Indian Standards (BIS) for furnishing crucial arsenic data obtained through analyses of polluted groundwater in various geographical areas. This joint initiative contributes significantly to our comprehension from both a geochemical and scientific standpoint, revealing insights into the distribution and concentrations of arsenic in diverse settings.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

## REFERENCES

1. Subramanian V. Sediment load of Indian rivers. *Curr Sci.* 1993, 64, 928–930p.
2. Acharyya SK, Lahiri S, Raymahashay BC, et al. Arsenic toxicity of groundwater in parts of the Bengal basin in India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea-level fluctuation. *Environ Geol.* 1993, 39, 1127–1137p.
3. Khan HR. Management of groundwater resources for irrigation in Bangladesh. FAO, Rome, 1994.
4. Milliman JD, Rutkowski C, Meybeck M. River discharge to the sea: a global river index (GLORI). NIOZ, Texel, the Netherlands, 1995.
5. Bhattacharya P, et al. Groundwater arsenic in the Holocene alluvial aquifers of Bengal Delta Plains: petrological, geochemical and isotope geochemical studies. In *Proceedings of International Conference on Arsenic in Bangladesh Groundwater: World's Greatest Arsenic Calamity* (ed. Allauddin, M.), Wagner College, New York, 1999.
6. Azam A. Groundwater Pollution by arsenic, Status of upcoming trends in biodiversity conservation, 1, Dr. Rachna Chauhan, Educational book service New Delhi 978- 93-86541-78-9; 2019.
7. Azam A, Dr Sharma BK. Contamination of groundwater by arsenic in Ballia and Ghazipur districts of eastern U. P. *JIGYASA, (IJIF)*. 2019;12(2):642–650.
8. Azam A. Arsenic polluted ground water in eastern U P, India *International Journal of Engineering and Management Research.* 2013;3(4):81–83.
9. Azam A, Kunwar A. Arsenic contamination in Groundwater in Eastern U.P., *RESEARCH MAGMA.* 2018;2,(1):1–9.
10. Azam A, Kunwar A. Hydrochemistry of arsenic in groundwater pollution in eastern Uttar Pradesh. *Journal of Water Pollution & Purification Research.* 2018;5(2):1–4.
11. Azam A, et al. A Review: Effect of Physicochemical and Hydro geochemical factors on arsenic sedimentation and Mobilization, *Biological forum-An International Journal.* 2023;15(2):1046– 1052.
12. Azam A, et al, "Assessing the Occurrence, Causes, and Health Effects of Arsenic Contamination in Groundwater: A Comprehensive Review", *International Journal for Innovative Research in Multidisciplinary field* 2023;9(7) 107-111.
13. Azam A. Study of seasonal variation of arsenic concentration in Groundwater in Ghazipur district of Uttar Pradesh. *Asian Journal of Advances in Research.* 2020;3(1):8–15.
14. Azam A. Temporal and seasonal variation of arsenic in Ballia district of Eastern U. P. *Asian. Journal of Advances in Research.* 2020;2(1):22-29.
15. Azam A., A study of groundwater with special reference to arsenic contamination and its consequences, Jal, Santan kumar Ram, Rachnakar Publishing house Delhi 978-93-87932-44-9; 2020.
16. Azam A., Relation between Energy and Environment, *International Journal of Engineering and Management Research*, Volume-4, Issue-3, June-2014, ISSN No.: 2250-0758 Page Numbers: 431-433.
17. Azam A., Path of Green Chemistry and Sustainable development , *Asian Journal of Advances in Research* 2(1): ISSN No.: 2582-3248, pg. No.18–21, 2019.
18. Azam A., Arsenic Polluted Ground Water in Eastern U P, India *International Journal of Engineering and Management Research*, Vol.-3, Issue-4, August 2013 ISSN No.: 2250-0758 Pages: 81-83.
19. Azam A, et al, "The Significance of Polymeric Ligand Exchange (PLE) Technique for Arsenic Removal from Polluted Groundwater: A Review" *Asian Journal of Advances in Research* 6(1): ISSN No.: 2582-3248, pg. No.577-583.
20. Azam A, et al, "Arsenic in Groundwater: Understanding the Pathways from Pollution to Human Health and Remediation via PLE Method" *INTERNATIONAL JOURNAL FOR INNOVATIVE RESEARCH IN MULTIDISCIPLINARY FIELD*, 9(12) ISSN No.: 2455-0620, pg. No.49-52,
21. Ali I, Rahman A, Khan TA, et al. Recent Trends of Arsenic Contamination in Groundwater of Ballia District, Uttar Pradesh, India, *GU J Sci* 2012, 25(4), 853–861p.
22. Katiyar S, Singh D. Prevalence of arsenic exposure in population of Ballia district from drinking water and its correlation with blood arsenic level, *J Env Bio.* 2014 (35) 589-594pp.

23. Singh R, Gond DP, Pal A. Assessment of ground water quality of Ghazipur district, eastern Uttar Pradesh, India, special reference to arsenic contamination, *Recent Res Sci Technol.* 2010, 2(3), 38–41p.
24. Chakraborti D, et al. Arsenic groundwater contamination in Middle Ganga Plain, Bihar, India: a future danger? *Environ Health Perspect.* 2003, 111, 1194–1201p.
25. Singh AK. Arsenic contamination in groundwater of Northeastern India. In *Proceedings of 11th National Symposium on Hydrology with Focal Theme on Water Quality*, National Institute of Hydrology, Roorkee, 2004, 255–262p.

