



SPECIATION OF ARSENIC ACROSS WATER - SEDIMENT INTERFACE OF PUNPUN RIVER

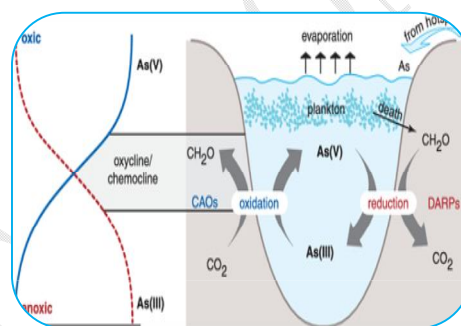
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ABSTRACT:

Arsenic is metalloid, which exists broadly in two different forms As (III) and As (V) and they are found in many different environments such as soil, fresh water, sea water and sewage¹⁻⁴. Arsenic mainly occurs naturally in rock and also produced by industrial mining and agricultural practices. It can leak out and pollute bodies of water including lakes or rivers⁴⁻⁵. Both the forms of Arsenic As (III) and As (V) are carcinogens causing skin, kidney, bladder and lung cancer. The extent of arsenic poisoning within an individual has been exposed to or has ingested. As a result, both the European Union and WHO⁶ allow a maximum arsenic concentration of $10 \mu\text{g L}^{-1}$ in water. However, many developing countries are struggling to establish a standard of even $50 \mu\text{g L}^{-1}$ and as such, it is of dire importance that the level and underlying mechanisms of arsenic pollution be understood.



KEYWORDS: industrial mining and agricultural, mechanisms of arsenic pollution.

1. INTRODUCTION

During some biological processes, arsenate (AsO_4^{3-}) is reduced to the lower valence state As (III) and then methylated microbiologically into Monomethyl arsine, dimethyl arsine and trimethyl arsine, all of which can then be oxidized by air to form the less toxic dimethyl arsenic acid $(\text{CH}_3)_2 \text{HAsO}_4$. As (III) species, however, are much more toxic than As (V), as methylation of As (III) increases its volatility and therefore the mobility of methylated arsenic increases

within the biogeochemical cycle⁷⁻⁸. Punpun is a religious landmark in Bihar, India that attracts people all over the India who came to observe the ritual of the departure soul of their ancestors. In particular the Punpun River, which passes through Punpun, is believed to be sacred to many people, who bathe in the river drink its water. As such this study aims to contribute to the this knowledge by revealing the speciation of arsenic across a specific example, in the case of water-sediment interface in the drainage sites between the Punpun river and Punpun city.

2. MATERIALS AND METHODS

2.1. Site Information

Water and sediment sample were collected before the monsoon 2018 from five sites at which the drainage of the city Punpun met the Punpun river. These sites identified as 1,2,3,4, and 5

2.2. Sample collection.

From each of the five sites the surface water was taken in one - litre, polythene bottles. These sample were then immediately acidified by 2N HCl filtered through whatman filter paper grade 42 and subsequently stored in clean polythene bottles. A grab sample filtered with a semi -

permeable bag was then used for the sampling of the sediments. One sample was taken from a depth of 0-0.5cm. and another from depth of 7-12 cm. Since the membrane was even impermeable to bacteria, the pore water was thus sterilized and then acidified properly and stored in clean polythene bottles.

2.3. Sediment analysis.

The arsenic speciation analysis of the surface water and pore water was carried out by Gas chromatography (GC) coupled to Inductive coupled plasma Mass spectrometry (ICP-MS). The nonvolatile methyl arsenic species were volatilized and then cryotrapped in a glass tube. The separation and quantification of various species were carried out by heating the trap and gas. Chromatography column coupled to an ICP - Mass previously detailed by Feldmann (1997). The quantification of organo-arsenic species, however was done by measuring a multiorgano arsenic standard containing $(\text{CH}_3)_3\text{As}(\text{ONa})_2$, $(\text{CH}_3)_2\text{AsO}(\text{OH})$ and $(\text{CH}_3)_3\text{As}$.

To estimate As (III) and As(V), They were separated by anion Exchange Chromatography (AEC). The inorganic arsenic species As (III) and As(V), however, occur as neutral or negatively charged depending on the pH. For the quantization of the two species As(III) and As (V), the anion Exchange chromatography (AEC) with inductively coupled plasma mass spectrometry (ICP- MS). The total arsenic determination was carried out by silver diethyldithiocarbamate, In this process, since As (III) is more efficient, all the arsenic was first converted into As (III) in a pre-reduction step using KI + Ascorbic acid. This As (III) is reduced into AsH_3 . by NaBH_4 in an acid solution. From here it was placed into an absorber tube containing silver diethyldithiocarbamate (SDDC) solution in pyridine. As combined with SDDC salt it formed the soluble red complex, i.e., $\text{As}[(\text{C}_2\text{H}_5)_2\text{N.CS}_2]_3$ which was measured at 535 nm against reagent.

RESULTS

3.1. Arsenic species in free water .

The study reports, the arsenic contamination in free water as shown in table 1. It revealed that all five sites the concentration of As(V) was significantly higher than that of As(III). Furthermore, negligible amount of organo arsenoid species were found, indicative of very minimum microbial activity, however this issue was not fully investigated.

Table 1. Concentration in $\mu\text{g/L}$ of the different species of arsenic in free water

Site No	As (III)	As (V)	MMAs	DMAs	TMAs	AS Total
1	0.850	1.21	0.12	-----	-----	2.252
2	0.731	0.96	0.10	-----	-----	1.781
3	0.782	0.96	0.22	-----	-----	1.722
4	0.750	0.91	0.10	-----	-----	1.601
5	0.923	1.48	----	-----	-----	2.301
Average	0.807	1.10	0.10	-----	-----	1.931
+ SD	+0.086	+0.3	+0.07	-----	-----	+0.328

-: no significant amount detected

3.2. Arsenic species in pore water from sediment:-

The results has been given in Table-2 reveal that across all five sites the pore water from sediment 0.5cm contain $\sim 6\mu\text{g L}^{-1}$ of As(III) $\sim 0.4\mu\text{g L}^{-1}$ As(V). As such the concentration of As(III) is significantly more than As(v).

Moreover, the pore water contained all three methylated forms of arsenic with the greatest concentration DMAs in all the five sites. Also at site 5 the concentration of As (III) and DMAs were found to be abnormally high.

Table 2. Concentration in $\mu\text{g/L}$ of the different species of arsenic in pore water from sediment 0 - 5 cm deep

Site No	As (III)	As (V)	MMAs	DMAs	TMAAs	AS Total
1	5.31	0.442	0.84	2.792	0.228	8.808
2	5.65	0.445	0.91	2.870	0.200	3.250
3	5.43	0.420	0.78	2.834	0.200	9.812
4	5.65	0.422	0.86	2.868	0.268	10.313
5	8.26	0.410	0.92	4.470	0.300	14.400
Average	6.06	0.427	0.87	3.166	0.242	10.336
+ SD	+1.25	+0.013	+0.07	+0.720	+0.046	+2.460

Table-3 Display the results of the analysis of pore water from sediment 7-12 cm deep. The data reveals that the concentration of As (V), as in terms of total arsenic further decrease from 3 - 5% , 0 - 5 cm depth , to 0.62-0.86% 7 - 12 cm depth. Though the concentration ($\mu\text{g/L}$) of As (III) increases in respect of total arsenic it decreases from 56-68%, 0 - 5 cm deep, to 42-44% 7 - 12 cm deep.

The concentration of MMAs increased at this depth while the concentration DMAs was found to be the greatest with an average value 5.608 $\mu\text{g/L}$. The concentration of TMAAs also increased but this increase was very minor. The value of total arsenic concentration showed a significant increase.

Table 3. Concentration in $\mu\text{g/L}$ of the different species of arsenic in pore water from sediment 7 - 12 cm deep

Site No	As (III)	As (V)	MMAs	DMAs	TMAAs	As Total
1	5.98	0.10	1.820	5.325	0.295	13.585
2	5.59	0.12	1.820	5.425	0.3350	13.405
3	5.62	0.11	1.925	5.385	0.312	13.450
4	5.88	0.10	1.885	5.425	0.330	13.580
5	5.64	0.11	1.980	6.490	0.312	15.695
Average	5.94	0.08	1.898	5.610	0.316	13.943
+ SD	+0.40	+0.01	+0.060	+0.490	+0.020	+0.970

4. DISCUSSION

4.1 As (III) and As (V) in Free pore water

The result from free water showed that As (V) was found in greater concentration as compared to As (III). This finding properties that is may be due to the aerobic condition, prevailing within free water, that the As (V) species are more stable than the As (III) species. However this higher concentration of As(V) may also be explained by a insignificant transformation of As(V) by microbial mat or other constituents present in the water, a concept by similar literature⁹⁻¹⁰ Furthermore , the organoarsenoid was found to be close to absent from the free water indicating very minimal to no Significant Microbial activity under the aerobic condition.

In contrast , the pore water from sediment both 0.5 cm deep and 7 - 12 cm deep , contained significantly greater concentrations of As (III) as compared to As (V), indicating that as soon as anaerobic conditions begin to develop, Arsenite (AsO_3^{3-}) is found in greater concentrations than arsenate. It is implicated that microbial species involving arsenic metabolism enhance such transformation processes As(V) into As (III) and support microbial driven biogeochemical cycle¹¹. The cycle represents oxidation reduction reaction involving As (V) and As (III) as well as methylated and thioarsenicals. Furthermore, As(V) reduction can occur in conjunction with sulphide oxidation and As (III) oxidation with nitrate reduction and therefore can be carried out in anaerobic environments.

Moreover, the pore water contained all there methylated forms of arsenic making it clear that microbial activities start within the sediment under anaerobic conditions. Also at site 5 the concentration As(III) and DMAs have been found to be abnormally high which may be attributed to the

greater microbial activities occurring in sediment at this site. The concentration of all the three methylated forms increased significantly one again within the pore water once again the indicative of the greater microbial activities going on under the more anaerobic conditions.

4.2 Depth dependence of methylation of arsenic.

The results revealed that the methylation of arsenic increases with increasing depth on sediment at all five sampling sites. This clearly indicates that methylation significantly influences both translocation of arsenic in sediment and the transformation of arsenic into DMAs as it is much faster than that of MMAs and TMAs.

Furthermore, some microbes metabolize arsenic via methylation, dimethylation, oxidation and reduction reactions to generate energy for their survival and biofilm production. Methylation reactions convert As(V) or As(III) into compounds such as MMA(V), MMA(III), DMA(V), DMA(III) and trimethylarsine oxide, as well as several volatile arsines, including monomethylarsine, dimethylarsine and trimethylarsine. Although many of the enzymes involved for such transformation remain unknown, a methyl transferase, ArsM, discovered from *Rhodobacter sphaeroides* confers resistance to arsenic and can generate trimethylarsine¹².

4.3. Depth Dependence of As (III), As (V) and Total As

As (III) significantly dominates over As (V) as the depth increases which may be attributed to increasing microbial activities that cause greater reduction of As (V) into As (III).

Furthermore, at 7-12 cm deep As (V) can be seen in negligible amounts which is probably a result of the greater adsorption of As (V) to Fe(III) and Al(III) oxide and hydroxide respectively which may have not passed into pore water due to their being insoluble. This also confirms the earlier reported result of As(III) being much less adsorptive on Fe(III) and Al (III) oxides, hydroxides and more mobile than As(V)¹³.

4.4. Biological interplay of Arsenic

Several microorganisms have been studied for the bioremediation of heavy metals and metalloids and their mechanisms are well understood. It is thought that As(V) reduction can be carried out in two distinct manners. One mechanism involves dissimilatory reduction of arsenate and was discovered in *Sulfurospirillum arsenophilum*¹⁴. Another mechanism of As (V) reduction involves ArsC and resistance genes¹⁵. There are different mechanisms by which such resistance genes operate, it has been found that in *E. coli*, *Staphylococcus* and yeast possess three components to their complex reduction system. These three components include the arsenate reductase ArsC, related to tyrosine phosphate-phosphatases; ArsB, the arsenite-specific efflux pump; and a source of reducing equivalents, thioredoxin or glutaredoxin¹⁶.

5. CONCLUSION

In every sample of free (surface) water and pore water from sediment, the concentration of total arsenic is greater than the maximum permitted VALUE (10 µg/L). These measures have been placed in light of the epidemiological evidence to support the carcinogenic nature of the ingested arsenic and its concentration with liver, lungs and kidney diseases and other dermal effects¹⁷. Considering this, in the pore water from sediment 7-12 cm. deep, the concentration of arsenic is much greater than the acceptable concentration which makes it of the utmost concern because this load of arsenic will subsequently release into river water making it toxic for domestic use. It is suggested that thermal, optical and pH biosensors should be used to regularly monitor the level of this arsenic species. It will be interesting to examine if these sites correspond to the microbial species abundance that actively participates in the arsenate reduction and methylation process. These investigations are currently in progress. Hence it is strongly recommended that the municipal, local and state authorities take it seriously to treat drainage properly before it passes on it into the river. The extent of arsenic poisoning within an individual is strongly correlated to the amount of arsenic the individual is in question.

has been exposed to or has ingested. Therefore, any action taken to solve the rising problem of arsenic contamination in the punpun river should be done promptly and efficiently so to reduce the impact of the adverse health effects of arsenic imposes.

6. ACKNOWLEDGMENT

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