

## RESEARCH COMMUNICATIONS

**Arsenic association and distribution in carbonaceous materials in northeastern India****M. K. Baruah<sup>†</sup>, P. Kotoky<sup>#,\*</sup>, J. Baruah<sup>#</sup>, G. C. Borah<sup>#</sup> and P. K. Bora<sup>#</sup>**<sup>†</sup>Department of Chemistry, NNS College, Titabar 785 630, India<sup>#</sup>Geoscience Division, Regional Research Laboratory (CSIR), Jorhat 785 006, India

**The present study on total arsenic distribution in carbonaceous materials across the four northeastern states of India warrants immediate continuous monitoring of the situation as it may cause a serious public-health concern to this heavily populated developing nation. Many studies on arsenic in India are already available, but to our knowledge data about this particular substrate, i.e. coal and bituminous matter, are not yet available.**

**The study attributed predominant association of arsenic in the hydrogenated units of organic matter. However, association in the aromatic units of organic matter is also observed. Both *in situ* and drifted nature of accumulation of arsenic is observed. The study revealed the principal nature of accumulation of arsenic by the formation of organo-arsenic complexes and exhibited a regional enrichment trend from east to west, with average arsenic content of 95.12 µg/kg. Apart from creating a strong database on arsenic distribution pattern for this virgin northeastern region of India, the study provides an effective demonstration that arsenic association, concentration, distribution and post-depositional mobility in carbonaceous matter can be used to construct a predictive model for a depositional geo-chemical set-up towards aquifer development, with optimum possible environmental risk.**

CONCENTRATION of arsenic (As) in the environment is increasing as a result of human activities and various natural processes. Arsenic enrichment has been found in hydrothermal<sup>1</sup>, oxic<sup>2</sup>, anoxic<sup>3</sup>, deep-sea<sup>4</sup>, sediments, lakes<sup>5,6</sup>, iron-rich<sup>7,8</sup>, clay<sup>9</sup>, carbonate<sup>10</sup>, arsenopyrite<sup>11,12</sup>, pyrite<sup>13</sup> and organically-associated<sup>11</sup> phases. Total arsenic displays nutrient-like behaviour in near shore and open ocean waters, whereas arsenite and methylated arsenic species productions are coupled with biological activity<sup>14,15</sup>. Vertical distribution of both solid and dissolved As (As<sup>3+</sup> and As<sup>5+</sup>) in recent sediment shows a novel pattern of the element<sup>16</sup>. Moreover, particulate arsenic entering estuaries<sup>17</sup> remained in the solid phase and accumulated in sedimentary deposits<sup>18</sup>. Our attention has been drawn to the recent havoc of increasing arsenic level in the groundwater in West Bengal, covering an area of 37,493 km<sup>2</sup> lying close to the metropolitan city of

Kolkata<sup>19,20</sup>, with maximum concentration being 3.7 mg/l (permissible limit of arsenic in potable groundwater is only 0.05 mg/l) which has caused a serious public-health concern, particularly in the eastern part of India. It is surprising that the problem has remained unattended for so long<sup>20</sup>. Moreover, increasing arsenic levels in groundwater have also been reported in neighbouring Bangladesh, mainly related to younger deltoid sediments<sup>21-24</sup>. Although As has been occurring in various natural systems, surprisingly there is no report available about its presence in the northeastern region of India. Organic matter is a natural concentrator of most metals; and therefore, being the progenitors can show current distribution pattern of the elements. The occurrence of arsenic is geologically related in a sedimentary environment with dominant carbonaceous materials and bears significant environmental consequences. The history of geological evolution of the sedimentary basins geographically located in West Bengal, and neighbouring Bangladesh is similar to the northeastern region of India. These sediments have high proportion of clay and contain relatively large amount of organic carbon<sup>23</sup>. Among the several likely sources, carbonaceous matter may be able to provide an answer towards initial retention and subsequent release of sedimentary arsenic contents to the groundwater aquifers. The mobility of this element in a heterogeneous natural system is significantly dependent on its association and chemical forms.

Biosynthesis and release of organo-arsenic compounds by marine algae<sup>25</sup> strongly suggest that carbon-rich substances have been playing a major role in As distribution. Depositing bacterial decomposition products of plant materials followed by various geological processes formed natural, carbon-rich substances. The humification process, comprising condensation of molecules due to gradual removal of polar groups<sup>26</sup> is continuous in the soil and peat, whereas in lignite and coal it has ceased<sup>27</sup>. Thus, organic matter from coal and that from soil differs in that the former is highly condensed, possessing fewer side chains and functional groups. Thus, the extent of association of inorganic materials with organic substances with varying carbon content differs widely. It is also possible that the mineral matter may occur as individual or combined forms. Thus, it is apparent that the carbon-rich samples, which have undergone different degrees of humification (or metamorphism), need to be studied in order to understand the nature of distribution of As. Here, we report a significant variation of As in natural organic matter of North-East India and the nature of accumulation of As in these substances. A significant amount of study on the occurrence of As in groundwater and younger recent sediments of India and Bangladesh has already been made; however, data on association of As in carbonaceous materials are not yet available. Within limitation in data resource and other logistics involved in the present phase of study, it is expected that it will open

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up an avenue towards in-depth investigation on the association and occurrence of As in natural, carbon-rich substrates.

Figure 1 shows the location of samples collected for the study. Five main areas include (i) eight carbon-rich (lignituous) samples collected from carbonaceous horizons encountered at depths ranging from 1000 to 1400 m (bore-hole) below the surface near Lakwa (Assam) where heavy production of crude oil has been in operation; (ii) eighteen surficial samples (sub-bituminous) from 6.0 m seam of Makum coal field in Assam; (iii) ten samples (lignituous coal) from Nagaland; (iv) twelve samples (sub-bituminous) from Meghalaya, and (v) twelve samples (graphitic coal) from Arunachal Pradesh. All the samples were collected from the Central Fuel Research Institute, Jorhat Unit. The representative fraction of the composite samples after grinding to 100-mesh size was taken out by coning and quartering process, and utilized throughout the present investigation.

Next, 0.5 g air-dried sample was digested in a Teflon-lined bomb at 140°C for 1 h using concentrated HF (48% v/v; 10 ml), HNO<sub>3</sub> (70% v/v, 4 ml), HClO<sub>4</sub> (70% v/v, 1 ml) and 5% (w/v) KMnO<sub>4</sub> (5 ml). After digestion, the materials were treated with 5% (w/v) NH<sub>2</sub>OH HCl (5 ml), water (20–30 ml) and H<sub>3</sub>BO<sub>3</sub> (5 g), and then filtered. The filtrate and the washings were collected in a 100 ml volumetric flask and double-distilled water was added to make up the volume<sup>28</sup>. Ten ml solution was taken from this parent solution in a reaction vessel and treated with 2 ml conc. HCl, 2 ml KI solution (20% w/v), 1 ml L-ascorbic acid (20% w/v) and the solution was made up to 20 ml with de-ionized water. Then, each solution thus prepared, including the blanks was treated with 2 ml NaBH<sub>4</sub> solution (3% w/v) and allowed to stand for

about 60 s. The generated arsine was then swept into the argon–hydrogen flame with argon gas, and arsenic was determined by cold vapour using Perkin–Elmer atomic adsorption spectrophotometer (AAS) (model 2380) having detection limit up to 0.01 µg/kg. The C, H and N are determined with the help of Perkin–Elmer CHN Analyser (Series-2400) using acetanilide as standard reference. The average of replicate C, H, N analysis and total As from the samples covering the four states of the North-eastern region of India is used for interpretation in the present study.

High purity Certified/Analar or its equivalent grade reagents (obtained from Aldrich, Sigma or Emerck only), double-distilled de-ionized water and Borosil glassware (A) were used throughout the course of work. A sub-boiling distillation unit (all quartz), purified HNO<sub>3</sub> and HCl were used in this study. Stock standard solution was prepared by dissolving ultra-pure metals/compounds (99.9%) obtained from Aldrich only. Blank and standard were run on every triplicate analysis to know the precision and accuracy of measurements throughout the study.

We were concerned about the influence of geological substrate (carbon-rich substances) on the trends of As concentration. Because our study encompasses highly variable geological materials, we did not expect a regular trend in As association and distribution pattern from these sources. Table 1 shows the quantity of As present in the samples under study. Analysis of samples representing all the four states showed significant differences in total As concentration among the samples under study, with an overall mean of 95.12 µg/kg. Apart from Meghalaya samples, average As concentration in bore-hole samples was found to be quite higher than those of other samples. Moreover, gradual decrease of As is observed with increase of depth in the bore-hole samples (Figure 2). Similar observation has been made by researchers

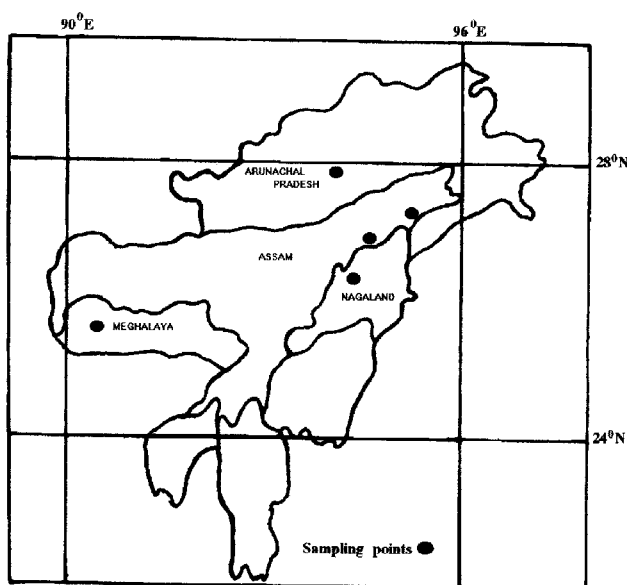


Figure 1. Location map of the area showing sampling sites.

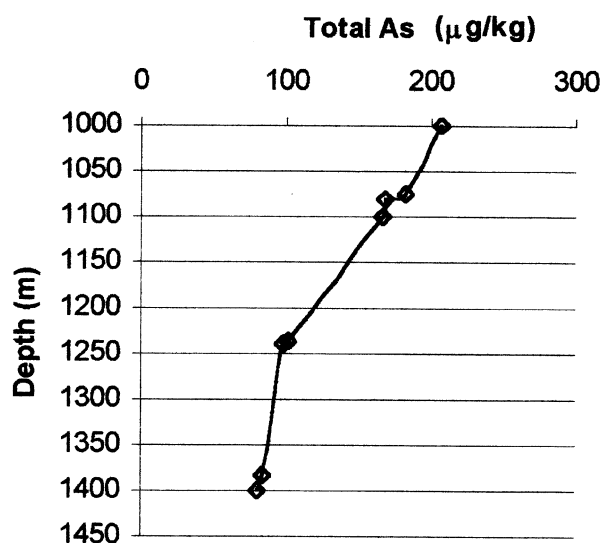


Figure 2. Variation of total arsenic with depth.

working on arsenic contamination in West Bengal, from Geological Survey of India<sup>23</sup> and in Bangladesh from British Geological Survey<sup>29</sup>. However, a contrasting argument in the vertical distribution of As content was also reported<sup>21</sup>. Roychowdhury *et al.*<sup>30</sup> reported more precise results where As content decreases at depths of over 22 m, while it increases for depths of less than 22 m, which agrees with our result. Perhaps, the most important implication of our results is that these may be useful to predict As concentration pattern in organic matter of different geochemical systems. The geochemical mobility of associated As in natural environment must be assessed from its quantity, directly related to the nature of its existence and formation. Moreover, aerial and microbial oxidation of base metals sulphides ultimately results in the formation of considerable amount of sulphate in the natural system and thereby enhances the release of As content from their sink. The post-depositional mobility of As<sup>14,31,32</sup> associated with the base metal sulphide (pyrite) content might have been catalysed by the organic matter contents and may create an environmentally unfriendly situation. The weathering of base metal sulphide associated with carbonaceous matter might have generated arsenic-rich oxy-hydroxides, which in turn release As (after reduction) to the existing sedimentary environment<sup>21,22</sup>. There is no wide variation of As in the Arunachal Pradesh and Nagaland samples, whereas samples from Assam and Meghalaya show significant variation in total As concentration. Moreover, the Meghalaya samples show quite high values of As; in one case, the concentration is much higher than the bore-hole samples. An interesting point to note is that except bore-hole samples, As concentration generally increases from east (Arunachal Pradesh) to west (Meghalaya).

On comparing the bore-hole and surface coal samples of Assam, one can observe a twofold increase in maximum values of As in the bore-hole samples. This would indicate that the different polar groups in the organic matter of the bore-hole samples may play an important role in As accumulation.

The role played by organic matter for enrichment of As can be explained as follows. Arsenic may be accumulated predominantly by either aromatic units or hydrogenated (non-aromatic) units of organic matter. The H/C ratios

indicate hydrogenation (increasing H/C) or amortization (low H/C). A relationship between As and the H/C ratio (wt.) is shown in Figure 3a. The comparatively higher H/C ratios together with their total As concentration can be attributed as the predominant enrichment of As in the hydrogenated units of organic matter, whereas samples with low H/C ratio reveal that As is predominantly accumulated in the aromatic units of organic matter. The general hydrogenation sequence of the samples with respect to their locations under study can be represented as Assam (bore-holes) > Meghalaya > Nagaland > Assam > Arunachal Pradesh. Bore-hole samples from Assam have shown the highest enrichment in hydrogenated units, while samples from Arunachal Pradesh have shown the highest amount of As enrichment in aromatic units.

The C/N ratios are representative of autochthonous/*in situ* (lower C/N ratio) or allochthonous/drifted (higher C/N ratio) origin of organic matter. A relationship between As and the C/N ratios (wt.) of the samples is shown in Figure 3b. On comparing the plots it has been found that the Nagaland and bore-hole samples of Assam with low C/N ratios are attributable to deposition of As in autochthonous organic matter, whereas other samples with high C/N ratio are indicative of As accumulation in allochthonous organic matter. The general sequence of C/N ratio within the samples under study can be represented as Arunachal Pradesh > Meghalaya > Assam (Surface) > Nagaland > Assam (bore-holes). It is now evident that the As in Assam (bore-holes) and Nagaland samples is syn-depositional in nature, while As content in Meghalaya, Arunachal Pradesh and Assam (surface) is mainly post-depositional in nature. From this study the nature of accumulation of As by the formation of organo-arsenic complexes during post-depositional diagenetic consequences can easily be assessed.

The occurrence of As in natural systems posed a problem that most geological materials react slowly under low-temperature weathering conditions, where the rate of release of the element in solution may be slow. The environmental impact on surface water may be lesser because of dilution effects, but with regard to groundwater this may be a serious concern. Even though many inorganic substances are known to be enriched with As, e.g. ferromagnesian nodules<sup>7,8</sup> and iron sulphide<sup>13,31</sup>, these are

**Table 1.** Distribution of total arsenic content in carbonaceous matter of North-East India

State	No. of samples and type	Carbon (wt%)	Arsenic ( $\mu\text{g}/\text{kg}$ )	
			Range	Average
Assam (bore-hole)	8 Lignitic	40.503–42.064	80.0–207.0	136.1
Assam	18 Sub-bituminous	70.381–71.143	44.0–78.0	61.0
Nagaland	10 Lignitic	53.825–56.124	56.0–68.0	62.0
Meghalaya	12 Sub-bituminous	58.202–58.791	106.0–238.0	172.0
Arunachal Pradesh	12 Graphitic	66.012–71.981	39.0–50.0	44.5

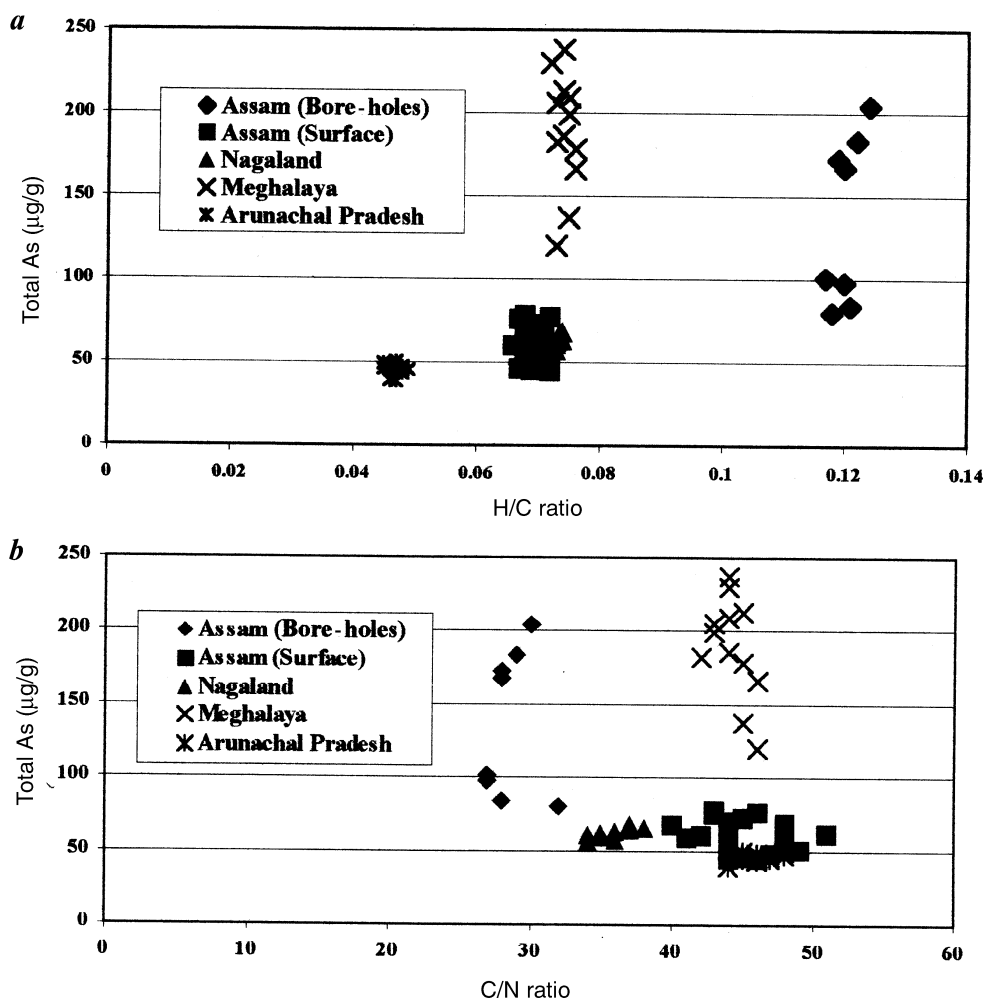


Figure 3. Relationship of total arsenic with (a) H/C ratio and (b) C/N ratio.

leached either quickly in the aquatic environment or may be released over a long period of time. The organic matter present in the system can easily take these metal ions. Organic matter promotes sulphate reduction during burial and diagenesis of sediments, and generates diagenetic iron sulphide (commonly called pyrite), which includes in its structure As in substitution from sulphur<sup>33</sup>. On the other hand, when drought occurs, water levels would drop and this process helps increase the potential for microbial oxidation of organic matter to release metals. These metals would be either taken up by plants or taken away by the water. Moreover, in times of drought, pH is decreased (<5.0) resulting in an increase of  $H^+$  ion concentration by which metals are released from the organic matter (Baruah and Kotoky, unpublished work). Thus, the released metal could flow out of the system, and play a significant role in interaction with the surface water system, causing a situation against life-sustaining processes. The acute environmental problem caused by arsenic in land and water is being actively pursued. It is known that the peat near the rim of a basin has a higher metal level than peat closer to the middle of the basin<sup>34</sup>.

This is understandable since humic acids are known to have many unfilled cation exchange sites capable of adsorbing metals with change of valence states<sup>35</sup> from the watershed influx. Further, the uptake of As by marine algae<sup>36</sup>, its metabolism in marine bacteria<sup>37</sup> and biological oxidation of arsenite<sup>38</sup> show enrichment of the element in organic matter. The interconversion of arsenate–arsenite in oxic–inoxic interfaces<sup>39,40</sup> results in drastically different As speciation in oxidation–reduction environments. Thus, the enrichment of As in organic matter is possible during decay of vegetable matter, especially humus soil<sup>41</sup>. The release of organo-arsenic compounds by marine algae and inorganically associated As<sup>11,42</sup> justifies the As accumulation in organic matter. Thus, our results provide an effective demonstration that As concentration in organic matter can be used to provide an answer to one of the severe environmental concerns of today.

Total arsenic content associated with the carbonaceous matter demonstrates that there is no wide variation in the Arunachal Pradesh and Nagaland samples, whereas the samples from Assam and Meghalaya show significant variation. The Meghalaya samples exhibited compar-

tively higher values in total arsenic content. Significant allochthonous arsenic association by forming organo-arsenic complexes with a comparatively higher proportion within the hydrogenated unit of the organic matters is clearly seen. Moreover, the total arsenic content shows an increasing enrichment from east to west of the north-eastern region of India. This trend along with the association/distribution pattern will definitely help to model a geochemical set-up to reconstruct the depositional sedimentary environment of the northeastern region of India.

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ACKNOWLEDGEMENTS. M.K.B. is grateful to the Department of Science and Technology, Govt. of India, for a Science and Engineering Research Council Visiting Fellowship. We are grateful to the Director, Regional Research Laboratory (CSIR), Jorhat for permission to publish the work. We thank the Central Fuel Research Institute, Jorhat Unit for the samples. We also thank Dr J. C. Sarma, RRL-Jorhat for help in elemental analysis of the samples.

Received 12 December 2002; revised accepted 11 April 2003

## Thermal structure of continental crust beneath Hrapur–Mandla deep seismic sounding profile across Narmada–Son Lineament

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**The Narmada–Son Lineament (NSL) in central India is a prominent tectonic feature; extending to about 1600 km from the west coast. Five deep seismic sounding (DSS) profiles were shot across the NSL to delineate its crustal structure. Some geothermal studies have suggested a high heat flow regime for this zone. In the present work, we have integrated seismic velocity, crustal structure and focal depth information for Hrapur–Mandla profile passing through Jabalpur and obtained a two-dimensional thermal structure along this profile. The results indicate a temperature of 510–535°C at the Moho depth (41–43 km). Surface heat flow varies between 45 and 47 mW/m<sup>2</sup>. Our results suggest a low mantle heat flow, which in turn, makes the lower crust brittle and amenable to the occurrence of deep, focused earthquakes.**

THE Narmada–Son Lineament (NSL) in central India is a major lineament zone which divides the Indian Shield into a southern Peninsular block and a northern Foreland block<sup>1</sup>. NSL extends from the west coast towards the northeast, underneath the Monghyr–Saharsa ridge<sup>2</sup>. This zone lies between long 72 to 88°E and lat 21.5 to 24°N. It

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