

vious investigations have shown increase in run-off of the Baspa basin¹³. However, in the long term, decrease in glacier extent will decrease in stream run-off during summer and autumn seasons, affecting local as well as national economy, since many villages are located on the banks of streams originating from glacier numbers 1–4. In addition, run-off of the Baspa river is also used for generation of hydropower. All these observations suggest that global warming has started to affect glacier melt in the Himalaya and poses questions to the conservation of precious water resources.

1. Flint, R. F., *Glacial and Quaternary Geology*, John Wiley, 1964, pp. 63–85.
2. Kulkarni, A. V. and Buch, A. M., *Glacier Atlas of Indian Himalaya*, SAC/RSA/RSAG-MWRD/SN/05/91, 1991, p. 62.
3. IPCC, Climate changes 2001: The scientific basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change (eds Houghton, J. T. *et al.*), Cambridge University Press, Cambridge, UK, 2001, p. 881.
4. Lozan, J. L., Grabl, H. and Hupfer, P. (eds), Summary: warning signals from climate. In *Climate of 21st Century: Changes and Risks*, Wissenschaftliche Auswertungen, Berlin, Germany, 2001, pp. 400–408.
5. Kulkarni, A. V. and Bahuguna, I. M., Glacial retreat in the Baspa basin, Himalayas, monitored with satellite stereo data. *J. Glaciol.*, 2002, **48**, 171–172.
6. Nye, J. F., The response of glaciers and ice-sheets to seasonal and climatic changes. *Proc. R. Soc. London Ser. A*, 1960, **256**, 559–584.
7. Paterson, W. S. B., *The Physics of Glaciers*, Butterworth-Heinemann, 1998, pp. 26–53.
8. Meier, M. F. and Post, A., Recent variations in mass net budgets of glaciers in western North America, IASH, 1962, **58**, 63–77.
9. Kulkarni, A. V., Mass balance of Himalayan glaciers using AAR and ELA methods. *J. Glaciol.*, 1992, **38**, 101–104.
10. Braithwaite, R. J., Can the mass balance of a glacier be estimated from its equilibrium-line altitude? *J. Glaciol.*, 1984, **30**, 364–368.
11. Singh, R. K. and Sagewar, C. V., Mass balance variation and its impact on glacier flow movement at Shaune Garang glacier, Kinnaur, HP, Proceedings of the National Meet on Himalayan Glaciology, 1989, pp. 1499.
12. Kulkarni A. V., Philip, G., Thakur, V. C., Sood, R. K., Randhawa, S. S. and Ram Chandra, Glacial inventory of the Satluj basin using remote sensing technique. *Himalayan Geol.*, 1999, **20**, 45–52.
13. Kulkarni, A. V., Mathur, P., Rathore, B. P., Suja Alex, Thakur, N. and Manoj Kumar, Effect of global warming on snow ablation pattern in the Himalayas. *Curr. Sci.*, 2002, **83**, 120–123.
14. Kulkarni, A. V. and Suja Alex, Estimation of recent glacial variations in Baspa basin using remote sensing technique. *J Indian Soc Remote Sensing*, 2003, (in press).

ACKNOWLEDGEMENTS. We thank Dr Shailesh Nayak, Group Director, Marine and Water Resources Group for suggestions during the investigation and for critical evaluation of the manuscript.

Received 27 February 2003; revised accepted 7 August 2003

Sediment contamination by arsenic in parts of central-east India and analytical studies on its mobilization

Piyush Kant Pandey*, Sumita Nair, Ashish Bhui and Madhurima Pandey

Department of Engineering Chemistry, Bhilai Institute of Technology, Durg 491 001, India

This communication reports arsenic contamination of sediments in parts of Chhattisgarh. It also investigates the nature of arsenic contamination and the conditions which may favour its release from this matrix. The contaminated sediment serves as a long-time source of arsenic because As mobility and transport in the environment are strongly influenced by its association with the solid phase in soil and sediment. The results establish the sediment contamination of certain water bodies, including a major river in the region. As levels in the contaminated sediments lie between 200 and 10.75 ppm, with a mean level of contamination at 68.00 ppm and standard deviation of 41.81 ppm. A direct result of this contamination has been noted in the form of lower productivity of the Shivrath river in fish population.

Sequential arsenic extraction procedures were adopted to differentiate the nature of arsenic species in the sediment and its mineral assemblages. Two analytical schemes were followed to identify the arsenic phases in the sediment. Sequential extraction analyses indicate that a large portion of the arsenic in Chowki–Rajnandgaon–Durg sediments is in complex silicate matrices or is calcium-bounded. This will limit the mobility of arsenic. Yet about 15% of As which is in the form of exchangeable fraction may get mobilized by changes in the ionic strength of the overlying matter. This indicates the need for a scientific management of the contaminated sediments in the region.

ARSENIC contamination of groundwater has become a worldwide menace. It is harming the developing countries more vehemently owing to obvious reasons. The Bengal Delta Plain (BDP) has become one of the most severely contaminated parts in the world. Yet, there could be many more BDPs in India, which are yet to be explored. Pandey *et al.*¹ first reported arsenic contamination of the groundwater and the consequent human affliction at a village named Kaurikasa in erstwhile Madhya Pradesh (now Chhattisgarh), which does not share boundary or geology with BDP. A further paper by Pandey *et al.*² established the contamination of surface water due to the probable mobilization of contaminated groundwater. Now it is logical to see if the sediments are also contaminated in the affected locations of central-east India.

*For correspondence. (e-mail: drpiyush_pandey@yahoo.com)

In the BDP, the contaminated sediments have been implicated for arsenic contamination of the groundwater by various researchers³⁻⁶. Even though the exact source and mechanism for mobilization of As in BDP aquifers is not well understood, researchers suggest that geochemical processes are involved in mobilizing As from the sediments. The mechanism of reductive dissolution of iron oxyhydroxides has gained wider acceptance⁷.

The aim of this work was to see the levels of contamination of the sediments, the chemical environments that may mobilize arsenic and finally the quantity of arsenic which may be mobilized in differing chemical settings. The focal theme of research is that the contaminated sediment is a major cause of environmental problems and a key factor in the impairments to beneficial uses of the water bodies. Hence, it is imperative to assess the quantity of As which may easily mobilize, because it can play an important role in aquatic health and human-risk assessment. Sediments with high arsenic concentration can play an important role in the groundwater quality also, because sediments usually act as a sink for pollutants. Consequently, sediment-associated contaminants can influence the concentration of trace metal in both the water column and biota, if they are desorbed or become available to benthic organisms.

The bottom sediments serve as a reservoir for heavy metals and therefore deserve special consideration in the planning and design of aquatic pollution research studies. An undistributed sediment column contains a historical record of geochemical characteristic in the watershed. If a sufficiently large and stable sediment sink can be located and studied, it will allow an investigator to evaluate geochemical changes over time and possibly, to establish baseline levels, against which current conditions can be compared and contrasted.

Recent field and column studies suggest that the mobile colloids that can play an active role in the transport of sparingly soluble contaminants such as metalloids, radionuclides, transition metals and hydrophobic inorganic⁸⁻¹⁰ matter can be mobilized and transported in the environment, in response to changes in solution chemistry¹¹⁻¹⁷.

After finding the sediment As levels, the specific objective of our work was to evaluate sequential chemical extraction for assessing the quantity of readily mobilized As from contaminated sediment and to investigate the speciation of arsenic in air dried sediment extracted by different reagents. This work also assesses the type of arsenic fraction present in that condition, which could be effective to evaluate the source of arsenic or the form of arsenic present in particular sampling sites.

A large number of sediment samples (about 350) were collected from various locations in streams and rivers flowing through the Rajnandgaon district, Chhattisgarh. Shivnath is the major river of the region, that is perennial in nature, whereas most of the smaller streams of the region are dry during the pre-monsoon period (February–May). Many of the sampling locations were located in and around the Chowki block of Rajnandgaon district which has an undulating topography. This topography favours a rapid flow of the water and consequently, the small streams support smaller sediment quantity. The entire area falls in the Shivnath river basin and the river flows in the plain lower-lying bedrock and supports a large quantity of sediments.

The sediments samples were collected up to a depth of 10 cm from the surface by hand using a stainless coring tube. This depth was selected as it represents the most active phase of any sediment bed. The total arsenic in samples was measured after HNO_3 -HF-HClO₄ digestion, following the standard method¹⁸.

For analytical studies concerning sequential extraction, five sampling sites were chosen which had shown high contamination level. Tables 1 and 2 summarize the sequential extraction procedure and the solid phase targetted by each extractant. The supernatant thus obtained was filtered with 0.45-micron filter. The residue was then washed with distilled water to avoid any cross-contamination and acidified with 10% solution of nitric acid until pH < 2 (if required) and analysed by HGAAS as soon as possible. This technique is very sensitive with a detection limit of 5 ng/ml under optimum conditions.

The procedure was standardized by adding known amounts of some common As-bearing minerals and phases (each done in duplicate) separately, to sub-samples of dried homogenized sediments. The arsenic phases tested were orpiment (As_2S_3) and arsenopyrite (FeAsS). Comparison of the spiked samples to the unspiked ones provided a means of standardization of the method and the appropriate corrections were made on the result.

The results obtained demonstrate a high degree of arsenic contamination of the sediments in the Chowki–Rajnandgaon–Durg (CRD) region (Table 3). The Shivnath river draining the entire Chowki block, where Pandey *et al.*^{1,2} had established the presence of arsenic in the groundwater, soil and surface water, has favoured this spread. A mean level of 68.0 ppm arsenic has been identified in the sediments of the CRD region, with a 95% confidence level of 17.25 ppm and standard deviation of 41.81 ppm (Table 4). The value of standard deviation is smaller than the mean, and kurtosis and skewness values are positive and small.

Table 1. Sequential extraction–scheme 1 (adapted from ref. 25)

Extractable form of arsenic	Extractant
Exchangeable fraction	1 M $(\text{NH}_4)_2\text{SO}_4$
Easily reducible fraction	0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 0.1 M HNO_3
Moderately reducible fraction	0.1 M oxalic acid + 0.175 M ammonium oxalate

These values testify a stabilized contamination, where the arsenic values are more or less in equilibrium.

The sediment values are strongly influenced by the water in contact with the sediment. Hence our previous report identifying the surface water contamination stands justified (Table 5)². We have analysed the sediments at the anney-cut dam and the filter plant sand (refuse) of the Municipal Water Treatment Plant at Rajnandgaon. Both have shown a mean contamination of 60 and 44 ppm respectively. This observation clearly denotes the presence of As in the raw water, which is drawn from the Shivnath river.

This communication draws the attention of the scientific community towards the great potential of the rivers draining the arsenic-contaminated regions, for mobilizing arsenic which leads to contamination in the deltaic regions. This hypothesis stems from the fact that the scientists have failed to identify the major sources of arsenic in the BDP sediments. If the rivers draining any geologically arsenic-contaminated regions like central-east India are able to mobilize arsenic to the tune of about 62 tons per

annum (Table 6)², the amount which may be carried by the Ganges–Brahmaputra may be very high due to the sheer volume of water and sediment load.

Johnson and Thornton¹⁹ studied the seasonal variation of arsenic in the Carnon river, south-west England. In the study, majority of arsenic was found in the particulate phase (~80%); the authors suggest that sorptive or co-precipitation processes are responsible for the regulation of dissolved concentrations of arsenic in these waters. These processes are largely independent of pH. Adsorption appears to be important in the removal of arsenic from solution, with 80% being removed on entering estuarine waters.

A similar fate could be envisaged for the particulate-associated arsenic in rivers like Shivnath, Ganges and Brahmaputra. The delta region where the flow of water is sluggish and the salinity may favour the deposition of colloidal arsenic, could be a major source of arsenic. Thus, the delta plain of any river may be susceptible to arsenic contamination due to the deposition of arsenic. The sediment-bound arsenic thus brought, may become soluble by oxyhydroxide reduction in anaerobic conditions. Such a condition invariably exists in the delta regions of all south-east Asian countries and hence is being reflected in large-scale arsenic contamination.

After establishing the sediment contamination and its probable role in arsenic contamination of the deltaic region, it is worthwhile to analyse if this contamination can have any adverse impact on ecological and human health. Adverse effects of contaminated sediments on biological resources and threats to human health generally occur only when there is a pathway to ecological or human receptors. In most cases, such a pathway will only exist when surface sediments (those within the biologically active zone) are contaminated. Contaminated sediments existing at depths below the biologically active zone are unlikely to result in such effects unless the overlying sediments are removed by natural (e.g. erosion, scouring, etc.) or anthropogenic (e.g. dredging, etc.) means, or there are other mechanisms

Table 2. Sequential extraction–scheme 2 (adapted from ref. 26)

Extractable form of arsenic	Extractant
Water-soluble fraction	1 M ammonium chloride
Iron and aluminium bound	1 M ammonium hydroxide
Occluded	1 M ammonium oxalate
Calcium-bound	1 M hydrochloric acid

Table 3. Arsenic contamination of sediments in the CRD region

Sediment location	Total arsenic (ppm, mean values of appropriate number of samples)
Bagdai river 1	10.75
Bagdai river 2	88.0
Bagdai river hole	52.0
Boirdih dam 4	45.0
Boirdih dam 1	70.0
Boirdih dam 2	44.0
Boirdih dam 3	44.0
Boirdih dam 4	48.0
Boirdih dam 5	60.0
Boirdih dam 6	48.0
Boirdih dam 7	60.0
Confluence point of Dhangarh stream	72.0
Dhangarh stream 1	96.0
Dhangarh stream 2	90.0
Dhangarh stream before stop dam	120.0
Dhangarh stream stop dam	24.0
Dongargaon stream 1	56.0
Dongargaon stream 2	56.0
Filter plant sand at (WTP) Rajnandgaon	44.0
Gunderdehi pond	167.45
Gunderdehi pond 2	44.0
Shivnath Anney cut Rajnandgaon	60.0
Shivnath river 1	200.0
Shivnath river 2	56.0
Shivnath river 3	45.0

WTP, Municipal water treatment plant.

Table 4. Arsenic contamination of CRD region sediments: statistical analysis of the results

Statistical parameter	Value
Mean	68.008
Standard error	8.36
Median	56
Mode	44
Standard deviation	41.81
Sample variance	1748.41
Kurtosis	4.05
Skewness	1.91
Range	189.25
Minimum	10.75
Maximum	200
Sum	1700.2
Count	25.00
Confidence level (95.0%)	17.25

Table 5. Arsenic contamination of rivers of the region (adapted from Pandey *et al.*²)

River	Location	District	Maximum level of arsenic (µg/l)	Season when noted
Shivnath	Ambagarh–Chowki	Rajnandgaon	190	Monsoon
Shivnath	Rajnandgaon	Rajnandgaon	180	Post-monsoon
Shivnath	Durg	Durg	300	Monsoon
Bagdai	Bagdai	Rajnandgaon	100	Post-monsoon
Kharun	Kumhari	Raipur	< 5	Annual mean

Table 6. Arsenic mobilized by the Shivnath river during the year 1999 (adapted from Pandey *et al.*²)

Month	Mean monthly flow (million cubic meter)	Mean arsenic (µg/l)	Total arsenic mobilized during the month (kg)	Total As mobilized (tons per annum)
January	5.78	0.00	0.00	0.00
February	2.84	0.00	0.00	0.00
March	0.90	0.00	0.00	0.00
April	0.22	0.00	0.00	0.00
May	0.00	0.00	0.00	0.00
June	96.35	6.00	578.10	0.58
July	448.11	60.00	26019.29	26.02
August	877.27	19.00	16130.45	16.13
September	453.06	40.00	18122.40	18.12
October	164.42	11.00	1750.28	1.75
November	35.19	0.00	0.00	0.00
December	7.49	0.00	0.00	0.00
Total	2091.63		62600.52	62.60

for the release of sediment contaminants that exposure may occur. Hence, the focus of sampling in the sediment source control programmes is generally on the sediments within the biologically active zone. Additionally, the surface sediment will most likely exhibit impacts from recent discharges of contaminants²⁰. In the present work, the sediments were sampled up to a depth of 10 cm only, which is the most biologically active zone.

The US-EPA has reported a background level of arsenic in different sediment samples²¹. Comparing the reported no effect level (NEL) and low effect level (LEL) of the sediments, it appears that the sediments in the CRD region are in a distressed condition as the arsenic concentration is about ten times higher than the low effect range of arsenic in freshwater sediments (Table 7).

On finding high contamination in the CRD region, we carried out a comparative study for the contamination levels in BDP rivers and other rivers of Chhattisgarh (CG). For this purpose, about 50 samples were collected from the BDP rivers (particularly Ajay river in Burdwan district, WB and Ganga in Kolkata) and two major rivers of Chhattisgarh, i.e. Indrawati in Bastar and Hasdeo in Korba. The aim of the work was to compare the results and use the reported sediment data as a quality control check. The entire sampling and analyses at both CG and BDP were carried out during 1999–2001. Table 8 shows that though

Table 7. Comparison of the results at the studied site with US-EPA-established sediment quality guidelines

Location	As (ppm)
Average concentration in CRD sediment (the present work)	68.00
Stream sediments in England and Wales ²⁷	5–8
Non-polluted great lakes ²⁸	< 3
No effect level ²⁹	4–8
Effects range low, marine sediments ³⁰	8.2
No adverse biological effects, marine sediments ³¹	57
Control sediments, southern California ³²	03–15
Control sediments, Puget Sound ³²	03–15
No effect threshold, freshwater sediments ³³	3
Lowest effect level, freshwater sediments ³⁴	6
Threshold effect levels for freshwater sediments ³⁵	5.9
Threshold effect levels for marine sediments ³⁵	7.24
Effects range low, freshwater ²⁴	13

the area of CRD is smaller than that of BDP, the level of contamination in CRD during 1999–2001 was far higher than that in BDP and other rivers of CG. Analysis of Indrawati river was particularly important, as its basin is adjacent to the Shivnath–Mahanadi basin. Similarly, the Hasdeo river is the hub of large-scale mining and industrial activities, viz. coal mining, power generation, aluminium production, etc. The results indicate that the level of contamination in both Indrawati and Hasdeo rivers is less compared to the

Shivnath sediment in the CRD region. We intend to extend the work in the entire Shivnath–Mahanadi basin to get a complete picture.

When the CRD region is contaminated, it would be logical to compare the contamination level with similar contaminated sediments in other parts of the world. This comparison (Table 9) establishes a comparatively lower level of contamination in CRD. Yet, these levels cause some biological effects. This fact is attested by lower productivity of the Shivnath river as far as fish population is concerned. Another study on assessing the sediment toxicity is being carried out at our laboratory.

Determining arsenic mobility from the contaminated sediment is the next priority. The same has been attempted here with the help of two sequential extraction schemes. Scheme 1 attempts to determine the chemical mobility of the sediment bound arsenic and the Scheme 2 attempts to determine the mineral assemblages of arsenic in the sediment.

Arsenic is widely distributed in a large number of minerals. The highest mineral concentrations generally occur as arsenides of copper, lead, silver or gold or as the sulphide. Major arsenic-containing minerals are arsenopyrite (FeAsS), realgar (As_4S_4), and orpiment (As_2S_3). The arsenic content of the earth's crust is 1.5–2 mg/kg; it ranks 20th in abundance in relation to other elements²². Table 10 presents the range of arsenic in general assemblages. However, minerals like gold, copper, uranium, etc. which are generally associated with sulfidic ores, may contain higher concentration of arsenic in any igneous or sedimentary sequence.

The natural level of arsenic in sediments is usually

below 10 mg/kg dry weight. Bottom sediments can become substantially contaminated by arsenic from man-made sources. Levels of up to 10,000 mg/kg dry weight were found in bottom sediments near a copper smelter in Washington, USA²³. The reason for high arsenic in the sediments of the CRD region appears to be geologic. Pandey *et al.*² reported that there exists a geological anomaly in this part of central India. The formations of this arsenic contaminated area belong to Lower–Middle Proterozoic age. The country rocks comprise phyllitic shales and haematitic quartzites, which are part of the Lower Proterozoic age formations popularly called the Bailadila group. This group consists of banded hematite/ magnetite quartzite and an iron-ore mine situated at Dalli–Rajhara about 25 km east of Kaurikasa. The western part of the Rajnandgaon district shows extensive volcanism and the rocks of 'Nandgaon group' consist of lower 'Bijli Rhyolites' and 'Pitepani volcanics'. This volcanic phase was followed by the emplacement of 'Dongargarh granites', intrusion of meta-dolerite dykes and quartz veins. The arsenic-contaminated area, which forms the eastern periphery of the Dongargarh granite batholiths, consists of metabasalt and metarhyolites. The area shows shearing parallel to N–S and NW–SE and a low-grade metamorphism. Pandey *et al.*² have identified the sporadic presence of arsenopyrites in the highly sheared, metamorphosed contact zones between the metabasalts and metarhyolites, which are auriferous and uraniferous at different locations. Thus, the origin of arsenic is clearly geologic, affected by the 'Nandgaon orogeny'.

Table 11 shows arsenic extracted using Scheme 1 and Scheme 2 extractants. The amount of arsenic extractable ranges between 26.4 and 7.9%. Matrix-wise, Scheme 1 has extracted about 12.5 and 18.5% and Scheme 2 has extracted about 12.5 and 16% arsenic from the river sediments and soils respectively. As the results in both schemes are in close proximity, both schemes essentially target similar types of mineral assemblages.

Sequential extraction experiments were conducted on ten samples of contaminated sediments. Five of these were stream sediments and rest were soil/deep-bore soil. The results present a significant outcome. Figures 1 and 2 show the chemical nature of arsenic-contaminated sediment ascertained by Scheme 1 and the mineral assemblages in which

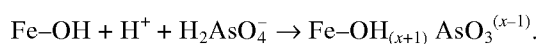
Table 8. Arsenic contamination of some sediment samples in CG and BDP rivers

Sample	Mean arsenic level (ppm)	Arsenic concentration range (ppm)
Indrawati river, Bastar, CG	2.5	0.5–14
Hasdeo river, Korba, CG	5.9	0.3–24
Ganga river sediment, BDP	2.6	1.2–11
Brahmaputra river sediment, BDP ³⁶	–	1.4–5.9
Meghna river sediment, BDP ³⁶	–	1.3–5.6
Ajay river, BDP	3	0–15
Shivnath CRD region, CG	68	8–209

Table 9. Comparison of the results with reported sediment contamination in other parts of the world

Sample site	Range (mg/kg)	Reference
Mining-contaminated lake sediment, British Columbia	80–1104	Azcue <i>et al.</i> ³⁷
Mining-contaminated reservoir sediment, Montana	100–800	Moore <i>et al.</i> ³⁸
Industrially polluted inter-tidal sediments, USA	0.38–1260	Davis <i>et al.</i> ³⁹
Soil and tailing, British Columbia	396–2000	Azcue <i>et al.</i> ³⁷
Soil and tailing-contaminated soil, UK	120–52600	Kavanagh <i>et al.</i> ⁴⁰
Soil below chemical factory, USA	1.3–4770	Hall <i>et al.</i> ⁴¹
Freshwater sediment in CRD region of central-east India	8–209	The present study

the arsenic is bound respectively. The data for total extractable and non-extractable arsenic by the respective scheme are also presented. Data analysis makes it clear that arsenic mobility from the CRD sediment is somewhat limited, but the reverse is true in case of the deeper soil. Exchangeable arsenic (64%) dominated the extractable arsenic (~ 19%) in deep-soil samples, signifying the geological presence of easily soluble arsenic which has not encountered the water. A lesser abundance of the exchangeable arsenic (~ 30%) and concomitant increase in the reducible fractions (~ 70%) indicate the possible adsorption of As (V) onto appropriate adsorbent in stream sediments. Both observations are consistent with the arsenic chemistry, where it is well established that As(V) sorbs onto sediments, and co-precipitation with iron and manganese oxyhydroxides is known to happen. The surface reaction which may take place is as follows:



This particular result obtained by us showing a higher presence of exchangeable arsenic in the deep soil of the arsenic contaminated region holds the key to the genesis of arsenic.

The probable associations of arsenic with various mineral assemblages were verified in Scheme 2 extractions (Figure 2). Here, it was observed that the average easily extractable arsenic (~ 15%) in soil and sediment matrices

is dominated by calcium bound arsenic (~ 40%) and is followed by Fe–Al-bound arsenic (~ 30%) and arsenic occluded in Fe–Al oxides (~15%). It is worth noting that total-in-sediment digestion method using $\text{HF-HClO}_4\text{-HNO}_3$ yielded high values. Hence, the amount of arsenic not extracted by Scheme 2 was as high as ~ 85%. This indicates that this arsenic is silicate-bound. The silicate compounds which were observed in the sediments of the CRD region were quartz (SiO_2), feldspar (KAlSi_3O_8 , $\text{NaAlSi}_3\text{O}_8$, $\text{CaAl}_2\text{Si}_2\text{O}_8$, and intermediate compositions), micas, amphiboles, pyroxenes, olivine and clays. The oxides and hydroxyoxides were corundum (Al_2O_3), hematite (Fe_2O_3), pyrolusite (MnO_2), ilmenite (FeTiO_3), sphene (CaTiOSiO_4), goethite and lepidochrosite (FeOOH), and ferrihydrite ($(\text{FeOOH})_5(\text{H}_2\text{O})_2$). The carbonates were mainly calcite (CaCO_3) and dolomite $\text{CaMg}(\text{CO}_3)_2$.

Based on the identification of the phases carried, the higher calcium-bound fraction in both the soil and sediment indicates that As is mainly clay-adsorbed. As(V) is expected to be strongly adsorbed by calcium carbonate because of the oxide-like character of its edges. Thus, it can be concluded that a large portion of the arsenic in CRD sediments is in a complex silicate matrix, or is calcium-bound. In either condition, its mobility will be severely limited. Still 15% easily extractable As species will mean the probable mobilization of 15 ppm arsenic from a sediment having As level of 100. This 15-ppm level may be contrasted with low effect freshwater level of 13 ppm prescribed by EPA³³.

The sediment of the CRD region is contaminated with arsenic. The enrichment factor of arsenic is as high as 40 compared to the average sediment background level of 5 ppm. We once again highlight our hypothesis that the adsorbed arsenic brought from upstream in the form of colloidal particles could be the major source of arsenic to the delta regions. Shrivnath river shows a moderate contamination compared to many other heavily contaminated sediment of the world. Yet, the levels surpass the sediment-quality guidelines and are expected to cause adverse effects on the aquatic environment.

Table 10. Arsenic concentration in crustal materials (adapted from ref. 22)

Rock	Type	As (ppm)
Ultrabasic	Igneous	0.3–16
Basalt	Igneous	0.06–113
Andesite	Igneous	0.5–5.8
Silicic, volcanic	Igneous	0.2–12.2
Limestone	Sedimentary	0.1–20
Sandstone	Sedimentary	0.6–120
Shales and clay	Sedimentary	0.3–490
Phosphorites	Sedimentary	0.4–188

Table 11. Arsenic extractability from the contaminated sediment

Sample site	Nature of sample	Arsenic concentration	Percentage extracted As in Scheme 1	Percentage extracted As in Scheme 2
Boirdih dam 1	Sediment	111	14.2	13.5
Dhanagarh stream 1	Stream sediment	96	11.8	12.7
Dhanagarh stream 2	Stream sediment	90	11.2	9.9
Dhanagarh–Shrivnath confluence point 1	Stream sediment	72	11.7	12.6
Dhanagarh–Shrivnath confluence point 2	Stream sediment	70	12.6	13.5
Murethitola 140–160 ft–1	Borehole soil	65	24.7	20.8
Murethitola 140–160 ft–2	Borehole soil	68	26.4	22.5
Murethitola 140–160 ft–3	Borehole soil	72	23.6	19.7
Murethitola 200–220 ft–1	Borehole soil	350	8.5	7.9
Murethitola 200–220 ft–2	Borehole soil	320	8.1	8.0

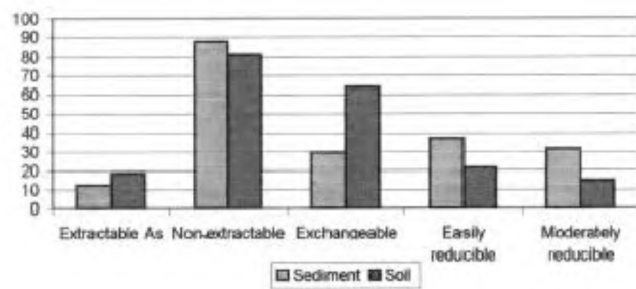


Figure 1. Chemical nature of arsenic-contaminated sediment ascertained by Scheme 1.

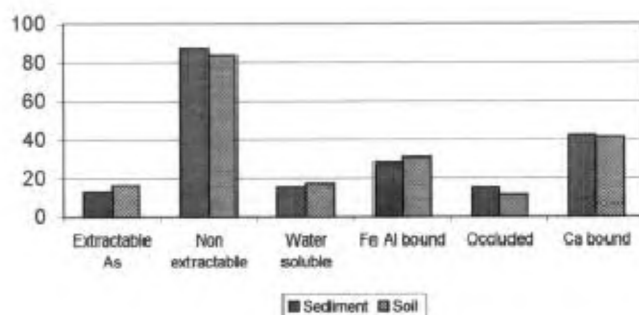


Figure 2. Determination of As-bearing phases by Scheme 2.

Sequential extraction analyses show that Scheme 1 has extracted about 12.5 and 18.5% arsenic and Scheme 2 about 12.5 and 16% arsenic from the river sediments and soils respectively. Arsenic mobility from the CRD sediment is somewhat limited, but the reverse is true in case of the deeper soil. Exchangeable arsenic (64%) dominated the extractable arsenic (~ 19%) in deep-soil samples, signifying the geological presence of easily soluble arsenic. A lesser abundance of exchangeable arsenic (~ 30%) and concomitant increase in the reducible fractions (~ 70%) indicate the possible adsorption of As (V) onto appropriate adsorbents in stream sediments.

Geochemically, the ionically exchangeable As present in this sediment may be released on increase in the ionic strength of water, as it happens in the case of increasing salinity of water by human activities or heavy draw-down of groundwater. Similarly, any increase in the competing ions, viz. PO_4 , NO_3 , etc. will result in a release of As strongly bound with Fe–Al oxides or clays. Such competing ions are invariably present in agricultural run-offs and their strength increases on the use of fertilizers. Thus, the sediment contamination of CRD should be a matter of concern, and care should be taken to monitor the geochemical conditions that may trigger its release to the overlying water column.

1. Pandey, P. K., Khare, R. N., Sharma, S., Sar, S. K., Pandey, M. and Binayke, P., Arsenicosis and deteriorating groundwater quality; Unfolding crisis in central-east Indian region. *Curr. Sci.*, 1999, **77**, 686–693.

2. Pandey, P. K., Yadav, S., Nair, S. and Bhui, A., Arsenic contamination of the environment: A new perspective from central-east India. *Environ. Int.*, 2002, **28**, 235–345.
3. Acharya, S. K., Chakraborti, P., Lahiri, S., Raymahashay, B. C., Guha, S. and Bhowmik, A., Arsenic poisoning in Ganges delta. *Nature*, 1999, **401**, 545.
4. Chowdhury, T. R., Basu, G. K., Mandal, B. K. and Biswas, B. K., Arsenic poisoning in the Ganges delta. *Nature*, 1999, **401**, 546.
5. Saha and Chakraborti, C., Geological and geochemical background of the As bearing groundwater occurrence of West Bengal. In Proceedings of the International Conference on Arsenic in Groundwater: Cause Effect and Remedy, Kolkata, 1995.
6. Nickson, R. T., McArthur, J. M., Ravenscroft, P., Bergus, W. G. and Ahmed, K. M., Mechanism of arsenic release to ground water, Bangladesh and West Bengal. *Appl. Geochem.*, 2000, **15**, 403–413.
7. Nickson, R., McArthur, J., Bergess, W., Ahmed, K. M., Ravenscroft, P. and Rahman, M., Arsenic poisoning of Bangladesh groundwater. *Nature*, 1998, **395**, 338.
8. Drever, J. I., *The Geochemistry of Natural Waters*, Prentice-Hall, Englewood Cliffs, NJ, 1982.
9. Linke, W. F., *Solubilities—Inorganic and Metal Organic Compounds*, A-Ir, Van Nostrand, New York, 1958, vol. 1, 4th edn.
10. Garrels, R. M. and Chrost, C. L., *Solutions, Minerals and Equilibria*, Harper and Row, New York, 1965.
11. Stumm, W. and Morgan, J. J., *Aquatic Chemistry*, Wiley-Interscience, New York, 1981, 2nd edn.
12. Swalin, R. A., *Thermodynamics of Solids*, Wiley Interscience, New York, 1972, 2nd edn.
13. Ryan, J. N., Master's thesis, Massachusetts Institute of Technology, 1988.
14. Baes, C. F. and Mesmer, R. E., *The Hydrolysis of Cations*, Wiley Interscience, New York, 1976.
15. Roy, S. B. and Dzombak, D. A., Dietary garlic extract in modifying clastogenic effects of inorganic arsenic in mice: Two generation studies. *Colloids Surf. A*, 1996, **107**, 245–262.
16. Lerman, A., *Geochemical Processes—Water and Sediment Environments*, Wiley-Interscience, New York, 1979.
17. Gschwend, P. M. and Reynolds, M. D., Monodisperse ferrous phosphate colloids in an anoxic groundwater plume. *Contam. Hydrol.*, 1987, **1**, 309–327.
18. APHA, American Public Health Association, Standard methods for the examination of water and wastewater, Washington DC, USA, 1992.
19. Johnson, C. A. and Thornton, I., Hydrological and chemical factors controlling the concentration of Fe, Cu, Zn and As in a river system contaminated by acid mine drainage. *Water Res.*, 1987, **21**, 359–365.
20. Guidance on the development of sediment sampling and analysis plans meeting the requirements of the sediment management standards, Washington State Department of Ecology, Ecology Publication No. 95-XXX, December 1995, Chapter 173–204 WAC.
21. USEPA, Determination of background concentrations of inorganics in soils and sediments at hazardous waste sites, EPA/540/s-96/500, 1995.
22. Medical and biologic effects of environmental pollutants: Arsenic, National Academy of Sciences, Washington, DC, 1977.
23. Crecelius E. A., The geochemistry of arsenic and antimony in Puget Sound and Lake Washington, Thesis, University of Washington, Seattle, Washington, 1974.
24. Ingersoll, C. G., Haverland, P. S., Brunson, E. L., Canfield, T. J., Dwyer, F. J., Henke, C. E. and Kemble, N. E., Calculation and evaluation of sediment effect concentrations. *Great Lakes Res.*, 1996, **22**, 602–623.
25. Brannon, J. M. and Patrick, W. H., Transformation and mobilization of arsenic in sediments. *Environ. Sci. Technol.*, 1987, **21**, 450–459.

26. Iverson, D. G., Holm, T. R. and Stanforth, R. R., An evaluation of column chromatography and flameless atomic absorption spectrophotometry for arsenic speciation as applied to aquatic system. *Environ. Sci. Technol.*, 1979, **13**, 1491–1494.
27. United Nations synthesis report on arsenic in drinking water, <http://www.who.int/watersanitation-health/Arsenic>, 2002.
28. US Army Corps of Engineers Ecological evaluation of proposed discharge of dredged or fill material into navigable water, Interim guidance for implementation of section 404(b)(1) of public law 92–500 (Federal water pollution control act amendments of 1972), 1977, misc. paper D 76–17.
29. Persaud, D., Jaagumagi, R. and Hayton, A., Development of provincial sediment quality guidelines, Ontario Ministry of the Environment, Water Resource Branch, Aquatic Biology Section, Toronto, Canada, 1989, pp. 19.
30. Long, E. R., MacDonald, D. D., Smith, S. L. and Calder, F. D., Incidence of adverse biological effects within range of chemical concentration in marine and estuarine sediments. *Environ. Manage.*, 1995, **19**, 81–87.
31. Sediment management standards, Washington State Department of Ecology, 1991, chapter 204.
32. Lee, H., Boese, B. L., Pelletier, J., Winsor, M., Specht, D. T. and Randall, R. C., *Guidance Manual, Bedded Sediment Bioaccumulation Tests*, US Environmental Protection Agency, Newport, OR, 1992, EPA/600/x89/302, ERLN-N111.
33. Criters intermimaries pour l'Evaluation de la quality des sediments du saint – Laurent, Environment Canada et Ministere de l'Environnement du Quebec, 1992.
34. Persaud, D., Jaagumagi, R. and Hayton, A., Guidelines for the protection and management of aquatic sediment quality in Ontario, Ontario Ministry of the Environment, Toronto, Canada, 1992.
35. Interim sediment quality assessment values, Manuscript report no. ECD, Ecosystem conservation, Directorate Environment Canada, Ontario, 1994.
36. Datta and Subramaniam (1997) In UN synthesis report on arsenic in drinking water, <http://www.who.int/watersanitation-health/Arsenic>, 2002.
37. Azcue, J. M., Mudroch, A. and Rosa, F., Hall GEM, Effects of abandoned gold mine tailings on the arsenic concentrations in water and sediments of Jack of Clubs Lake, BC. *Environ. Technol.*, 1994, **15**, 669–678.
38. Moore, J. N., Ficklin, W. H. and Johns, C., Partitioning of arsenic and metals in reducing sulfidic sediments. *Environ. Sci. Technol.*, 1988, **22**, 432–437.
39. Davis *et al.*, in ref. 36.
40. Kavanagh, P. J., Farago, M. E., Thornton, I. and Braman, R. S., Bioavailability of arsenic in soil and mine wastes of the Tamar Valley, SW England. *Chem. Spec. Bioavail.*, 1997, **9**, 77–81.
41. Hall, L. L., George, S. E., Kohan, M. J., Styblo, J. and Thomas, D. J., *In vitro* methylation of inorganic arsenic in mouse intestinal cecum. *Toxicol. Appl. Pharmacol.*, 1997, **147**, 101–109.

Received 21 June 2003; revised accepted 18 September 2003

Ammonites as biological stopwatch and biogeographical black box – a case study from the Jurassic–Cretaceous boundary (150 Ma) of Kutch, Gujarat

Sabyasachi Shome^{†,*}, Soma De[#], Pinaki Roy[#] and Shiladri S. Das[‡]

[†]Geological Survey of India, 15 Kyd Street, Kolkata 700 016, India

[#]Department of Geological Sciences, Jadavpur University, Kolkata 700 032, India

[‡]Geological Studies Unit, Indian Statistical Institute, 203 B.T. Road, Kolkata 700 035, India

Some ammonites provide high time resolution and some others record precise palaeolatitudinal position of the sedimentary basins which harboured them. The Late Jurassic fossil record in Kutch was poor until recently. The present discovery of four genera, viz. *Micracanthoceras*, Spath, 1925; *Durangites*, Burckhardt, 1912; *Coronogoceras*, Spath, 1925 and *Tithopeltoceras*, Arkell, 1953 helps in drawing precisely the Jurassic–Cretaceous system boundary in Kutch and in palaeocontinental reconstruction. Besides, faunal migrational pathways across different palaeobiogeographical provinces have been discussed.

THE nature of the fossil record reveals that many taxa spent 'a little hour of grace' on the earth yet flourished and had wider and rapid biogeographic dispersal. They are aptly described as 'fleeting fossil'¹. Many ammonites are fleeting fossils and had great geochronological importance. In fact, they were used as zonal indices for slicing up the earth's rocks, especially the Mesozoic into finer time segments. Hence they are the biological stopwatch.

Besides, ammonites are environmentally sensitive. They are exclusively marine and often climatically and latitudinally restricted. Since the Jurassic, when the earth's last continental fragmentation started, land masses were wandering in different directions. Some continents broke away, while others collided. India, once a member of the lost Gondwana supercontinent, started rifting during the Late Cretaceous (90 Ma ago)² and made a solitary journey of about 5000 km before hitting the Asian plate; the collision resulted in the upheaval of the mighty Himalayas. The wandering continents, however, acted as a 'Viking funeral ship' or 'Noah's ark' and rafted fossils albeit ammonites with them. Ammonites, mostly being biogeographically and climatically restricted, inscribed their latitudinal signatures in the rock book like geomagnetic anomalies and thus acted as a black box^{2–4} thus helping reconstructing the continental disposition of the past^{5–7}.

During the Middle Jurassic, the Kutch basin came into being⁸. The first phase of Gondwana fragmentation separated West Gondwana comprising Africa and South

*For correspondence. (e-mail: sabyasachi60@hotmail.com)