Direct and indirect arsenic release from soaps by unhygienic use in tubewells

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Microorganisms have been implicated in the release of arsenic into drinking water involving bio-electrochemical reactions. Iron reducer has been shown to release captive arsenic from insoluble ferric oxyhydroxide–arsenic oxide adduct. Sulphate reducing bacteria (SRB) and Enterobacteriaceae may play a similar role by releasing hydrogen sulphide. The case of arsenic mobilization in water may be complex and varied. Arsenic contamination in Kanpur, northern India, 1000 km upstream of the Gangetic delta, added a new dimension to understanding the cause of its release in water. We propose that passive arsenic carried by the Ganges in the soil for centuries may be activated by unhygienic use of tubewells during the past three decades. We modelled the soil redox-chemistry prevalent under such conditions. We show that SRB grow in the vicinity of tubewells due to the availability of abundant food as fatty acids and sulphate as electron acceptors from soaps and detergents to release arsenic. In the absence of soap, Enterobacteriaceae play the same role. We also show that 26 commonly used soaps and detergents in India contain alarmingly high concentration of soluble arsenic, contaminating surface water.

Keywords: Arsenic, contamination, detergents, soaps, tubewells.

ARSENIC present in the Gangetic valley as alluvial deposit is primarily believed to have originated from the Himalayas. Soil samples on the bank of the Ganges were collected randomly from Kolkata (West Bengal) to Hardwar (Uttaranchal) and also from the banks of the Yamuna river from Delhi to Allahabad (Uttar Pradesh). Around 100 sites were tested and found to contain 1–4 $\mu g g^{-1}$ of dormant arsenic. The presence of arsenic in water at Kanpur has been detected in November 2004, nearly 20 years since the first report of arsenic contamination in the Bengal delta[1]. Arsenic contamination in Ballia, eastern Uttar Pradesh has also been reported[2]. The Ganges valley has been affected from Kolkata to Kanpur. In contrast, there is no report of arsenic contamination in the waters of the Yamuna valley region so far. Arsenic contamination upstream of the Ganges ruled out any special geological role of the Gangetic delta.

Before 1970, the source of potable water was similar for the entire Ganges and Yamuna regions. In the seventies, irrigation programmes using fertilizers started in northern India, including the Bengal delta. Hence this may not be the main cause of site-selective arsenic release. In contrast to the largely dry parts of northern India, the Bengal delta suffers from heavy rainfall and submersion of low-lying areas under stagnant water for almost the entire year. Therefore, the only notable difference could be the use of water from the large number of tubewells to avoid infected surface water in the Bengal region. Digging of tubewells started upstream of the Ganges from Bengal to northern India with the passage of time. The time gap of roughly 20 years of arsenic release between the Bengal delta and Kanpur may be synchronized with the time lag of digging these tubewells for drinking water in these regions[3–5].

Figure 1 *a* represents a tubewell in Shuklaganj, Kanpur being extensively used by a large number of people for drinking, bathing, washing and other household purposes. Water from this tubewell showed the presence of arsenic (10 $\mu g l^{-1}$). About 200 people on an average utilizing 10 g of bar soap/detergent per person dump roughly 2 kg of soap per day in the vicinity of any such tubewell. To have an understanding about localized arsenic mobilization, we assumed that if soap and detergent can supply fatty acids as food and sulphate as electron acceptors for sulphate reducing bacteria (SRB), then their presence in the mud near these tubewells would provide an important clue.

Water from 20 tubewells situated in congested localities and distributed on both banks of the Ganges at Kanpur was tested. Only eight samples tested positive for the presence of arsenic. This may be the beginning of arsenic release into water at Kanpur. Therefore, we decided to find out the distribution pattern of arsenic release among tubewells which have been in use for the same period of time and are situated close to each other. We could identify two tubewells separated by a distance of 0.5 km, which showed sharp difference in arsenic contamination. Tubewell-1 showed the presence of arsenic (8 $\mu g l^{-1}$) and its mud is black showing the presence of Fe(II) and sulphide. Tubewell-2 did not contain any detectable level (0.05 μg) of arsenic and its mud (brown) showed only the presence of Fe(III) (Figure 1 *b*, *c*).

Incubation of mud washed water (tubewell-1) in the presence of ten commonly used soap and detergent solutions revealed that all such solutions aggressively help proliferate SRB (Figure 2).

Water leached out from freshly collected mud from these two sites was tested for the presence of SRB and Enterobacteriaceae (Figure 3 *a*). For tubewell-2, precipitation of FeS is negligible under identical conditions (Figure 3 *b*).

However, both the mud-washed water samples responded to form FeS readily under SIM medium. All these soap/detergents contained appreciable quantity of phosphate and sulphate. Surprisingly, all of these widely used soap/

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detergents, contained high concentration of free arsenic (μg g^{-1}) in soluble form: e.g. Liril (6.0), Lux (6.0), Hamam (6.5), Breeze (5.0), Pears (1.5), Wheel (5.0), Rin (10.0), Surf Excel (5.5), Rin Adanced (4.5), Vim (7.0) from Hindustan Lever; Cinthol (7.0), No-1 (4.0) from Godrej; Nirma soap (4.5), Nirma detergent (5.0) from Nirma Ltd; Mysore Sandal (6.0) from Karanataka Soaps; Johnson baby soap (2.0) from Johnson and Johnson; Fresh (4.5) from Vanesha Herbal; Ghari soap (6.0), Ghari detergent (4.0) from Kanpur Detergents and Chemicals; Plus (4.0) from Corana Plus Industries; Cycle (6.0) from Shyam Detergent; PSM (3.0) from Kanpur; Doctor (0.2) from Kanpur; Ariel (4.0), Tide (1.0) from Proctor and Gamble and Henko (0.0) from Henkel. Interestingly, Oil of Olay soap made in USA (Proctor and Gamble) contained least arsenic (0.2) amongst the body soaps tested. All these soaps and detergents readily released arsenic in surface water. Henko detergent does not contribute any fresh arsenic in water, and Johnson baby soap and Doctor brand soap do not contain any phosphate.

At this stage we made a water-insoluble mixed oxyhydroxide adduct comprising Fe(III)–Mn(II)–As(V) (125 : 25 : 1) at pH ~ 7. This adduct was treated as a model arsenic-infected soil. The mud extract containing SRB was then incubated along with the model soil in two different culture media. One was the SIM and the other was a modified bactosulphate API (SR)-soap medium[6] using soap solutions as the source of carbon (fatty acid). After initial three days, arsenic was released and reached a stationary phase after 10 days (Figure 4 *a*). Under SIM medium, the enhanced release of arsenic is due to the added activity of Enterobacteriaceae along with SRB. With modified soap media, the delay in release of arsenic is due to the activity of SRB only, as known strains of Enterobacteriaceae did not grow in this medium. The modified soil showed formation of FeS during progress in the incubation period.

Reduction of arseniferric oxyhydroxide holding the As(V)-oxide is the key factor to the release of arsenic in water. Subsequently, the generated H_2S can have four options

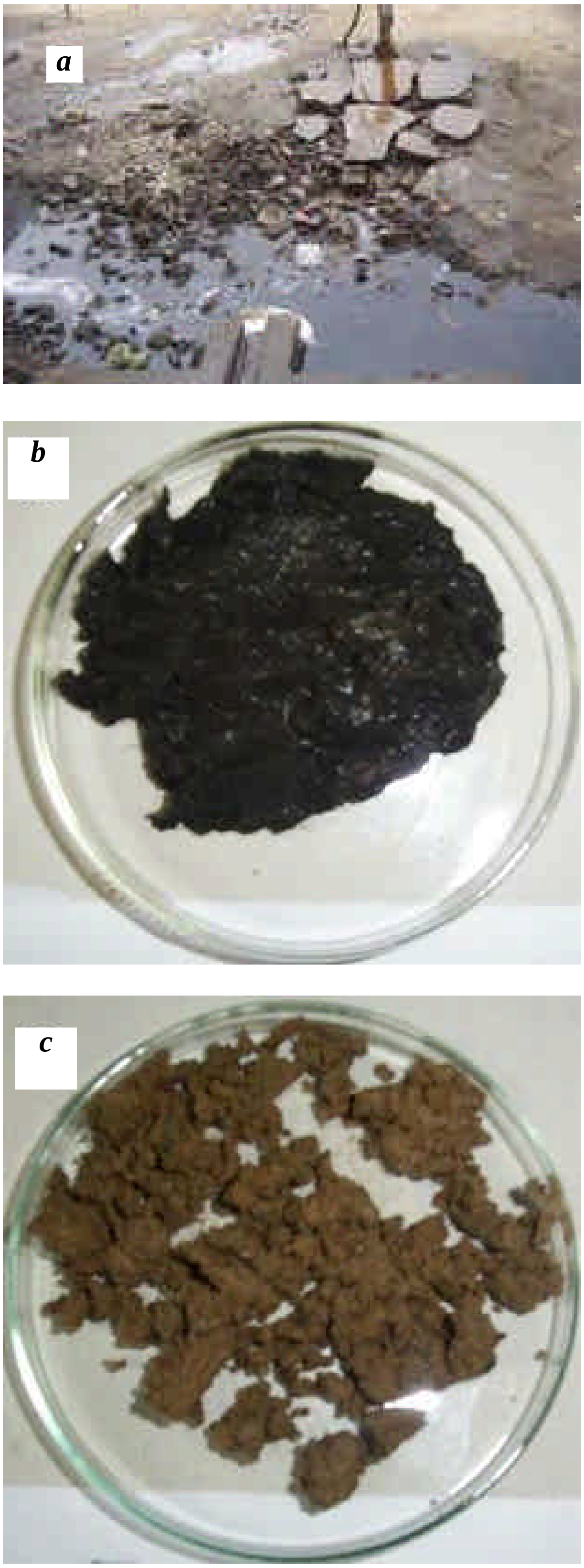

Figure 1. ***a***, A typical widely used tubewell contaminated with arsenic (Shuklaganj, Kanpur) displaying unhygienic surroundings with water-logged, stagnant condition. ***b***, ***c***, Mud collected from Bhagwatghat tubewell-1 (***b***), and tubewell-2 (***c***) (separated by 0.5 km). Both tubewells are 8 years old and have moderate depth.

Figure 2. The precipitation of FeS due to activity of SRB containing different soap–detergent solution (as the only carbon source) modified media after 5 days of incubation with mud-leached water from tubewell-1, and control (C, extreme right).

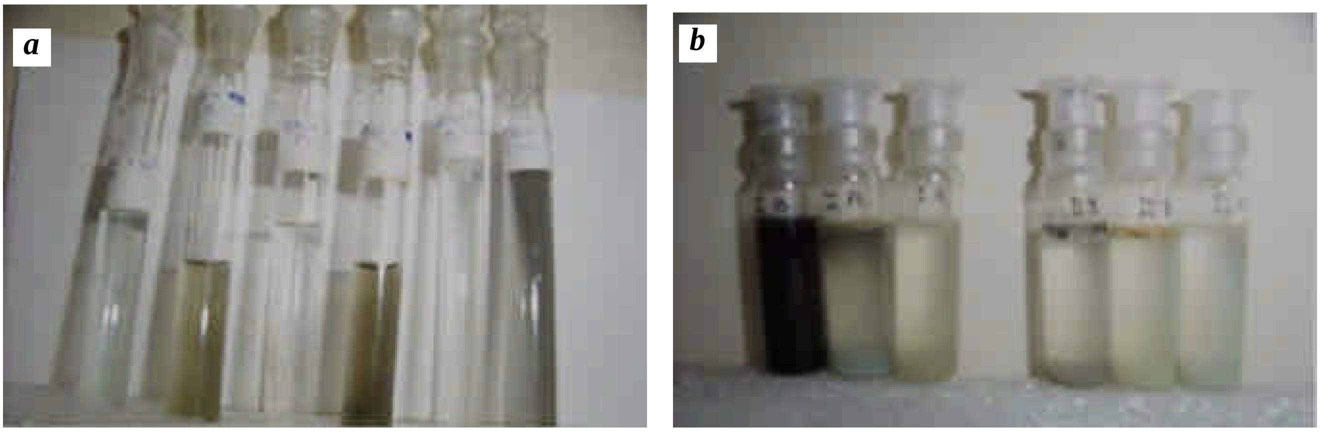

Figure 3. ***a*** (left and middle pair tubes) Salmonella and *Proteus vulgaris*, sulphide-yielding Enterobacteriaceae in modified bactosulphate API (SR)-soap medium (left tube, no growth) and in SIM medium (right tube, growth). (Right pair) Control tube and (extreme right), mud extract from Bhagwatghat tubewell-1 in modified sulphate API (SR)-soap medium. ***b***, (left) Mud extract from Bhagwatghat tubewell-1 incubated with three different soap-containing modified sulphate API (SR)-soap medium. (Right) Mud extract from Bhagwatghat tubewell-2 after 7 days of incubation showing (cf. left panel) trace amounts of FeS precipitation.

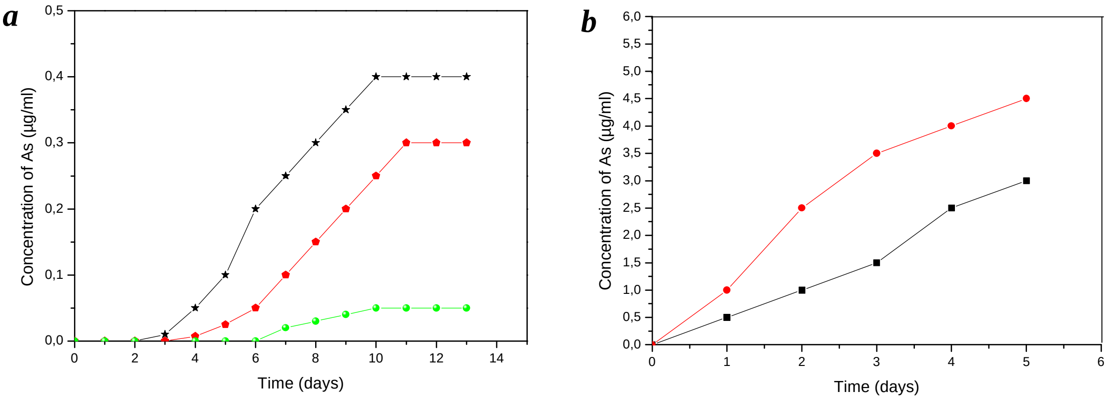

Figure 4. ***a***, Arsenic releasing profile under SIM (black) and under modified soap medium (red), control (green); ***b***, Dissolution profile of arsenic from pure As_2S_3 (black) and FeS/As_2S_3 (red) at pH 7. Data were average of three determinations from the same batch.

to act: (i) reduction of available Fe(III); (ii) reaction with metals ions like Fe(II) to precipitate FeS; (iii) Reaction with As(V) to reduce it to As(III) and (iv) Precipitation of As_2S_3. Controlled reactions established that the reduction of Fe(III) to Fe(II) is the first step followed by precipitation of FeS at a pH around 7. As(V), if present, is partly absorbed by the precipitating FeS, but remained in solution in fairly high concentration. Reduction of As(V) to As(III) is a slow process. When As(III) is directly used instead of As(V), As_2S_3 is largely coprecipitated with FeS. Pure As_2S_3 or when co-precipitated with FeS, is able to release arsenic into water by its slow dissolution around pH 7 (Figure 4 *b*).

The case of arsenic mobilization in water may be complex and varied[7–12]. Microbes like iron reducing bacteria and SRB present in the anoxic environment produce Fe(II) and sulphide ions, resulting in the desorption of arsenic from the insoluble ferrihydroxide adduct. Furthermore, members of the Enterobacteriaceae family normally present in aerobic environment can utilize organics near tubewells to augment the release of arsenic by sulphide reduction of Fe(III). However, precipitated FeS under aerobic exposure readily converted back to ferric oxyhydroxide. The anaerobic microorganisms may become segregated into zones according to the electron acceptor, owing to competitive exclusion. SRB find plenty of food near the tubewells, where unhygienic human acts readily supply large quantities of fatty acids. They may not show any dependency on obligate, anaerobic, methanogenic microbes to acquire fatty acids. In the presence of abundant electron acceptor like sulphate and ready supply of large quantity of fatty acids, SRB can out-compete ferric reducer and obligate anaerobe methanogens and may dominate the ecological niche near the tubewells.

For the past three decades, the use of soaps and detergents has been steadily increasing here[13], as also the digging of tubewells for drinking water[4]. Before mid-sixties, the large Indian population relied on dug wells or ponds earmarked for supply of drinking water in a locality. No washing or bathing was permitted near these water sources. Furthermore, soaps were rarely used during those days and it was only soap nut, soda ash or sodium carbonate that was commonly used for washing. Recipes from natural ingredients involving milk cream or vegetable pulp and oil, turmeric and sandalwood paste, pulse powder and other herbal ingredients were used for bathing.

Later, however, soaps and detergents became readily available along with the extensive use of tubewells[4,13] for washing and bathing purposes. The original aim of these tubewells was to provide clean drinking water, avoiding Enterobacteriaceae as contaminants. As the source aquifer was not visible, rampant use of the base of the tubewell for activities like bathing and washing had started. Most tubewells do not have a good drainage system (Figure 1 *a*). Stagnant water surrounding a tubewell allowed the accumulation of phosphates (from soap) to promote algal growth. Under this algal anaerobic blanket, SRB started proliferating with the regular supply of fatty acids and sulphate. These bio-geochemical redox reactions require a stagnant pool of water, with continuous replenishment of water lost due to evaporation. In contrast, drier parts of India do not allow proliferation of these microbes round the year. The steady release of arsenic from detergent and soaps may similarly remain apparently invisible in the rest of the country, as migration of released arsenic through the soil is prevented due to the absence of stagnant water. On ageing, free arsenic may be trapped by ferric ion and thus remain unavailable in water at a later stage. A proper drainage system with a good flow of water may also prevent local accumulations of food sources and the necessary anoxic conditions for growth of these microbes. It is important to stress that members of the Enterobacteriaceae family normally augment the release of H_2S and thereby help in releasing trapped arsenic. Proliferation of such microbes is generally slowed down in the presence of soap and detergent, which in turn facilitates the growth of SRB. Ironically, soap and detergent also directly dump soluble arsenic. Thus arsenic release is anthropogenic in nature due to improper utilization of basic civic facilities coupled with the use of arsenic-infected soaps and detergents. Solid soaps and detergents use sodium sulphate and phosphate mainly as binders. And these are the sources of arsenic in soaps. To prevent algal growth, the use of phosphate in soap has been questioned and to some extent its use is restricted in a few countries. Therefore, proper drainage and hygiene management near a tubewell and the use of liquid soaps and detergents (which will be arsenic-free) are the key factors to be seriously considered to prevent its release in water.

Mud from Bhagwatghat tubewells 1 and 2 in Kanpur was freshly collected at a depth of 15 cm and 2 m away from the drainage outlet of the tubewells, in sterilized containers using N_2 balloons to make it anaerobic and transported to the laboratory within half an hour before sunrise. About 20 g of mud was mixed with 50 ml distilled water and agitated for 30 min under N_2 atmosphere. Mud was allowed to settle and the supernatant water was filtered and taken out using hypodermic syringe through the butyl rubber septum. Aliquots of this water were incubated with standard SIM[14] and modified soap-detergent bactosulphate API (SR) medium[6]. Bottles or vials used for growth were sealed with rubber septum or plastic cap followed by parafilm sealing twice. Model synthetic soil (2 g) was used with 100 ml culture medium (SIM or modified soap–detergent bactoSulphate API (SR)) followed by injecting 25 ml of mud-leached water. Aliquots (2 ml) of growth solution were syringed out everyday under N_2 and tested for the presence of dissolved arsenic after filtering from suspended FeS followed by complete drying of the filtrate and decomposing it by concentrated sulphuric and nitric acid mixture, as done with soap samples. From control solutions, trace amounts of released arsenic were subtracted to get the actual data.

Arsenic was estimated by standard AsH_3 test using $HgBr_2$ and also by $HAuCl_4$ to detect its presence in trace amounts. Digestion of the soil or soap (1 g) was made using concentrated H_2SO_4 and HNO_3 (10 : 20 ml) in 1 : 2 ratio slowly and finally on a hotplate to fume H_2SO_4, so that the nitric acid was completely removed. On cooling and extraction with water, the soluble part was filtered out and concentrated to reduce the volume to 20 ml. Next 0.5 ml H_2O_2 (20 vol.) was added; and NaOH solution was added to make it alkaline and digested to oxidize any trace of unoxidized sulphur after HNO_3 treatment (for toilet soap) to sulphate. It was reacidified using 4 M HCl and 1 g arsenic-free granulated zinc was used to generate AsH_3 which turns freshly impregnated $HgBr_2$ paper from yellow to orange-brown[15–18]. Blank test was routinely done in parallel to assess the presence of arsenic from the reagents used[19]. For sulphate test, digestion was carried out in concentrated nitric acid following standard $BaSO_4$ test and for phosphate by following phosphomolydate test. Test for Fe(II) was made with 1,10-phenanthroline and for Fe(III) with thiocyanate, and confirmed by bleaching with NaF. Manganese was tested with bismuthate/red lead oxidation in nitric acid to yield permanganate. A standard $SnCl_2$-thiocyanate reagent in dilute HCl and using diethyl ether to extract red molybdenum complex protocol was followed for the test of molybdenum[20]. Test for sulphide was done using lead acetate paper[15].

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20. Kanpur soil contained chromium and concentration of molybdenum in northern India was very low.

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Signature of increasing total column water vapour and surface temperature at Maitri, Antarctica

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Measurement of total column water vapour has been carried out at Maitri (70°45′S, 11°44′E), Antarctica using Microtop sun-photometer during the 16th, 21st, 22nd and 23rd Indian Antarctic Scientific Expedition. The annual mean water vapour was found out to be 0.24 cm in 1997, while it was 0.42 cm in 2002 and 0.45 cm in 2003. Monthly mean water vapour was maximum during January in all years studied and increased by 48.8% in 2002, 57.7% in 2003 and 66.6% in 2004, compared to 1997. Total column water vapour corresponding to surface temperature has also been studied. Years 2002 and 2003 were found to be warmer by 11.72 and 4.1% respectively compared to the year 1997. The observation showed signature of increasing total column water vapour at Maitri. Measurement also showed increase in surface temperature and was especially pronounced in the month of January at Maitri. In the present communication, a comparative study of water vapour and surface temperature is discussed in detail.

Keywords: Antarctica, regional warming, surface temperature, water vapour.

WATER in its various phases constitutes the critical link between the chemical component of global change and the dynamics, radiation and climate components. In the upper troposphere and lower stratosphere, the radiative[1] and chemical[2] effects of water vapour are large and atmospheric concentration varies considerably with temperature and relative humidity. In global climate models, almost half of the projected increase in temperature due to a doubling of carbon dioxide in the atmosphere results from the effects of increased water vapour[3]. Increase in water vapour in the stratosphere has resulted in considerable cooling, similar to that due to ozone depletion. Recent studies have shown a stratospheric cooling in regions of H_2O increase, of magnitude similar to that due to stratospheric ozone loss indicating a significant additional cause for the observed decrease in stratospheric temperature. However, doubling of water vapour in the stratosphere could lead to a 1°C rise in surface temperature[4]. Total column water vapour (very low amounts in Antarctica), however, plays a significant

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