

A Study of Impact of groundwater Arsenic Contamination

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Abstract Arsenic poisoning, or arsenicosis, occurs after the ingestion or inhalation of high levels of arsenic. Arsenic is a type of carcinogen that's gray, silver, or white in color. Arsenic is extremely poisonous to humans. What makes arsenic especially dangerous is that it doesn't have a taste or odor, so you can be exposed to it without knowing it. While arsenic is naturally occurring, it also comes in inorganic (or "man-made") formulas. These are used in agriculture, mining, and manufacturing.

- 1. Introduction** Arsenic is a crystalline metalloid found in the Earth's crust, but in its free form it is quite rare. The element is typically found in minerals, such as arsenopyrite, realgar and orpiment. Under standard atmospheric pressure, arsenic sublimates, or changes directly from the solid state to the gaseous state without becoming a liquid. However, it will turn into a liquid when put under high pressure.

Table 1

Atomic Number	:	33
Relative Atomic Mass	:	74.9216
Mass Number	:	74
Electronic Configuration	:	$1s^2. 2s^2 2p^6. 3s^2 3p^6 3d^{10}. 4s^2 4p^3$
Atomic Volume	:	$12.97 \text{ cm}^3 \text{ mol}^{-1}$
Number of known Radioactive nuclides	:	17*
Elemental Radius	:	139 pm
Covalent Radius	:	121 pm
Ionic Radius	:	69 pm
Ionisation Energies	:	947, 1798, 2734, 4834, 6040 and $12300 \text{ kJ mol}^{-1}$
(For 1 st to 6 th ionisation energies)		
Electronegativity	:	2.2 (according to Pauling scale)
Melting point	:	1090 K at 3.7 MPa for the Y-variety
Sublimation point	:	886 K at 0.1 MPa
Electrical Resistivity	:	$24 \times 10^{-8} \text{ ohm.m}$ at 273 K
Electrical Conductivity	:	$4.17 \times 10^6 \text{ ohm}^{-1} \text{ m}^{-1}$ at 273 K
Specific Heat Capacity	:	$329 \text{ J kg}^{-1}\text{K}^{-1}$ at 291 K and $344 \text{ J kg}^{-1}\text{K}^{-1}$ on average between 273 K and 373 K

Linear Thermal Expansion Co-efficient :	$5.0 \times 10^{-6} \text{ K}^{-1}$
Electrode Potential (at 298 K) :	0.24 V
$\text{As}^{3+} / \text{As} \text{ (} 1/3 \text{As}^{3+} + \text{e} \rightarrow 1/3 \text{As)}$	
Relative Densities :	2.026, 4.70 and 5.727 for α-, β-, and γ – varieties respectively
Allotropes :	α- or Yellow arsenic, β-, γ- or metallic arsenic

Arsenic occurs ubiquitously in nature; and at present, a great deal of attention has been attributed to its natural and anthropogenic sources wherefrom it is emitted to the atmosphere. A meticulous study to estimate natural and anthropogenic influx of arsenic to land, air and oceans has been made by many a scientist, the summary of which is provided below.

2. Sources and History of Arsenic

Arsenic Emitted In Tonnes per Year¹

Sources	Reference A	Reference B	Reference C
Volcanoes	7000	280	17150
Low temperature volatilisation	160	16000	26200
Wind erosion	240	2500	1980
Forest fires	160	--	125
Sea spray	28	194790	27
Total	7800	213570	45480

In addition to the data given above, recent measurements of the concentration of arsenic in the atmosphere have been applied to provide a rain-out flux. Although the information regarding the anthropogenic inputs to rivers and coastal waters are limited but a tentative estimate of the oceanic flux has been provided by Chilvers et al ¹ which will be discussed in this section later on.

The results given in Table 2 can be clarified to show how and in what percent is arsenic emitted as a constituent of the total global emission. This has been highlighted in Table 3.

Table 3

Source	Global Production (ton year ⁻¹)	Emission Factor of Arsenic ($\mu\text{g g}^{-1}$)	Total Arsenic Emitted (ton year ⁻¹)	% of Arsenic (overall)
Volcanoes	25×10^6	686 of ash	17150	37.62
Low temperature volatilisation*			26200	57.68
Wind erosion	330×10^6	6.0 of soil	1980	4.34
Forest fires	250×10^6	5.0 of vegetarian	125	0.30
Sea-salt spray	550×10^6	0.053 of sea-salt	27	0.06
Total			45482	100.00

Smelting of metals like copper, lead, zinc and alloys like steel; as well as burning of coal and the use of arsenicals such as pesticides and insecticides are the major anthropogenic sources from which the environment is being subjected to arsenic-pollution. In Table 6, the relative proportion of the global production of the above mentioned metals along with the emission and distribution of arsenic per year have been furnished.

Table 4

Emission and Distribution of Arsenic to the Environment from Anthropogenic Sources

Source	Global Production (ton year ⁻¹)	Emission Factor (kg of Arsenic ton ⁻¹ of Production)			Input of Arsenic to (ton year ⁻¹)			Total Arsenic (ton year ⁻¹)
		To Air	To Land	To Water	Ambient Air	Land	Water	
Copper smelting	8.05 x 10 ⁶	1.50	5.88	3.50	12080	47290	28175	87454
Copper Refining (non thermal)	8.60 x 10 ⁶	Insignificant	1.23	0.03	Insignificant	10580	230	10810
Lead Smelting	3.58 x 10 ⁶	0.40	1.00	Insignif.	1430	3580	Insignificant	5010
Zinc Smelting	1.20 x 10 ⁶	0.65	5.04	Insignif.	780	6050	Insignificant	6830
Steel production	645.00 x 10 ⁶	0.09x10 ⁻³	9.1x 10 ⁻³	Insignif.	60	5850	Insignificant	5910
Coal Combustion	3696.00 x 10 ⁶	Various	9.5 x 10 ⁻³	-	6240	35100	-	41340
Wood fuel	850.00 x 10 ⁶	0.50 x 10 ⁻³	-	-	425	-	-	425
Clearance of								
i) tropical forest	3200.00 x 10 ⁶	0.50 x 10 ⁻³	-	-	1600	-	-	1600
ii) woodland, Savanna	640.00 x 10 ⁶	0.50 x 10 ⁻³	-	-	320	-	-	320
Burning of Pasture land	2000.00 x 10 ⁶	0.50 x 10 ⁻³	Insignif.	Insignif.	1000	Insignificant	Insignificant	1000
Herbicides	8.00 x 10 ³	430	570.00	-	3440	4560	-	8000
Wood preservatives	16.00 x 10 ³	9.25	Insignif.	Insignif	150	Insignificant	Insignificant	150
Desiccants	12.00 x 10 ³	Insignificant	100.0%	-	Insignificant	1200	-	12000
Glass manufacture	4.00 x 10 ³	117	-	-	467	-	-	467
Waste incineration	150.00 x 10 ⁶	0.52 x 10 ⁻³	-	-	78	-	-	78
Total	11202.47 x 10⁶					Greater than		181475

It is apparent from the table that the Smelting and Refining of copper is at the top of the list of the anthropogenic sources from where the environment is being polluted with arsenic..

3. POLLUTION OF GROUND WATER

Groundwater is a precious and most widely distributed resource of earth and unlike any other mineral sources it gets annual replenishment from meteoric precipitation. Groundwater which is a part of the hydrological cycle that controls the total water circulation of the world, differs from surface water in the fact that in its way from recharge area to discharge area, groundwater dissolves different minerals from the soil layers through which it passes. As a result, ground water contains several minerals and toxic elements in trace quantities. Lead, mercury, cadmium, hexavalent chromium, arsenic and sometimes selenium are the common toxic elements which are generally found in ground water. Higher quantities of these elements in groundwater cause serious pollution problem. Major pollution creating sources are industrial wastes, sewage and mining activities.

Arsenic can exist in various oxidation states in natural environment but rarely elemental form. In oxidation states, arsenic can form many organic and inorganic compounds among arsenates and arsenites of metals, methyl arsenic acid, $\text{MeAsO}(\text{OH})$ are the main arsenical present in natural waters ⁴².

i) ABSORPTION THROUGH ORAL INTAKE OF FOODS AND GRAINS

Experiments on both animal and human revealed that about 90 % of an ingested dose of dissolved inorganic trivalent or pentavalent arsenic is absorbed from the gastrointestinal tract ⁴². Organic arsenical compounds coming from seafoods are also absorbed through gastrointestinal tract in an amount greater than 80% ⁴⁶, although arsanilic acid (the important organic arsenical compound, which has been proved to be a growth promoter) is absorbed to the extent of only 15 – 40% ^{47,48}. The absorption of other growth promoters, such as 4-nitrophenyl arsenic acid, 3-nitro-4-hydroxyphenyl arsenic acid and arsenobenzene is also very low and also within 40%. It should be noted here that as arsenic (III) oxide, As_2O_3 is little soluble in water, its absorption through gastro-intestinal tract is dependent on the pH of the gastrointestinal juice and also on the size of the absorbed particles.

ii) CONSUMPTION WITH DRINKING WATER

The common arsenical compounds which are highly soluble in water and generally consumed with water are sodium arsenite, sodium arsenate and calcium arsenate. R.S. Braman and C.C. Foreback ⁴⁹ reported about the presence of arsenate, arsenite, methyl arsenic acid, dimethyl arsenic acid in natural waters among which the methylated forms are present in lower concentrations in comparison to the inorganic ones. However, rigorous works are necessary in this field and the chemical form of arsenic in different ground water is hitherto largely unknown. The absorption of arsenates or arsenites is even greater than 90% from gastrointestinal tract ⁴². The organic arsenical compounds are also well absorbed through the same route but the percentage of absorption is slightly lower.

4. Arsenic in Food Chain

During field survey in arsenic affected localities, it was noticed that a considerable fraction of the villagers use groundwater (collected from hand pumps) not only for drinking purposes, but they also cook their meals using the same water. Trials were given to find out the gain in arsenic (if any) in rice and lentil preparations cooked in arsenic contaminated tube well water (obtained from the affected localities) in the laboratory. It was observed that such preparations were always associated with heavy arsenic mineralisation.

Preparation of food items with arsenic contaminated water

Rice and Lentil

Parboiled rice and lentil samples were collected from the local market of the affected locality. Grains of parboiled rice and lentil were separated from dusts by hand picking and usual domestic clarifying practices.

Rice and pulse preparation

- (1) Washing : 100 g sample of parboiled rice was first washed with 100 mL of tubewell water containing arsenic collected from a hamlet (Halderbagan, village : Gangapur of Barasat Block) of North 24-Parganas (the physico-chemical characteristics of the water sample are shown in Table 2) thoroughly; washed water was decanted off in a beaker and kept for arsenic estimation. Similar washing was done for 100 g pulse sample by 100 mL of water.
- (2) Cooking : Washed grains were cooked in a neutral glass beaker (corning) in 500 mL of same water (for 100 g of rice) and 200 mL of the water (for 100 g of pulse, water added sequentially). Excess cooked water was carefully decanted off and almost liquid free boiled rice was retained. For liquid lentil (boiled pulse) preparation, grains were boiled to desired softness, retaining excess cooked water with the boiled grains.

The gruel was digested with a mixture of hydrochloric acid perchloric acid, evaporated to almost dryness, dissolved in distilled water, filtered and the filtrate was carefully analysed for arsenic.

In Table 1, is presented a survey report in relation to the average daily water consumption by a person in rural West Bengal. From the table, it is apparent that a person living on normal diet consumes approximately 2.5 litres of water from rice, lentil and curry etc., which is almost twice the drinking water he or she consumes throughout the day.

The amount of arsenic retention in the cooked food items is shown in Table 2, which indicates that

- (i) The toxic species is retained considerably (more than 90% of the water-arsenic) in cooked food items, if cooked water is not discarded (discarding of gruel of the cooked rice etc.) and
- (ii) Total amount of arsenic ingestible from cooked food items would be more than that consumed through drinking water.

It is worthwhile to mention here that certain percentage of poor villagers of our country do not discard the gruel when they eat rice as a staple. Thus the arsenic present in the gruel increases the amount of ingested arsenic in those people who do not discard the gruel of the cooked rice. It is thus proved that food items cooked in arsenic contaminated water are also as much potential contributor of arsenic to produce arsenic poisoning in human being as drinking water itself.

TABLE 1

AVERAGE CONSUMPTION OF DRINKING WATER PER CAPITA PER DAY				
Mode of Consumption	Volume of Water consumed (in L)		Amount of Arsenic ingested (in mg)*	
	During Summer	During Winter	During Summer	During Winter
Only drinking	1.5	1.2	0.15	0.12
Through rice	0.4	0.4	0.04	0.04
Through pulses	0.4	0.4	0.04	0.04
Through vegetables	0.3	0.3	0.03	0.03
Through curry	1.0	1.0	0.10	0.10
Total intake	3.6	3.3	0.36	0.33
*considering the average concentration of arsenic in the ground water as 0.1 mg L ⁻¹				

TABLE 2

PHYSICO-CHEMICAL PARAMETERS OF THE WATER SAMPLE USED AS COOKING MEDIUM										
Depth of the tubewell (m)	Type	pH	Hardness (mg L ⁻¹ of CaCO ₃)	Chloride (mg L ⁻¹)	Metallic radicals and arsenic (in mg L ⁻¹)					
					K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Fe ²⁺	arsenic
20	metallic	6.5	300	30	5.5	90	48	60	5.3	0.502

TABLE 3

ARSENIC IN RICE AND LENTIL THROUGH THE COOKING MEDIUM							
Item	Mass (g)	Cooking water added (mL)	Arsenic in cooking water (mg)	Arsenic with discarded water		Arsenic retained in cooked items	
				mass (mg)	% of arsenic	mass (mg)	% of arsenic
Rice	100	500	0.251	0.094	37.45	0.157	62.55
Lentil	100	200	0.1004	0	0	0.1004	100

5. Conclusion

Although uncertainties are associated with the presented data and rigorous works under the headings are necessary, still it may be concluded that the anthropogenic emission of arsenic to environment should be controlled to minimum with the greatest care, else it may pose a serious problem in different areas nearer the anthropogenic sources of arsenic. As it comes to the food chain, the faunas become easy target of Arsenicosis. Apart from other mitigation policies, Rainwater harvesting and using more surface water and less groundwater can lead us towards a less Arsenic threatened society.

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