Arsenic

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Arsenic is an element known throughout history as a classic poison. Currently, very small but highly significant concentrations of this element in drinking water supplies are causing massive health problems to many millions of people in some of the world's poorest nations. More localised sources related to mining and processing are also a concern. A review of background information on arsenic chemistry, occurrence in the Earth, production and uses, as well as its toxic properties, leads in to the other articles in this issue of *Elements*.

KEYWORDS: arsenic, poison, mine wastes, drinking water

INTRODUCTION

When, in his play *Under Milk Wood*, the Welsh poet and humorist Dylan Thomas created the henpecked husband character of Mr Pugh, a man whose favourite reading was drawn from *Lives of the Great Poisoners*, it was clear that the poison of his fantasies was arsenic (…whispering as he took breakfast tea to his wife's room "Here's your arsenic, dear. And your weedkiller biscuit… Here's your… nice tea, dear"). So it is that, from ancient times until the present day, the word arsenic has been associated with the poisonous properties of this material.

As one of the hundred-plus known chemical elements, arsenic is a fitting topic for a magazine with the name *Elements*. But it is, again, because of its poisonous nature that it forms a subject worthy of an issue of this magazine. In the last few years, it has been recognised that arsenic contamination of groundwater supplies used for drinking and irrigation, particularly in places such as West Bengal and Bangladesh, is giving rise to massive human health problems. In this case, it is long-term exposure to low concentrations of dissolved arsenic. The seriousness of this problem, which is affecting millions of people in some of the poorest countries of the world, has led the World Health Organization to describe it as "the greatest mass poisoning in human history". For example, an estimated 35 million people in Bangladesh and 6 million in West Bengal are at risk. As we shall see, the threat to human health from arsenic contamination of waters and soils is not confined just to these regions, although it is there that the scale of the problem is most disturbing. Extensive arsenic poisoning ('arsenicosis') has also been reported from Argentina, Chile, Mexico, China, Thailand and Taiwan. Furthermore, the realisation that even extremely low concentrations of arsenic in drinking water may be a serious long-term health hazard raises concerns in many other countries, including the USA and parts of Europe.

The major themes that are essential to understanding the 'arsenic problem' will be developed in the articles that follow, but before that we need to recall key background information about arsenic as an element; about the distribution of arsenic in the Earth; about the mining, processing and utilisation of arsenic; and about the toxicity of arsenic compounds. As well as putting the human health problems of this element into a global context, we also need to recall that it does have both traditional uses and applications in modern industries.

In the 4th century BC, the Greek philosopher Aristotle referred to a substance which was probably the arsenic sulphide mineral realgar (AsS), and it seems certain that arsenic compounds were used in the murders by poisoning that were so much a part of imperial Rome. Although the element arsenic does occur naturally in the native state, it is rarely found in this form. The 'arsenic' of assassins and murderers generally refers to the trioxide form, As_2O_3 (also known as 'white arsenic' or the mineral arsenolite). Although minerals containing arsenic have been known since ancient times, the discovery of the element itself is generally attributed to the German scholar Albertus Magnus in roughly 1250 AD. But it was, ironically perhaps considering its impact on human health, the medieval physician Paracelsus who provided the first detailed recipes for the preparation of elemental arsenic.

MINERALOGY AND GEOCHEMISTRY

Of course, today we know a great deal about the chemistry and geochemistry of arsenic. Some of the salient facts are given in TABLE 1, in particular, information on the properties of the element and its average concentration in the rocks, sediments, soils and waters of the Earth. Arsenic has only one stable isotope (^{75}As) and is 47th in abundance among the 88 naturally occurring elements. The average crustal abundance of arsenic is 1.5 mg kg^{-1} (1.5 ppm). Mudstones, shales and slates have the highest concentrations among the common rocks, although extremely high concentrations can be found in some coals. Typical concentrations in natural waters are much lower, of course, with higher levels seen in river and sea waters than in rain or lake waters. The data given in TABLE 1 are for background (or 'baseline') concentrations. Much greater levels are found locally in waters, soils and sediments where arsenic associated with mining, smelting or other industrial activities, or with geothermal systems, can dramatically enhance concentrations (by factors of 100 to 1000, or even more).

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Arsenic does not readily substitute into the structures of the major rock-forming minerals. It is found mainly as minerals where the As occurs as the anion or dianion (As$_2$), or the sulfarsenide anion (AsS); these anions are bonded to metals such as iron, cobalt or nickel (e.g. FeAs$_2$, FeAsS, CoAsS). It can also occur as a minor component in the relatively abundant sulphide mineral pyrite. More rarely it occurs combined with copper or silver, and there are also simple arsenic sulphide minerals such as realgar (AsS) and orpiment (As$_2$S$_3$) (see FIG. 1). When these primary minerals are exposed at or near the surface of the Earth, reaction with the atmosphere and surface waters causes alteration; simple arsenic oxides or more complex phases containing various metals combined with arsenic, oxygen and other anion species are formed. A large number of 'secondary' arsenic minerals are produced in this way.

FIGURE 1 Crystals of the arsenic sulphide mineral orpiment

USES, MINING AND PRODUCTION

Although the use of arsenic by industry has greatly declined, partly because of a much fuller appreciation of its toxicity at even low levels, it has played an important role as a component of insecticides, weedkillers and wood preservatives. Historically, it was also used in pigments to colour wallpapers, paints and ceramics, and it has been used in certain specialist alloys and in glass manufacture. Two other aspects of the uses of arsenic present a very different picture of this element; one is in the manufacture of components for the modern electronics industry, the other is its largely historical application in medicines. In the former case, the semiconducting properties of compounds such as gallium arsenide have been used to great effect in the dramatic advances that have occurred in electrical device development over the past half century. In the latter case, arsenic compounds have been successfully used to combat disease. For example, the great German medical researcher Paul Ehrlich (1854–1915), who effectively invented the treatment of diseases using chemotherapy, was convinced that the toxic properties of arsenic could be used to attack pathogenic microbes if only a form could be found which at the same time was safe for human ingestion. A long and painstaking search (see also O'Day in this issue) led to the discovery of an organoarsenic compound which was sold commercially as Salversan and which, although later overtaken by other drugs, revolutionised the treatment of syphilis.

Because arsenic occurs in association with minerals commonly exploited for their copper, nickel, cobalt, lead, silver and tin, it has been produced as a by-product of the mining of those metals. A good historical example is provided by the mines in Cornwall (SW England), which

<table>
<tr><td colspan="4">**TABLE 1** **ARSENIC CHEMISTRY AND GEOCHEMISTRY**</td></tr>
<tr><td colspan="2">CHEMICAL SYMBOL: As
ATOMIC WEIGHT: 74.92
VALENCE STATES: -3,-1, 0, +3, +5</td><td colspan="2">ATOMIC NUMBER: 33
ELECTRONIC STRUCTURE: [Ar] 3d10 4s2 4p3
STABLE FORM: grey arsenic
RARER ALLOTROPES: yellow arsenic,
black amorphous arsenic</td></tr>
<tr><td colspan="4">GREY ARSENIC:
DENSITY = 5.73 g cm^{-3}; MELTING POINT = 817°C (28 atm); SUBLIMES ~614°C</td></tr>
</table>

ARSENIC CONCENTRATIONS IN ROCKS, SEDIMENTS AND SOILS*

Rock/sediment/ soil type	Average As conc. (mg kg^{-1})	As conc. range (mg kg^{-1})
Basalt	2.3	0.18–113
Andesite	2.7	0.5–5.8
Granite	1.3	0.2–15
Slate/phyllite	18	0.5–143
Mudstone/marine shale	3–15	< 490
Sandstone	4.1	0.6–120
Limestone/dolomite	2.6	0.1–20.1
Evaporites	3.5	0.1–10
Coals	–	0.3–35,000
River sediments (world average)	5	
Continental margin sediments	–	2.3–8.2
Peaty soils	13	2–36
Acid sulphate soils (Canada)	–	1.5–45

TYPICAL ARSENIC CONCENTRATIONS IN NATURAL WATERS

	Average As conc. (µg L^{-1})	As conc. range (µg L^{-1})
Maritime rain water (baseline)	0.02	–
Terrestrial rain water (baseline)	–	0.013–0.032
River water (baseline)	0.83	0.13–2.1
Lake water, British Columbia	0.28	< 0.2–0.42
Seawater, deep Pacific/Atlantic	–	1.0–1.8
Groundwater (baseline UK)		< 0.5–10

* Data derived from Smedley and Kinniburgh (2002)

were first developed by the Romans following their conquest of Britain in 43 AD. Mining, mainly of copper and tin, continued uninterrupted here for 2000 years, until the late 20th century. The heyday of Cornish mining was in the 19th century, with arsenic becoming an important by-product after about 1870. Before the ores from the mines could be sent to smelters to extract and refine the tin, the arsenical impurities had to be removed, and this was done by driving them off in roasting ovens and allowing them to condense in long zig-zag tunnels ('lambreth' flues). A picture of such a system, designed to trap the condensed white arsenic oxide 'soot' on its walls, is shown in FIGURE 2. Men, whose only concession to safe working practices was wearing cotton-wool nose plugs, periodically removed the 'soot' by scraping it from the walls of these flues.

considerable uncertainty regarding the toxicity of species such as the organic compounds and arsenosugars towards humans. The importance of speciation in relation to toxicity also has geological relevance. The primary arsenic-bearing minerals such as the metal arsenides and sulfarsenides (arsenopyrite, etc.) are virtually non-toxic, because they are highly insoluble. Problems arise when these primary minerals break down and enter solution or form much more soluble species such as the oxides.
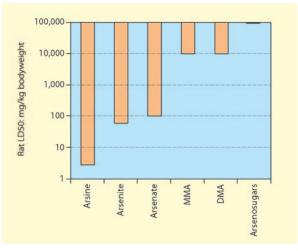

FIGURE 2 The remains of structures (lambreth flues) used to roast and drive off the arsenic from the ores mined for tin in Cornwall during the 19th century. This archaeological heritage site is at Botallack in West Cornwall. PHOTOGRAPH COURTESY OF THE COUNTY OF CORNWALL AUTHORITIES

FIGURE 3 Bar diagram illustrating the relative toxicity of different forms of arsenic The 'rat LD 50 test' shows the quantity, in milligrams/kilogram bodyweight, of the various arsenic compounds required to kill 50% of a test population of rats. MMA is monomethylarsonic acid and DMA is dimethylarsinic acid. FIGURE BASED ON A COMPILATION OF DATA BY DR JIM BRYDIE

The worldwide commercial production of arsenic has been steadily declining, with a world total of 37,500 tons of As_2O_3 being produced in 2004. By far the biggest producers were China (16,500 tons) and Chile (8000 tons), with the arsenic being produced as by-products of mining of metals, such as copper in Chile. World reserves are estimated to be about 20 times the annual world production. The price of arsenic metal in the USA has generally fluctuated between ~$3.00 and 50 cents per pound (0.454 kg) over the past 40 years. The dominant use for arsenic has been for the manufacture of chemicals such as chromated copper arsenate (CCA) used as a wood preservative, or in fertilisers, herbicides and insecticides. Much smaller amounts have been used in the manufacture of glasses and certain nonferrous alloys, and very small amounts (a few tons) of high purity arsenic are consumed by the electronics industry for the manufacture of semiconductor materials. However, as awareness of the harmful effects of even low concentrations of arsenic in the environment has grown, consumption has been rapidly declining. For example, the wood-preserving industry in the USA agreed voluntarily to stop using arsenic (CCA) preservatives by the end of 2003 and to use various substitute products.

SPECIATION AND TOXICITY

Arsenic provides a very good example of the importance of *speciation* in relation to toxicity. Simply put, the exact form in which the arsenic occurs dramatically affects the extent to which it is a poison for humans or other organisms. FIGURE 3 gives results for a standard test of toxicity, the 'rat LD 50' test; the figure shows the amount, in milligrams per kilogram bodyweight, of particular arsenic compounds required to kill 50% of a test population of rats. Here, the most toxic form of arsenic is in the gas arsine (AsH_3), followed by the arsenite (AsO_3^{3-}) and then the arsenate (AsO_4^{3-}) forms, both of which can be carried in solution. The organic (methylated) arsenic compounds [e.g. $(CH_3)_3As$] are much less toxic, and certain arsenic compounds such as the arsenosugars are not at all toxic. It is important, however, to emphasise that there is still

When the toxicity of arsenic is discussed, the focus is most often on the fatal effects of relatively large doses of compounds such as the trioxide (white arsenic). The fact that a 'pea-sized' quantity of such a material can cause death in a matter of hours was what made it the favoured chemical weapon of the assassin and murderer from the time of the Roman emperors onwards. It was also easy to obtain and lacked odour or taste when mixed in food or drink. Before modern analytical chemistry and the autopsy made arsenic readily detectable as a cause of death, the similarity of the victim's symptoms to relatively common conditions in the ancient and medieval worlds, such as food poisoning, also favoured its use. Arsenic could be delivered as a single large dose, provoking violent abdominal cramping and vomiting, often followed by death from shock. Alternatively, a series of somewhat smaller doses produced chronic poisoning, with a loss of strength, confusion and paralysis.

Perhaps the most famous person believed to have been a victim of arsenic poisoning was the French emperor Napoleon Bonaparte. After his final defeat at the Battle of Waterloo, Napoleon was imprisoned on the remote Island of St Helena. His death several years later, from what was officially recorded as stomach cancer, has proved controversial. Some writers have claimed that his death was the result of arsenic poisoning and cite evidence from analysis of what is believed to be a lock of his hair showing elevated levels of arsenic. If true, this could have been the result of deliberate poisoning, but a more intriguing argument centres on the wall decorations of Napoleon's quarters on the island. These reportedly included green-coloured wallpapers, which were very fashionable at the time. The pigments used to impart the green colour in such papers and paints were made from arsenic compounds. Stories of sickness amongst servants and others living alongside Napoleon lend credence to this hypothesis. The problem of

arsenic ingestion, given that even the most desperate of prisoners is unlikely to eat his prison walls, has been ingeniously solved by suggesting that the wallpaper in that dank Atlantic Ocean climate was attacked by a mold, causing minute fragments to break off and be inhaled. Whatever killed Napoleon, it seems likely that some of his contemporaries were poisoned by their fashionable salon decorations.

The pathophysiology of arsenic is complex. At high dosage levels, arsenic disrupts the fundamental functioning of cells in numerous organs; it does this, for example, by binding to the sulfhydryl groups of cellular enzymes or by substituting for phosphate in glycolitic and cellular respiration pathways. However, the great concerns over arsenic and human health today centre upon the long-term ingestion of low concentrations, chiefly in drinking water, although more indirect routes via food are also possible. Until recently, the long-standing legally acceptable limit imposed by the United States Environmental Protection Agency (EPA) for the concentration of arsenic in drinking water was 50 µg L^{-1} (50 parts per billion, ppb). However, in 2001, the EPA revised this limit downwards, so that it is now 10 µg L^{-1} (10 ppb). This followed on from recommendations made by the World Health Organization (WHO) in 1993, which were based on both an increased awareness of As toxicity and the ability to measure its concentration quantitatively. In many parts of the world, however, including India, Bangladesh and all other affected developing countries, this limit remains at 50 ppb. These are very small quantities, and their detection at these levels in waters is technically demanding. (Detailed accounts of water sampling procedures are given in references such as Wilde and Radke 1998; analytical methods are reviewed in ATSDR 2000, Rasmussen and Andersen 2002.) The reasons for these limits are the overwhelming evidence that consuming arsenic-contaminated water over the long term causes skin cancer and increases the risk of cancers of the bladder, lung, kidney, liver, colon and prostate. There is also evidence that the long-term consumption of arsenic-contaminated water is associated with cardiac, vascular and pulmonary disease, and with diabetes. Chronic arsenic ingestion is associated with delayed symptoms (at least five years, often more), adding to the problems of convincing those at risk of the need for action. The uncertainties surrounding the health impact of even very low arsenic concentrations have led the EPA to set a 'maximum contaminant level goal' at zero for drinking water.

ARSENIC IN WATERS AND SOILS WORLDWIDE

That high levels of arsenic in waters and soils are a global phenomenon can be seen from FIGURE 4. Here, three kinds of features associated with high arsenic concentrations are plotted on a map of the world, and all of the inhabited continents are seen to be affected. One of the three features concerns arsenic in association with geothermal waters, such as the hot springs of Yellowstone Park, USA (see FIG. 5) or Warakei, New Zealand. A second feature involves arsenic concentrations related to mining operations, where mine wastes or wastes from mineral processing are the sources. Southwest England, including Cornwall, and Lavrion in Greece are historically important examples, and more recent examples include parts of British Columbia (Canada), the Ashanti Region (Ghana) and parts of the Republic of South Africa and of Zimbabwe. The third locus of relatively high arsenic concentrations is in certain aquifers, that is to say, bodies of sediment with interstitial water that can be drawn off via wells or springs and used for agriculture or human consumption. All three types of arsenic sources are potential health hazards, although it is the contamination of shallow aquifers in areas such as West Bengal and Bangladesh that is creating the massive human health impacts noted above. In addition, highly localised sources of arsenic can present health hazards to individuals and local communities. The arsenic produced from metalliferous mining operations would usually be an impure
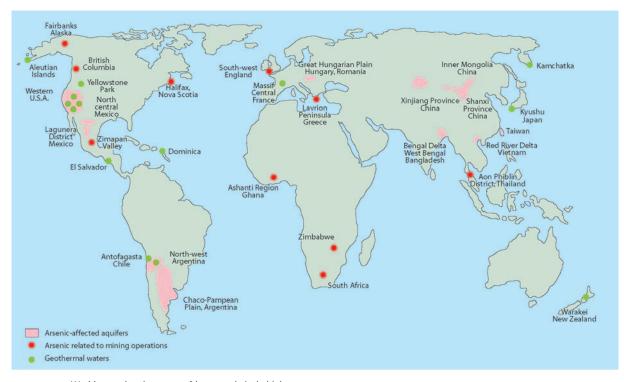

FIGURE 4 World map showing areas of known relatively high concentrations of arsenic. These are generally associated with hydrothermal areas (hot springs), mining activities or contaminated aquifers. FIGURE REDRAWN AFTER SMEDLEY AND KINNIBURGH 2002

material requiring further processing. For example, in the 19th century there were at least eight arsenic works in SW England where the arsenical 'soot' mentioned above would be taken to be refined. The refined product could then be transported to factories where products such as insecticides, weedkillers and wood preservatives would be manufactured. Contamination from former industrial sites is a serious concern, and as seen in the articles following this one, a fundamental understanding of how arsenic moves through soils and watercourses is critical to assessing the risks to the environment posed by these sites.

IN THIS ISSUE

In the articles that follow, the mineralogy, geomicrobiology, environmental geochemistry and toxicology of arsenic are further explored. Peggy O'Day, in discussing the chemistry and mineralogy of arsenic, draws attention to the ability of the element to readily change oxidation state and bonding configuration, which helps to explain its diverse properties. The critical role played by microbes in the biogeochemical cycling of arsenic in a wide variety of natural settings is addressed in the article by Jon Lloyd and Ron Oremland, and this leads to considering the behaviour of arsenic in a variety of environmental systems. Georges Calas and Guillaume Morin discuss examples of studies of soils, mine wastes and former industrial sites. They draw attention to the importance of both bacterial activity and sorption of As onto the surfaces of fine-particle mineral phases such as the hydrous iron oxides. Studies of arsenic in shallow ground-waters in southern Asia and the complexities of the inter-play between geological, microbial and human factors in causing this environmental health disaster are outlined by Laurent Charlet and David Polya. The final contribution provides a medical perspective on the health problems of low-level arsenic contamination via drinking water or the food chain. Claudia Hopenhayn reviews epidemiological evidence for the health effects of arsenic; she also discusses the complicating factors that may exacerbate toxicity, such as genetic susceptibility and concurrent exposure to other substances.

As will be seen, matters of very great concern centred on this most capricious of elements, such as the problems of contamination of shallow aquifers, are both complex and controversial. The origins of such problems and, hence, possible solutions are still hotly debated.

FIGURE 5 Hot springs at the Norris Geyser Basin, Yellowstone Park, Wyoming, USA, where siliceous sinters deposited from the hot springs can carry up to 5% As_2O_5. PHOTOGRAPH BY DAVID J. VAUGHAN

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