

Materials Flow Analysis of Arsenic in the United States

Executive Summary

The largest anthropogenic source of arsenic is the use of arsenic treated wood products. Very little recycling occurs throughout the anthropogenic flow of arsenic. One main leak of arsenic to the atmosphere is emissions, which occur in energy production, mining smelting and refining, and consumption processes. Another major source of arsenic is leaching from arsenic treated wood products. The amount of arsenic that is available within waters depends highly upon pH. This is an interaction of concern because increasing acidification of water bodies will cause more arsenic to be available. Therefore, a reduction in the emissions of sulfuric and nitrous oxides will have an added benefit of reducing arsenic levels. Finally, the amount and rate of arsenic removal from the earth's crust has been greatly increased by human activities and concerns over human health may lead to a long term decline in arsenic use.

Step 1: Characterization of the Anthropogenic Flows of Arsenic

Arsenic is an extremely toxic metal that poses such a significant environmental health hazard that the EPA placed it at the top of the list of 200 hazardous substances targeted by the 1990 Clean Air Act in terms of carcinogenic risk. Its historical and current uses have been primarily as a biocide. It was introduced as Paris green, an insecticide, in 1867 to combat the Colorado potato beetle. Lead arsenate and calcium arsenate were introduced to control the gypsy moth, codling moth, and cotton pests such as the boll weevil. Arsenic was also used in the nineteenth century as a coloring agent for dyes, in fireworks, in tanning, as a depilatory, a preservative for furs, and even in health tonics. Its use as a pesticide in the U.S. declined after the introduction of organic pesticides after World War II. Arsenic acid was used extensively by cotton growers as a leaf desiccant, but the EPA banned this use in 1993.

Current use in the U.S. is primarily as a wood preservative in the form of chromated copper arsenate (CCA). Arsenic is still used in some agricultural chemicals as a herbicide, although its use has been declining. Arsenic metal is used in the production of some nonferrous alloys. Arsenic metal is used as a minor additive (0.01% to 0.5%) to strengthen the posts and grids of lead-acid storage batteries. It is also used in copper alloys to improve corrosion resistance and tensile strength. An estimated 15 tons per year of high-purity arsenic metal is used in the manufacture of crystalline gallium arsenide, a semiconductor material used in optoelectronic circuitry, high-speed computers, and other electronic devices. Arsenic acid is used by the glass industry as a fining agent to disperse air bubbles.

Very little arsenic is recovered from consumer end-product scrap. An estimated 35 % to 50% of the arsenic used in nonferrous alloys is recovered and reused in the recycling of lead-acid storage batteries. However, this is a relatively small quantity due to the small amount of arsenic that is used in the batteries. Process water and contaminated runoff at wood treatment plants are collected and reused in pressure treatment. Gallium arsenide scrap from the manufacture of semiconductor material is reprocessed for gallium and arsenic recovery. No arsenic is recovered domestically from arsenical residues and dusts at nonferrous smelters. Figure 1 depicts the anthropogenic flows of arsenic within the United States.

With an estimated demand of approximately 30,100 metric tons (mt), the United States is the world's largest consumer of arsenic. More than 95% of domestically consumed arsenic is in compound form, primarily as arsenic trioxide. The production of chromated copper arsenate (CCA) accounts for more than 90% of arsenic trioxide consumption. Since 1985, the U.S. has had no domestic production of arsenic and, consequently, relies on imports. China is the principal supplier of arsenic metal and compounds to the U.S. market. 1998 U.S. imports of arsenicals consisted of 38,600 mt of arsenic trioxide, 2 mt of arsenic acid, and 997 mt of arsenic metal.

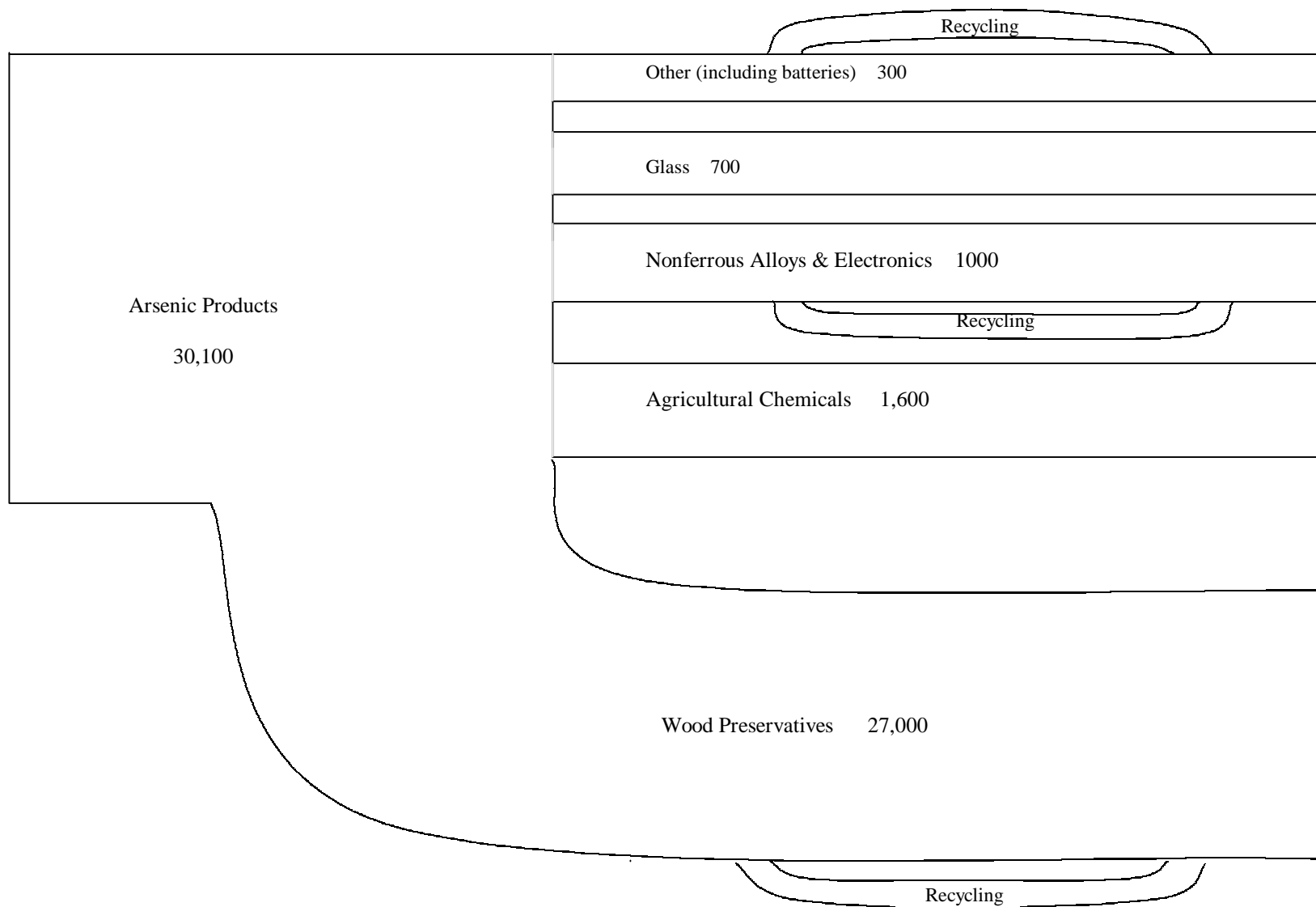


Figure 1. Flow of arsenic through the U.S. economy in 1998. Data is in metric tons. Recycling of lead in lead acid batteries results in a small amount of arsenic recycling. Scrap is recycled during the manufacture of gallium arsenide electronic devices. Process water from the production of pressure treated wood is collected and reused. Sources: U.S.G.S. (1998), U.S. Bureau of Mines (1994).

Step 2: Characterization of Environmental Leaks of Arsenic

Arsenic is mainly used in the United States as a wood preservative. Wood is usually pressure treated with chrome-copper arsenate. However, being applied to wood does not permanently sequester arsenic. A major source to the environment is through leaching of arsenic treated wood. Eventually, as the wood comes into contact with both soil and water, the arsenic will be released to the environment. Some forms of anaerobic bacteria will methylate the arsenic, making it water soluble or extremely volatile. Therefore, there is currently a rising level of arsenic in the environment that is biologically available and accessible.

However, arsenic can be immobilized by adherence to the surface clay particles that are found either in soils or in riverbeds. In addition, deposition of arsenic in marine sediments is another sink. However, this immobilization may not be permanent and changes in abiotic factors may increase the bioavailability of arsenic. For example, as acidity increases, the sequestration of arsenic decreases. Therefore, in highly acidified waters a large amount of arsenic may be mobilized. As the arsenic becomes more available in acidified waters, elevated levels of arsenic will be found within organisms living in these waters. Eventually, the increased bioavailability will result in arsenic accumulation within food chains.

In addition to accumulating in soil, water and food chains, arsenic can also accumulate in the atmosphere. Emissions are a significant source of atmospheric arsenic. Arsenic is highly volatile, which indicates that it will evaporate very quickly when exposed to air and will be widely dispersed by atmospheric processes. Atmospheric releases of arsenic occur in energy production, mining, smelting and refining, industrial processes, waste incineration and pesticide use (Table 1). Table 1 reveals that energy production, primarily in the form of coal burning, is the largest source of atmospheric arsenic. The second largest source is mining, smelting and refining.

Table 1: Emissions of arsenic to the atmosphere for the United States, mid-1980s.
Source: Ayers and Ayers (1999)

	Emissions (kilo megatons/year)
Energy Production	0.470
Mining, Smelting & Refining	0.370
Industrial Processes	0.0530
Waste Incineration	0.003
Pesticide Use	-0.700
Anthropogenic Total	1.000

In addition to releases occurring through production processes, arsenic can also be emitted to the atmosphere by consumption processes. Table 2 lists some emission coefficients for typical consumption processes. These coefficients are a measure of the fraction of the material released in mobile form within a decade. Emissions from consumption processes are greatest for non-agricultural uses and dental/medical uses.

Table 2: Emission coefficients for arsenic consumption processes.

Source: Ayers and Ayers (1999)

	Emission Coefficient
Metallic Use	0.001
Paint & Pigments	0.5
Electron Tubes & Batteries	0.01
Chemical Uses, Embodied	0.05
Agricultural Uses	0.5
Non-Agricultural Uses	0.8
Medical, Dental	0.8
Misc.	0.15

Arsenic can be found in many different chemical forms within the soil, water and atmosphere (Figure 2). Bacteria within soils and sediments can transform arsenate to arsenite, which can be converted into methylarsenic acid. Also within the soils and sediments, bacteria can transform methylarsenic acid into dimethylarsinic acid. All of these forms of arsenic can then become available within the water. Molds can convert methylarsenic acid into trimethylarsine, which can then also be available within water. In addition, molds and bacteria can convert dimethylarsinic acid into both trimethylarsine and dimethylarsine in water. Once in water, trimethylarsine and dimethylarsine can volatilize into the atmosphere. Therefore, different forms of arsenic can be found in the soil, sediments, water, atmosphere and the food chain.

Step 3: Comparison of Leaks to the Environment to the Biogeochemical Flows of Arsenic

The main reservoir of arsenic is the earth's crust. Through natural processes, like erosion and bacterial methylation, a very small amount of arsenic is released to the environment. Natural weathering processes result in gradual leaching of arsenic from rocks and soils. These erosion processes eventually transport arsenic into streams and rivers. In these waterways, arsenic can be deposited in sediments, or transported to the oceans. Once reaching the oceans, burial of marine sediments will eventually immobilize the arsenic.

Mainly through mining, humans have greatly increased the amount of arsenic found in the environment. During the mining process, small amounts of arsenic volatilize and are emitted to the atmosphere (Table 1). In addition, during the use phase of certain products, like paint and pigments, arsenic is also emitted (Table 2). Once in the atmosphere arsenic can be widely dispersed by atmospheric processes. Figure 2 shows the biogeochemical cycle for arsenic including the effects from anthropogenic sources.

Also, when arsenic treated wood products are used, the arsenic eventually leaks into the environment. This arsenic will be transported in streams and rivers and eventually will reach the ocean and be buried with marine sediments. However, as already discussed, as streams, rivers, and lakes become acidified, more arsenic will be available in these waters. By increasing the amount and rate of arsenic removal from the earth's crust, by increasing arsenic emissions to the atmosphere, and by acidifying waters, human activities have greatly increased the amount of arsenic found within the biogeochemical cycle of arsenic.

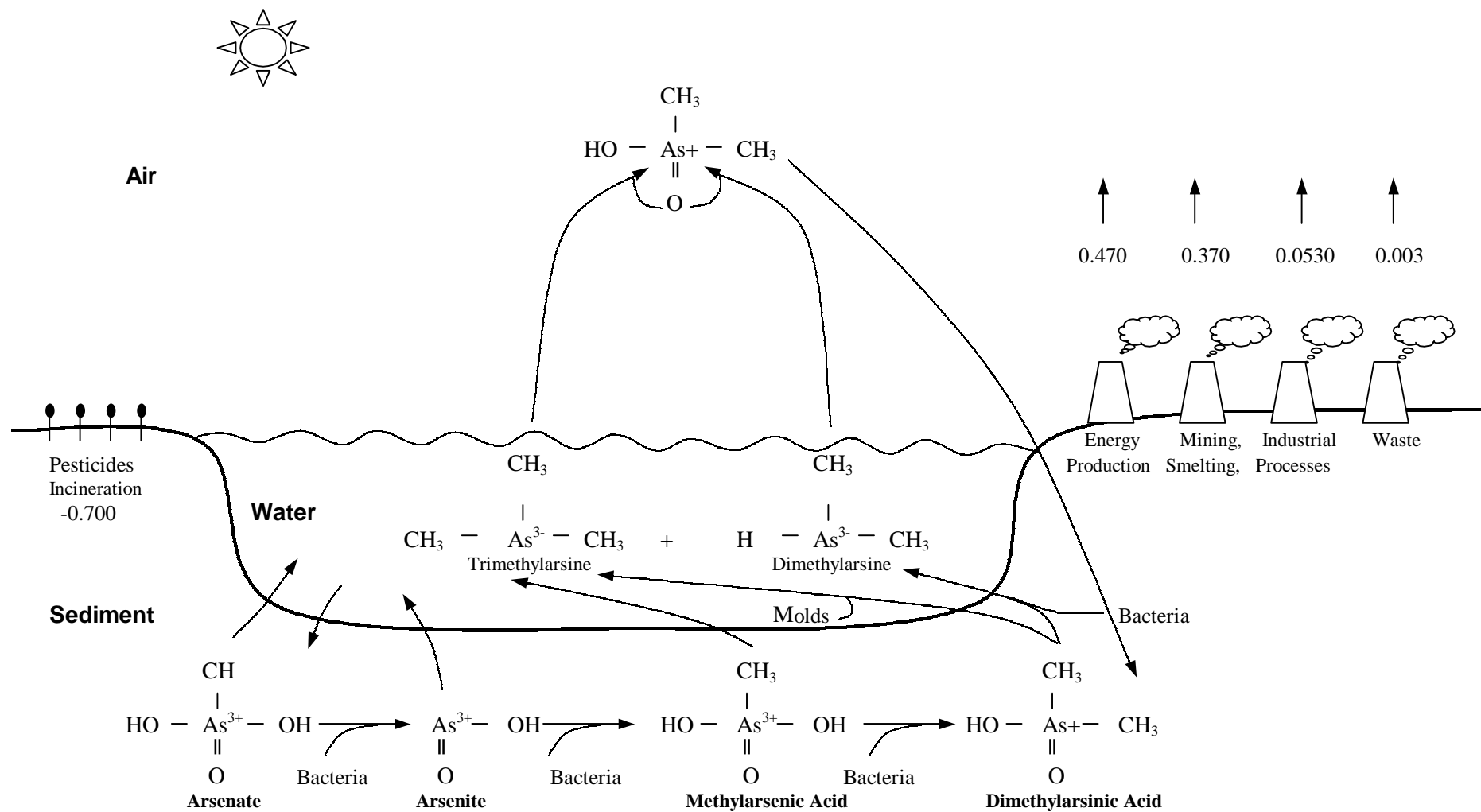


Figure 2. Biogeochemical cycle for arsenic. Sources: Ayres & Ayres (1999, Figure 6.4), and Ayres & Ayres (1999, Table 6.1).

Step 4: Examination of Interactions within the Arsenic Cycle

The main interaction found within the arsenic cycle derives from the fact that arsenic is not mined alone. Instead, arsenic is produced as a byproduct of other non-ferrous metal mining. Usually, arsenic is produced as a byproduct of copper mining, although the mining of lead, zinc and iron ores can also produce arsenic. Therefore, if the mining of these other metals was eliminated, the production of arsenic would also cease.

The largest reduction in arsenic atmospheric emissions would occur if the reliance on coal burning for energy production was significantly decreased. A reliance on natural gas or hydroelectric energy to meet energy production needs would result in drastically reduced atmospheric arsenic emissions. Furthermore, since mining and smelting is the second largest source of atmospheric arsenic emissions, a reduction in these processes would also significantly decrease the emissions of arsenic.

In addition, there is a crucial interaction between acidity and arsenic availability. Since a reduction in the pH of waters greatly increases arsenic availability, acid rain is a major concern in reducing arsenic exposures. Therefore, in order to decrease the level of arsenic that is bioavailable, a reduction in atmospheric sulfuric and nitrous oxides is necessary. If precipitation continues to become more acidic due to anthropogenic sulfur and nitrogen oxide emissions, a corresponding increase of arsenic within the environment is expected. This would increase the arsenic found within food chains, which can eventually impact human health.

Finally, since arsenic is mainly used as a biocide in wood treatments, a reliance on a different biocide would greatly reduce the amount of arsenic found in the environment. The markets of new home construction and renovation is expected to drive future demands for arsenic. Recently, concerns over worker and child exposures to arsenic have been increasing. Currently, inhalation through the respiratory tract is the main route of human exposure. Therefore, a reduction in arsenic emissions would greatly reduce human risk levels. The EPA has classified arsenic as having a high carcinogenic risk, although this risk analysis has been contested. Children are especially at risk since playgrounds may be built with wood that has been treated with arsenic. As a result of these human health concerns, for certain applications, the use of chromated copper arsenate is prohibited. In addition, the use of alternative preservatives has become more widely accepted. These factors are expected to decrease the long-term demand for arsenic.

Sources of Information

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