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Industrial Contributions of Arsenic to the Environment

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Arsenic is present in all copper, lead, and zinc sulfide ores and is carried along with those metals in the mining, milling and concentrating process. Separation, final concentration and refining of by-product arsenic as the trioxide is achieved at smelters. Arsenic is the essential consistent element of many compounds important and widely used in agriculture and wood preservation. Lesser amounts are used in metal alloys, glass-making, and feed additives. There is no significant recycling. Current levels of arsenic emissions to the atmosphere from smelters and power plants and ambient air concentrations are given as data of greatest environmental interest.

Arsenic is a bad word, but actually it is a very useful substance. Arsenic trioxide, which is the arsenic of commerce, is the basic raw material for insecticides, herbicides, fungicides, algicides, sheep dips, wood preservatives, feed additives and human and veterinarian medicinals, about in that order, perhaps, of volume of consumption. As the element itself, arsenic is useful in alloys, particularly in lead alloys for lead shot or lead battery grids and it is a constituent element of gallium arsenide, which is responsible for the nice colors on your digital watches. It's in the light-emitting diodes of watches and other instruments. So arsenic has very significant, substantial uses in this country and in the world in general.

The world production, is about 50,000 tons per year, as arsenic trioxide; reduce that by 25% to get the tonnage of the element. The United States consumes about half the total world production and the United States produces for its own use about half of what it consumes. That production is solely at the Asarco smelter in Tacoma, Washington. Current production rates there are about 1,000 tons of arsenic as the trioxide per month. The remainder of the U. S. supply, another 12,000 tons per year or so, comes from Mexico, Sweden, and France, in that order.

There are two grades of arsenic trioxide: A crude grade containing about 96–97% arsenic trioxide and a refined grade containing about 98.5–99%. The source of arsenic trioxide is the smelting industry. Arsenic is a by-product of the smelting of copper, lead, and zinc concentrates. No one would ever build a smelter to produce arsenic; it simply would not be economical. Arsenic is actually an undesired constituent of the copper, lead, and zinc concentrates which come into copper, lead, and zinc smelters. There are usually penalties attached to the purchase of these concentrates because of the arsenic content. We really want pure ore concentrates. But because arsenic is inevitably present and must be removed, it is removed in the course of smelting and is finally separated as a relatively pure by-product.

The amounts of arsenic in the various copper, lead, and zinc concentrates range all the way from parts per million up to as high as 15%. In general, foreign concentrates such as those from the Phillipines and from Peru contain higher percentages of arsenic. Concentrates from the northern Rocky Mountain regions of the Country contain substantially lesser but still moderate amounts in the tenths percent range. In the southwestern part of the United States, where there are numerous copper deposits, the amount of arsenic is present in the hundredths of percent or less.

The largest amount of arsenic being received by nonferrous smelters comes to the copper smelters in trace percentages in copper concentrates. The concentrates are wet and not dusty, containing 12–14% moisture except for some surface drying.

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As the concentrates are processed, however, there are numerous opportunities for dust and fume evolution. Table 1 lists of the melting points of the various elements which are contained in copper, lead, and zinc concentrates. The melting point of arsenic is quite high but is well below the melting point of copper. Thus arsenic can be volatilized readily. The arsenic is oxidized to arsenic trioxide, which has a sublimation point of 190°C. Its appreciable volatility is largely responsible for its emissions at varying stages of the smelting process.

Table 1. Element melting and boiling points.

Element	Melting point, °C	Boiling point, °C
Antimony	530	1380
Arsenic	817	—
	sublimes at 613	
Bismuth	271	1560
Cadmium	321	765
Copper	1083	2595
Indium	157	2000
Lead	328	1744
Selenium	217	685
Tellurium	450	990
Thallium	304	1457
Zinc	419	907

All of the processes of copper recovery do not involve dust and fume production. Copper refining, for example, is a wet process, all electrolytic. There are some fugitive emissions from smelting. One example is the fume evolved when hot slag is dumped. In that fume there are traces of arsenic. This is a very intermittent operation, and total mass emission of arsenic from this source is rather low and insignificant in the overall.

Arsenic roasters are charged with crude flue dusts recovered from various smelter processes. These flue dusts may contain from 20 to 40% arsenic. The flue dusts are simply heated, and the arsenic trioxide is sublimed off. The vapor passes through ducts and condenses in long labyrinthine brick chambers which are known as arsenic kitchens. At periodic intervals the chambers are opened and the material is chopped out of the chambers. It is a rather hard crystalline material. The removed material is hauled off, pulverized, and packed.

In addition to wearing completely protective work clothing and respirators, it has been the custom of arsenic workmen in some smelters to wash out their nostrils at the end of a work shift. This is a precautionary measure in case there have been leakages in the respirators and arsenic trioxide dusts have been deposited on the septum. There could be irritation, ulceration, and eventually perforation. They very carefully wash each other's noses and successfully prevent septum damage.

Surprisingly, the smelters are not the principal emission source for arsenic in the United States, as nearly as we can tell. According to studies conducted by the Oak Ridge National Laboratory and estimates based on annual consumption of 400 million tons of coal by power plants, the mass emission of arsenic from power plants is of the order of 3,000 tons per year. But of course power plants are many and are spread all over the country, which mitigates the possible problem. Pollution is really a matter of concentration not just mass emission. So far as I know there has been little concern expressed about the arsenic concentrations surrounding power plants. There have been some concerns abroad and perhaps we'll hear more about them from Dr. Bencko later. But there have been very serious concerns about the emissions from smelters, in particular the copper smelters, and especially the Tacoma plant operated by my company.

The current rate of emission of arsenic as As is 400 lb/day at the Tacoma plant. There is a substantial reduction in prospect when approximately a $7 million program will be completed in the next two years, if the court cases pending can be settled reasonably soon. The 400 lb ought to be reduced by about 90%. A figure of 400 lb sounds like a lot, and it is if you were to put it in one spot; but, in fact, that amount of arsenic is dispersed over the course of a day in nearly 600 million cubic feet of air and gases going up the principal stack. The volume is actually calculated as about 576 million standard cubic feet per day. The gases are hot and occupy a greater volume than that. The concentration of arsenic in the stack is about 10 or 11 mg/m^3. Again, this sounds as though it is a high concentration; from a physiological standpoint it is. But there is tremendous dilution after the gases are vented from the top of the stack so that the actual ground concentrations are very much reduced. Another point about the emission concentration is that we may be approaching the limit of practicable technology. I would call your attention to the fact that the new source performance standards adopted by the Environmental Protection Agency allow particulates concentrations of 50 mg/m^3 from smelting operations, and by contrast we have about 10 or 11 mg of arsenic as a particulate. We are meeting the new source performance standards for total particulates, and we may be nearing the limit of technology in the removal of these substances. Near perfection is attainable, but at an enormous and impossible cost.

The other principal source of arsenic emission to the atmosphere in the United States besides power plants and copper smelters is reported to be cotton ginning dusts. Arsenic compounds are used in the cotton industry. Treatment with arsenic com-

pounds to dessicate the cotton plants makes possible mechanical picking in the cotton fields. Without it, the costs of cotton would be significantly higher. Cotton ginning dust and the combustion of cotton gin wastes have been reported as creating significant concentrations of arsenic in the air downwind from these operations.

The ambient air concentrations near the Tacoma smelter are another point. Our sampling for arsenic in ambient air is done with low-volume samplers operating with membrane filters at a sampling rate of about 1 ft^3/min. Filters are changed at weekly or biweekly intervals. We have plenty of material usually to analyze. We don't worry about nanograms; we have plenty of micrograms to measure.

The concentration, of course, varies with the distance from the smelter. At the sampling station closest to the stack at our property line, the monthly averages during 1975 ranged from 0.5 to 2.5 $\mu g/m^3$. At about 1000 ft away, in our parking lot, As concentrations ranged from 0.13 to 0.76 $\mu g/m^3$; at 2000 feet, 0.26-1.46 $\mu g/m^3$. This is something at an anomaly: we get a little higher concentration at this particular distance. At about 1 mile, As concentrations are 0.09–0.39, $\mu g/m^3$; 4 miles, 0.02–0.11, and at 8 miles, 0.02–0.13. These distances by the way are in the directions of the prevailing winds. The winds are generally either northerly or southerly, really northerly or southwesterly, in the Tacoma area. These concentrations are, for the most part, under 1 $\mu g/m^3$. The total dose you would receive via the air if you were to breathe about 15 m^3/day (a generous estimate) would be 15 μg of arsenic if the airborne arsenic trioxide particles are all inhaled and all absorbed. This compares with an estimated daily intake of arsenic in food ranging from about 20 μg to several hundred or more, depending on the nature of the food eaten.

Going on to two other copper smelters operated by my company where the arsenic concentrations in the raw materials are substantially lower, we have in a smelter in Arizona, which shows ambient arsenic levels from 0.03 up to 0.25 $\mu g/m^3$ maximum at two sampling stations. At El Paso we have at varying distances 0.02 to 0.17 $\mu g/m^3$.

One smelter operated by another company reported 0.02–0.73 $\mu g/m^3$ within a 2-mile radius, with a mean of 0.12 $\mu g/m^3$. Another reported only about 3 ng up to 80 ng/m^3 within about a mile of the operation.

I have not accumulated in any systematic way the data on arsenic in the soil, but I wanted to just mention an interesting thing about the elements in dustfall and therefore elements in the soil. In the 40's and 50's a lot of work was done on dustfall measurements. This was a simple way of recording and measuring air pollution. It was found in those days that the average urban rate of dustfall ranged from about 25 to 72 tons per square mile each month. If you were to take a very conservative suburban dustfall rate of 20 tons per square mile per month that would mean you would have about two-thirds of a ton per day, from natural sources as well as man-made, deposited over each square mile. If you emitted one pound per day of any element in that square mile and deposited it each day uniformly over the square mile, you would contribute to the dustfall an amount of that element equal to a concentration of 750 parts per million. My point is this, that a very small emission rate can contribute very significantly to the accumulation of any element in the soil as it is deposited. Dustfall is of course a very important part over the whole world of soil deposition. It's been shown very positively that the top layers of soil of the Caribbean Islands came from the Sahara Desert. Transport of particulates is worldwide and goes on on a grand scale.

Some time ago, in a paper by Blot and Fraumeni of the National Cancer Institute (*1*), it was suggested that lung cancer rates in smelter counties of the United States were higher than normal and that arsenic emissions from the smelters might be contributing to the excess lung cancer rate. There were several things wrong with this analysis. One of them was that no distinction was made between smelters and refineries. Refineries are quite different operations with little or no arsenic emission. Secondly, no differentiation was made among copper, lead, and zinc smelters, and as I have said, most of the arsenic is taken into copper smelters. The paper also did not have any ambient air data or any emission data. So there were large questions as to why they could even suggest a relationship between arsenic and lung cancer rates. In Table 2 are

Table 2. Comparison of U. S. national average lung cancer mortality rates with the rates experienced by counties in which copper smelters are located (ICD 162, 163).[a]

County	Lung cancer (white males) mortality rate
Deer Lodge, Montana	65.2
Gila, Arizona	46.3
Pima, Arizona	39.7
Chochise, Arizona	38.1
NATIONAL AVERAGE	38.0
Pierce, Washington	35.8
El Paso, Texas	33.9
Greenlee, Arizona	32.0
Pinal, Arizona	31.7
Ontonagon, Michigan	29.2
Polk, Tennessee	28.8
Grant, New Mexico	26.3
Salt Lake City, Utah	26.2
White Pine, Nevada	20.0

[a]NIH data (*2*).

listed the copper smelting counties of the nation and the lung cancer rates, from Blot and Fraumeni's data, for these counties. As you can see, there are more counties below the national average rate for lung cancer than there are above. Table 3 shows the great variation in percentages of arsenic in the feeds of smelters around the country and the lung cancer rates for the counties in which the smelters are located. If you study those figures, I think you will see no apparent correlation between the feed rates of arsenic into the smelter and the lung cancer rates. Indeed, there is no correlation. The whole point I'm trying to make is that the simplistic conclusions or suggestions that are made on the basis of such ignorance of the industry are in my mind outrageous and something we should protest at every opportunity. That's what I'm doing now.

Table 3. As in smelter feeds and lung cancer rates.

Smelter (Company)	Arsenic in feed, %	Lung cancer SMR Male	Lung cancer SMR Female
Tacoma (Asarco)	5.200	35.8	6.4
Anaconda (Anaconda)	0.96	65.2	4.3
El Paso (Asarco)	0.800	33.9	7.6
Garfield (Kennecott)	0.135	26.2	3.5
Hayden (Asarco)	0.040	46.3	7.3
Hayden (Kennecott)	0.015	46.3	7.3
San Manuel (Magma)	0.007	31.7	7.8
Hurley (Kennecott)	0.005	26.3	10.8
White Pine (Copper Range)	0.002	29.2	2.0
U. S. Average		37.98	6.29

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