

Health risk and sources of arsenic in the potable water of a mining area

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Abstract Exploitation of ore bodies has promoted urban development near mines since ancient times. Silver, copper, lead, zinc and gold ore deposits are often accompanied by arsenic. In these areas, tailings, mine water and smelter fumes constitute potential sources of pollution to the groundwater. Oxidation of sulphide ores may release arsenic, which is then transported through aquifers. Due to its toxic properties, limits on the level of arsenic in drinking water have been established (0.01 mg l⁻¹ WHO guideline; 0.05 mg l⁻¹ Mexican standard). In México, groundwater polluted with up to 1.0 mg l⁻¹ of arsenic was used as a potable source in Zimapán, Hidalgo. To solve this problem several aspects had to be studied. The concentration of arsenic and the source of groundwater contamination were determined. Since no surface water bodies are located in the valley, an evaluation had to be made to assess the possibility of tapping a sufficient amount of high quality water. The investigations included sampling and chemical analyses of rocks, water and soils, as well as hydrogeological and geological studies. A water treatment procedure was tested on wells that were contaminated. Wells without arsenic were not considered since they do not produce a sufficient amount of water.

ARSENIC IN MINING AREAS

Arsenic is a widespread constituent of many types of mineral deposits. Arsenic commonly accompanies deposits of Cu, Ag, Au, Zn, Cd, Hg, U, Sn, Pb, P, Sb, Bi, S, Se, Te, Mo, W, Fe, Ni, Co and Pt, particularly those containing sulphides and sulpho-salts (Boyle & Jonasson, 1973). The commonly identified arsenic-bearing minerals are realgar (AsS), orpiment (As₂O₃), arsenopyrite (FeAsS), claudetite (As₂O₃), arsenolite (As₄O₆), arsenic pentoxide (As₂O₅), and scorodite (FeAsO₄·H₂O). Within this group of minerals, arsenopyrite probably is the most common arsenic mineral (Boyle & Jonasson, 1973; Welch *et al.*, 1988).

It is known that oxidation of sulphide ores, particularly those rich in pyrite, introduces high concentrations of metals such as arsenic, hydrogen ions and sulphate ions into the waters of many mining regions (Toran, 1987; Plumlee *et al.*, 1992). Natural concentrations of metals in non-acid waters in proximity to ore deposits can exceed nonmineralized background concentrations by hundreds to thousands of times, even in areas that have not been mined (Runnels *et al.*, 1992). Arsenic from natural

and anthropogenic processes has polluted streams and groundwater in a gold-mining area of Ghana (Smedley *et al.*, 1996). Sulphide oxidation at Levant mine (UK) has produced high concentrations of arsenic in the groundwater (Bowell & Bruce, 1995). In some mined areas of the western US, pollution of aquifers with arsenic has also been observed (Welch *et al.*, 1988).

Human activities related with mineral processing might also produce high levels of arsenic in the environment. Acid mine drainage, tailings, and waste rock deposits are the main source of metals close to the mining area. Smelting of ore concentrates releases metals to the atmosphere and may be another source of pollution (Gray *et al.*, 1994; Salomons, 1995; Rybicka, 1996). In soil, up to 560 ppm of arsenic was measured 0.8 km (one half mile) downwind from a smelter in Rhodesia (Rose *et al.*, 1990). Near the copper smelter of Garfield Utah, the arsenic levels in surface soils within a 22 km radius of the plant varied from 5 to 540 ppm (Yan-Chu, 1994). In San Luis Potosí, México, the washing out of tailings by rainfall, dispersion of dump material by wind, and irrigation with mine water, has produced high concentrations of arsenic in soils (Castro-Larragoitia *et al.*, 1997).

ARSENIC TOXICITY

All humans are exposed to low levels of arsenic. Arsenic exposure occurs mainly by ingestion of contaminated drinking water or by inhalation and/or ingestion of polluted soil. A fatal dose of ingested arsenic as As_2O_3 is about 1.0–2.5 mg As per kg body weight. The current European and US Environmental Protection Agency limit for arsenic in drinking water is 0.05 mg l^{-1} , although the World Health Organization has recently reduced its recommended limit to a provisional value of 0.01 mg l^{-1} (Morton & Dunnette, 1994; Yamauchi & Fowler, 1994).

Above-average levels of exposure are usually observed among people who live in areas where the drinking water has an elevated natural level of inorganic arsenic, among workers and nearby residents of metal smelters, and among persons who manufacture or use arsenic-containing pesticides (Sthöhrer, 1991; Lianfang & Jianzhong, 1994). Arsenic enters the human body through ingestion, inhalation or skin absorption. Most arsenic is well absorbed through the gastrointestinal tract and lungs into the bloodstream. It is distributed to a number of organs, including the lungs, liver, kidneys and skin. The most typical effects of chronic exposure to arsenic in drinking water are skin diseases, including hyperpigmentation, hyperkeratosis and skin cancer. Renal, gastrointestinal, neurological, haematological, cardiovascular and respiratory symptoms can also be observed as a result of arsenic exposure (Chen & Lin, 1994).

THE ZIMAPAN CASE

The Zimapán valley is located in the flanks of the Sierra Madre Oriental range, approximately 200 km north of México City. The township is 894 km^2 and has 35 000 inhabitants, 8700 of which are from Zimapán. The main source of drinking water is the aquifer system. Exploitation of Ag, Au, Zn and Pb has occurred since the seventeenth

century in mines located to the north of the valley. The main arsenic-bearing minerals accompanying the mineral deposits are arsenopyrite, lollingite, tennantite, adamite, olivinite and scorodite. Until the first half of this century, tailings from the mineral processing accumulated in the southern edge of Zimapán. In addition, nearly 40 smelters operated in the town until 1940.

The local geology defines a complex heterogeneous aquifer system with sharp lateral contrasts. The Zimapán fanglomerate acts as an unconfined aquifer with partial hydraulic communication with Cretaceous fractured limestones.

Fractured limestones define the main aquifer. The limestone aquifer contains wells that are deeper than 50 m. Perched aquifers, which are present in some areas within the limestones, the fanglomerate and the Las Espinas volcanic rocks, have shallow dug wells (10–15 m depth) used for agriculture and occasionally for drinking water. The volcanic rocks and the El Morro conglomerate have low permeability, but locally they may have secondary permeability and so form perched aquifers.

The regional groundwater flow has a north–south direction. Most of the aquifer recharge comes from the precipitation in the surrounding mountains. Precipitation in the valley is less than 400 mm year⁻¹.

METHODS

Water samples were taken from shallow and deep wells located in different parts of the valley. Temperature, pH, conductivity and alkalinity were measured in the field. Major ions and arsenic were determined in the laboratory following the methods described in APHA (1989). Arsenic was measured by colorimetry through arsine formation and reaction with silver diethyldithiocarbamate. The lower detection level was 0.014 mg l⁻¹ of arsenic.

Soil samples were taken, using a shovel, near tailing ponds and former smelters, following the wind direction. Samples were also taken from tailings. Two or three samples of soil, each weighing 100 g, were obtained from different depths at each point. Samples were dried at room temperature, ground and subsampled. Arsenic in soil and tailings was determined by electrothermal atomic absorption spectrometry. For total arsenic, 1 g of prepared soil was digested with HNO₃ and HClO₄. For soluble arsenic determination, another 1 g of the soil was added to 25 ml of de-ionized water, shaken for 2.5 h and filtered. Soluble arsenic was quantified in the filtrate.

RESULTS

The highest concentrations of arsenic in the groundwater (up to 1.097 mg l⁻¹) were measured in some of the deepest wells drilled in the limestones. The presence of arsenic is related to oxidation of the arsenic-bearing minerals contained in the aquifer (Armienta *et al.*, 1997a). Background total arsenic concentrations (i.e. in soils of nonmineralized zones) ranged from 74 to 151 mg kg⁻¹. Arsenic concentrations in soils near mineralized zones and from areas anthropogenically polluted, reached 768 mg kg⁻¹. Trace element (arsenic and copper) enrichment in soils related to mineralization and contamination has also been observed in England (Abrahams & Thornton, 1987).

Arsenic levels of up to 0.437 mg l^{-1} were measured in the water from the shallow dug wells near the tailings. Higher sulphate levels were determined in these waters compared to the levels found in water from wells not contaminated by the tailings. Concentrations of total arsenic in the tailing dumps varied between 10 000 and 22 000 mg kg^{-1} , whereas soluble arsenic ranged from 2.5 to 3.4 mg kg^{-1} . The soil samples from the area surrounding the tailing dumps had total arsenic levels of 294 to 2580 mg kg^{-1} . Most of the higher concentrations were found in surface samples. Concentrations of soluble arsenic, which varied from 0.97 to 8.40 mg kg^{-1} , were much lower than total arsenic levels (Fig. 1). The weathering and leaching of arsenic from the tailings into the water is responsible for the contamination of the dug wells.

Less than 0.10 mg l^{-1} of arsenic was detected in all but one (having 0.529 mg l^{-1}) of the dug wells near former smelters or foundry wastes. The total arsenic in the soil in these areas ranged from 79.5 to 4176 mg kg^{-1} . The water-soluble arsenic varied from 2.10 to 18.95 mg kg^{-1} . Concentrations of soluble arsenic were higher at 30 cm and 50 cm depth than at the surface (Fig. 1). The increasing concentration of soluble arsenic with depth shows that infiltration of arsenic from the surface of the soil, to the groundwater, has taken place. Smelter stack particulates containing arsenic have settled on the ground and percolated through the soils.

The proportions of major ions were different between the samples taken from the limestones and those from the volcanics, as shown by Stiff diagrams (Fig. 2). None of the water samples from the volcanic area had arsenic concentrations above 0.05 mg l^{-1} , and the majority had concentrations below the detection level.

The main water supply to Zimapán is obtained from the most productive deep wells tapping the limestone aquifer. The deep and shallow wells drilled in the volcanics are arsenic free, but have low productivity. Mixing of water containing different arsenic concentrations produces drinking water with 0.3 mg l^{-1} of arsenic. The most productive well, which in turn is also the most polluted (1.097 mg l^{-1} of arsenic), was suspended in early 1996. Another naturally-contaminated well (0.526 mg l^{-1} of arsenic) is still connected to the municipal water supply system.

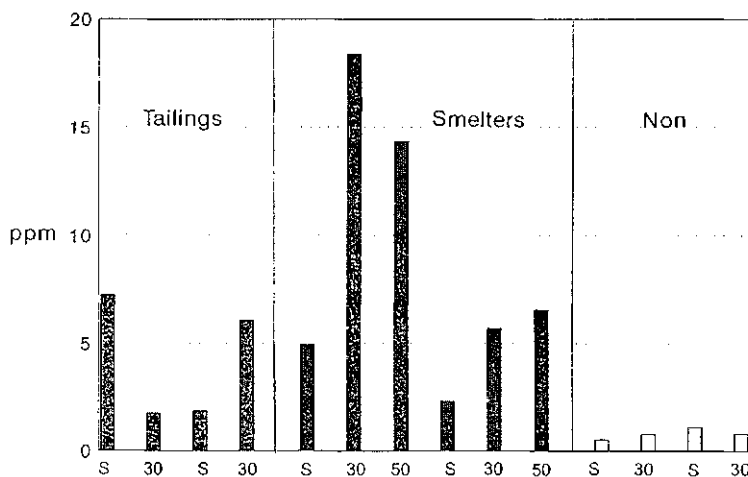


Fig. 1 Concentrations of soluble arsenic in soils at various depths. S = superficial, 30 = 30 cm, 50 = 50 cm.

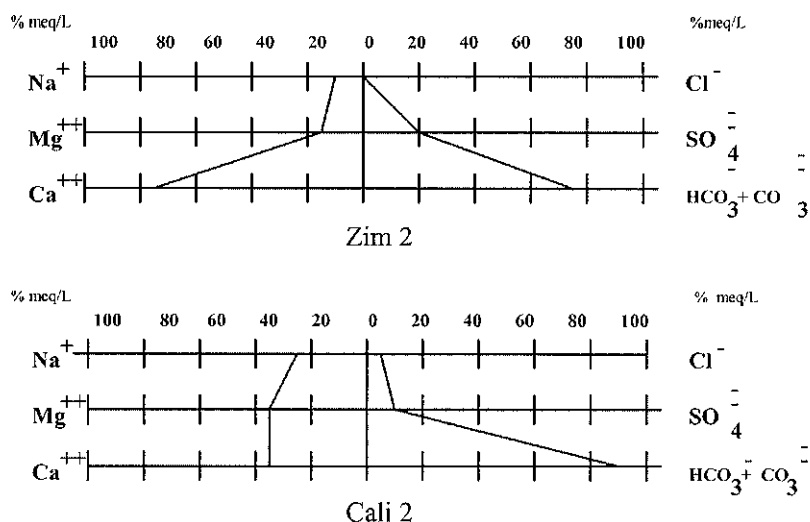


Fig. 2 Examples of Stiff diagrams of water coming from the limestones (Zim 2) and from the volcanics (Cali 2).

ALTERNATIVES

In the absence of meaningful information on natural background concentrations, targets for cleanup may be set that require water to be purer than that which existed originally. Such targets may be scientifically unrealistic and economically unachievable (Runnels *et al.*, 1992).

Since the most important groundwater contaminant source is the natural one, alternatives to dealing with the arsenic pollution should be based on this fact. The lack of water sources combining quantity and quality in the Zimapán valley led us to test a procedure to clean up the water.

Arsenic can be removed from the water by means of various treatment procedures. Adsorption on activated alumina, ionic exchange, inverse osmosis, lime treatment after oxidation and precipitation-coagulation processes, are some methods used for arsenic removal. Arsenic removal by metal ions is the most frequently applied technique (Bellack, 1971; Hathaway & Rubel, 1987; Jekel, 1994). A conventional treatment procedure (coagulation-flocculation-sedimentation-filtration) was tested in the laboratory using ferric sulphate as a coagulant. The procedure was applied in the most polluted well (El Muhi) before suspension of its operation (Morales, 1994). More than 94.9% of arsenic was removed by treatment with 80 mg l⁻¹ of Fe₂(SO₄)₃. A final arsenic concentration of 0.046 mg l⁻¹ (below the national drinking water standard of 0.05 mg l⁻¹) was obtained with this dose.

Treatment with ferric sulphate was also tested in a mobile water potabilization plant. The plant was produced at the Center for Development and Technological Applications of the Ministry of Health (CEDAT-SSA) México. The plant was originally developed as a means for producing safe drinking water in remote communities with scarce economic resources. Its suitability for arsenic removal was evaluated with artificial arsenic-polluted water. The plant is made up of dosifiers to

supply reagents, a sedimentation-flocculation tank, and two filtration tanks (Fig. 3). To complete the treatment, ozone and chlorine were added to the water. A solution of ferric sulphate, calcium hydroxide, chlorine and ozone was added through the reaction tube of the plant. One tank with a mixture of silica sand and anthracite, and another tank with activated charcoal, were used for filtration. Different reagent doses and water flows were tested for treating a solution containing 1.09 mg l^{-1} of arsenic. The water was circulated twice within the plant before its final outlet. A concentration below the detection level was obtained with a maximum water flow of 50.9 l min^{-1} in 20 min of treatment (10 min each run). The cost of the plant is about US\$17 600, and the operation cost is US\$0.19 (19 cents) per cubic metre of treated water. Considering a weekly consumption of 40 litres per family, the monthly payment would be US\$0.27 (27 cents) per family (assuming a 6 year depreciation of the plant, and a water supply to 975 families per each plant).

The operation of water treatment plants is not common in many parts of México. Generally, the lack of high quality water is solved by drilling more wells, or pumping surface water from nearby areas. In Zimapán, the nearest high quality water body is located about 30 km southeast, and water would need to be pumped up approximately 120 m from there, to reach the Zimapán valley. The cost of pumping would be very high. More than five deep wells have been drilled in the valley without successfully accessing water of adequate quantity and quality.

To solve the pollution problem, the authorities needed to be willing to spend a significant proportion of the local budget, which is small due to the low income of the inhabitants. A study on the health effects produced by arsenic has been used to convince them. Arsenic concentrations in hair and diseases possibly related with the

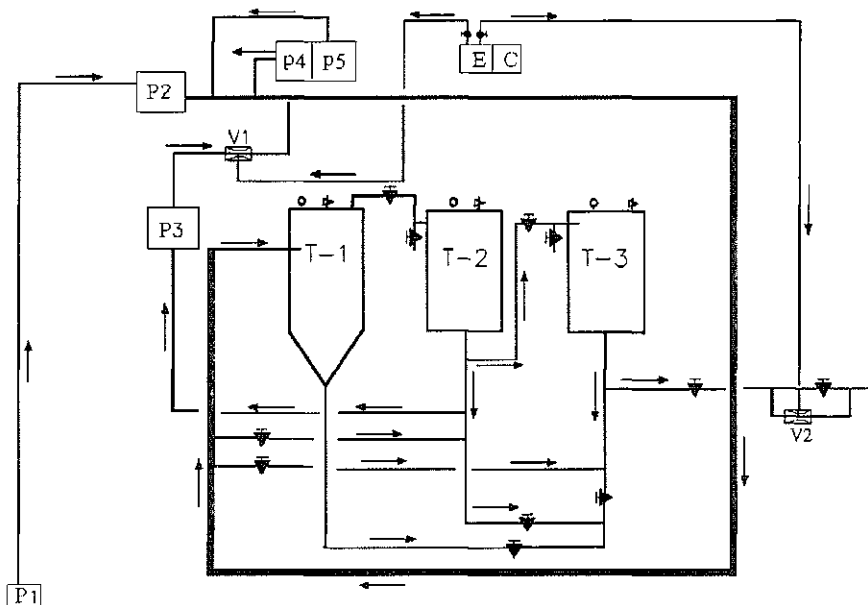


Fig. 3 Diagram of the treatment plant. P = pump; V = valve; T = tank; EC = electrolytic cell. Modified from CEDAT (1997).

ingestion of arsenic-polluted water were evaluated in the population (Armienta *et al.*, 1997b). Of the 120 sampled inhabitants of Zimapán, 97 showed some degree of skin effects. Significant differences in the arsenic content of hair samples were found in people having some degree of skin disease compared to those with no visible health effects. Arsenic concentrations in hair were significantly different ($p < 0.05$) between people drinking water with arsenic levels of 0.5 mg l^{-1} or greater, and people drinking water with lower levels of arsenic. This study provides evidence of the adverse health effects associated with the ingestion of arsenic-polluted well water in Zimapán.

Pollution problems might be present in mining areas in developing countries. In México, 13 000 jobs are directly related to mining activities, and 100 000 people work in activities indirectly linked with mining. Solutions to contamination problems must be considered to preserve both the environment and the economic benefits of mining. The solutions must be based on studies to determine the degree and the actual sources of pollution. The target and the alternatives should be determined for each location, considering its social and economical framework.

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