Natural Occurrence of Arsenic in Southwest Ground Water

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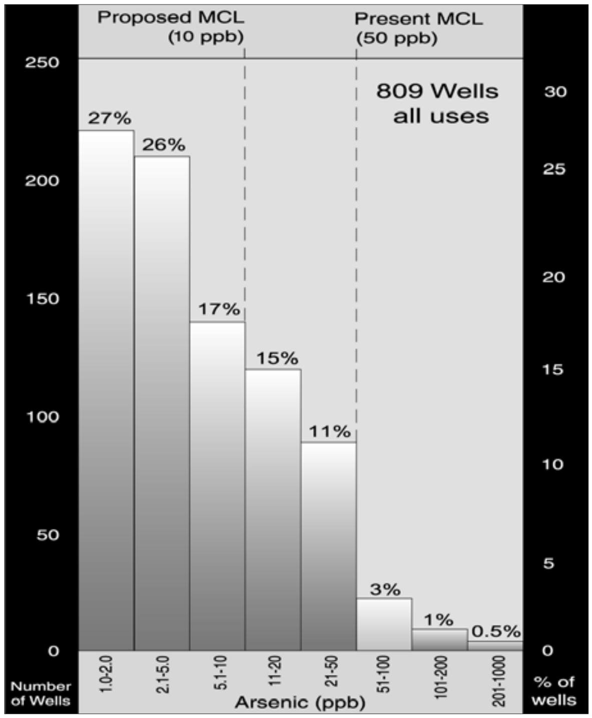
Arsenic is a naturally-occurring chemical element that is present in virtually all geologic materials at concentrations of typically 1 to 5 parts per million (ppm). Rocks and sediments in some geologic environments contain much higher levels of arsenic. Naturally elevated concentrations occur in ground water where concentrations in aquifer materials are high and where arsenic is easily mobilized from aquifer materials. Much remains to be learned about the processes that determine the amount of arsenic in aquifer materials and the readiness with which it is leached into ground water.

In the western United States, ground water with elevated arsenic concentrations is known to be associated with four types of geologic environments (Welch et al., 1988):

- Cenozoic lake beds, particularly in arid environments
- Intermediate to felsic volcanic rocks and associated sediments
- Geothermal environments
- Areas with gold and uranium deposits.



Arsenic levels in water from 809 Arizona wells. Figure reprinted with permission from Arizona Geology. (Spencer, 2000).

Cenozoic Lake Beds

The Southwest is characterized by numerous late Cenozoic sedimentary basins filled with sand, gravel, and conglomerate. The high-quality ground water contained in these sediments sustains many cities and communities in the Southwest. In most of the Southwest, surface water flows through these basins and is not trapped by lakes or playas. However, 5 to 35 million years ago, when these basins were actively subsiding due to movement on basin-bounding normal faults, many basins were closed and contained lakes and playas. As a result, lake sediments are common in the subsurface and include shale, claystone, calcareous siltstone, limestone, and enormous quantities of salt, gypsum, and anhydrite (Rauzi, 2002).

Clay and shale deposited in these ancient lakes may contain substantial arsenic adsorbed onto the very fine grains that make up the sediments. In contrast, sandstones and carbonates generally contain significantly less arsenic than clay and shale. The greater surface area of clay and shale particles for a given volume, plus an affinity for adsorbing trace elements, are probably responsible for this difference. High groundwater concentrations of arsenic are found in the Verde Valley of central Arizona, and are likely related to the abundance of clay-rich sediments in the underlying late Tertiary Verde Formation.

Volcanic Rocks

Volcanic rocks and sediments derived from them are also associated with elevated arsenic levels in ground water. This may be true not because volcanic rocks contain more arsenic than other types of rocks, but because the arsenic is more readily mobilized from volcanic rocks and derived sediments. In the northeastern half of the Tucson basin, where sediments are derived largely from granitic rocks, arsenic concentrations in ground water are generally less than 2 parts per billion (ppb). In contrast, in the southwestern half of the basin, underlain by sediments derived substantially from volcanic rocks, arsenic is found in much higher concentrations in ground water (Spencer, 2000).

Robertson (1989) concluded that the chemistry of ground water changes as the water flows from basin-margin areas of recharge to basin-interior areas where fine-grained sediments are typical. Specifically, as ground water flows through such systems, weathering reactions remove dissolved CO_2, increasing water pH. As pH increases, arsenic becomes more soluble. In basin interiors, where sediments are fine-grained and total sediment surface area is large, arsenic is apparently liberated from grain surfaces in significant quantities and transferred to the ground water. Volcanic rocks and derived sediments, especially where altered to clay minerals, may be especially prone to yielding arsenic to groundwater under such conditions.

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Groundwater arsenic concentrations greater than 50 ppb have been identified in the interiors of many basins in southern and central Arizona, including the Safford and San Pedro basins in southeastern Arizona (Robertson, 1989). In these areas, elevated arsenic levels are associated with fine-grained clastic sediments and slightly alkaline water chemistry, with pH levels of 7.5 to 9.5.

Geothermal Environments

Arsenic is also associated with geothermal areas, probably because trace elements such as arsenic are more readily mobilized and transported by warm or hot water. Brandvold (2001) found the highest concentrations of arsenic in ground water (40 ppb) in the Socorro Valley of central New Mexico to be associated with thermal springs or wells located near the city of Socorro and the Bosque del Apache Wildlife Refuge. Hem (1991) reported an arsenic concentration of 4.0 ppm in ground water from a 186ºC thermal well at Steamboat Springs, Nevada.

Mineralized Zones

Arsenic concentrations in rock and soil are highest in areas of sulfide mineralization, where arsenic is especially concentrated in minerals such as arsenopyrite, orpiment, realgar, and some copper sulfides. Arizona's abundant sulfide mineral deposits are not commonly associated with high arsenic concentrations in ground water; however, data are sparse, as water production wells are rarely installed in mineralized bedrock or in sediments near such bedrock.

Brandvold (2001) cited many geochemical factors that appear to be associated with arsenic in ground water in the Albuquerque area. Total and dissolved arsenic correlated positively with temperature (r = 0.5 - 0.8), fluoride (r = 0.6 - 0.8), silica (r = 0.7 - 0.9), sodium (r = 0.7), chloride (r = 0.7), and specific conductance (r = 0.4 - 0.7). Where depth to groundwater measurements were available, a slight correlation with arsenic (r = 0.32) was also observed. However, these correlations did not hold south of Socorro in the thermal springs area, where only a slight negative correlation with hardness was noted.

In conclusion, Cenozoic basins provide much of the ground water used by Southwestern communities, and these basins commonly contain subsurface lakebeds or sediments derived from volcanic rocks. Such materials may be the primary source of elevated arsenic concentrations in ground water. Arsenic is associated with specific geologic environments in the Southwest, but it is also clear that much remains to be learned about arsenic in ground water in this geologically diverse region.

Aqueous Speciation of Arsenic

The most common aqueous species of arsenic are the oxyanions arsenate (in the As(V) oxidation state), or arsenite (in the As(III) oxidation state). Arsenate is most prevalent as the monovalent $H_2AsO_4^-$ for pH < 7. At pH > 7, the divalent $HAsO_4^{2-}$ predominates. Arsenite typically occurs as the uncharged H_3AsO_3. Treatment technologies are generally more efficient for the arsenate species because they carry a negative charge.

Reducing conditions favor the uncharged arsenite. In order to increase removal efficiency when As(III) is present, the EPA suggests pre-oxidation to the As(V) state.

Sources

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