

# **ARSENIC IN ARIZONA GROUND WATER** Source and Transport Characteristics



### **Regulations**

Following on the U.S. Environmental Protection Agency's 'Arsenic Rule' decision to lower the allowable arsenic content in drinking water from 50 to 10 parts per billion (ppb) or less, public water systems were required to meet the lower limit by January 23, 2006. Private well owners are not subject to the rule because, under Arizona law, it is the sole responsibility of the private well owner to determine the quality (potability) of their private well water. However, private well owners across the state have realized the importance of testing their own water supply for arsenic.

#### Distribution

Arizona's Department of Environmental Quality (ADEQ) Ambient Ground Water Monitoring Program regularly conducts sampling to monitor regional ground water quality, as shown on the cover figure. This is done to detect the presence of new and existing pollutants, including arsenic and other naturally occurring constituents. Measurable levels of arsenic are found in ground water across the state.

Regional studies have been conducted by ADEQ since 1995 in 29 of the 51 ground water basins designated by the state. Arsenic was not detected above the minimum reporting level of 5 ppb in 1,117 of the 1,346 ground water sites sampled (83%). However, at 229 of the sample sites (17%), arsenic was detected at concentrations above the 10 ppb drinking water standard. These elevated arsenic concentrations occurred within each of the sampled basins, most frequently in wells or springs having older ground water such as characterizes the deep, artesian aquifer found in the San Simon sub-basin of the Upper Gila River Watershed (Towne, 2004). Arsenic concentrations above the 10 ppb limit are also found in the Casa Grande area, along the San Simon and Gila Rivers, and in scattered areas of Mohave and Maricopa Counties. Concentrations in excess of 2,000 ppb have been found in private wells in the Verde Valley of Yavapai County. (ADEQ, 2004).

### **Health Effects**

Arsenic poisoning is easy to diagnose and treat, with the most common symptoms ranging from garlic breath to "pins and needles" sensations in the hands and feet. Acute poisoning and death may occur when one tenth of a teaspoon (about 0.5 grams) of (inorganic form) arsenic is ingested at once. But no harm occurs when the same amount of arsenic is ingested by eating shrimp and other seafood. These foods have a non-poisonous organic (carbon-based) form of arsenic (Lee, 2007). To date, Food and Drug Administration has not set limits for allowable concentrations of arsenic in food sources because there are no known health hazards. However, there are numerous other forms of organic and inorganic arsenic that are considered very toxic. In general, arsenic containing chemicals are very poisonous when dissolved in and ingested with water. (Norman, 2005)

Chronic arsenic exposure may increase the risk of cancer and mimic the symptoms of diabetes, although arsenic is used in some cancer treatments and was used to treat syphilis prior to the discovery of antibiotics. Arsenic is readily excreted in the urine. Therefore, chronic exposure to this chemical is routinely determined by measuring arsenic levels in urine. Longer chronic arsenic exposures can be determined by measuring the concentration of arsenic retained in the hair and/or fingernails. Research has shown that arsenic's effects on human health are variable, with some ethnic populations exhibiting greater tolerance.

### **Geology Rocks!**

Arsenic chemically binds with other elements such as oxygen and sulfur, and often replaces certain elements in arsenic-containing minerals. For example, arsenic forms arsenopyrite [FeAsS] by replacing the sulfur (S) in this common arsenic mineral. In geologically ancient Arizona, granitic magma pushed upward into the host rock eventually forming granitic plutons and mineralized veins of copper, silver, gold ore – and minerals containing arsenic like arsenopyrite. It is generally true that regions of granite bedrock with gold ore in Arizona also contain elevated concentrations of arsenic. In the Cascade Mountains of Oregon and Washington, arsenic has been found in association with basaltic volcanic glass, but a proven relationship between basalt and arsenic in Arizona is not found in the literature. Historic Jerome in Yavapai County, known as the 'Billion Dollar' copper, gold and silver mining camp, contains mineral specimens of Jeromite, which consists of arsenic chemically bound with sulfur and selenium [As(S,Se)2].

Following on the report of an unusually large number of livestock deaths during the recent drought in the Verde Valley, arsenic poisoning was suspected as the probable cause. Arsenic concentrations in the animals' watering trough were tested and found to be between 400 and 500 ppb, and an intensive water quality study was launched. It was assumed that leachate from mine tailings was contributing to ground water quality degradation, but tailings concentrations were found to be around 200 ppb. Montezuma's well (several miles distant) was also tested and found to contain 100 ppb of dissolved arsenic. The study's authors concluded that the arsenic in ground water was not significantly impacted by mining activities but due to ground water in contact with the arsenic bearing minerals found in the Supai and Verde formations (Foust, et al., 2003).

The geology of northern Arizona and southern Utah consists of layers of ancient sedimentary rock, including the older Redwall Limestone, overlain by progressively younger rocks such as the sandstones, limestone, and shale observable in the exposed cliffs of the Grand Canyon. An extensive cave system was formed over 325 million years ago within the Redwall Limestone, similar to the solution limestone

caves of Kartchner Caverns State Park. Over geologic time, the weight of overlying rock layers that had accumulated on top of the caves in the Redwall Limestone collapsed, resulting in thousands of feet of vertical pipes that filled with rock rubble. These solution-collapse 'breccia' pipes acted as drains, filling with ground water that contained dissolved chemicals from the adjacent sedimentary rock as shown on the figure below. Thus, arsenic, metals, and uranium were deposited and concentrated within this lowoxygen environment. For example, arsenopyrite mineral precipitated within the localized breccia pipes of the Supai formation (Kenny, 2003). Within the past 2 to 5 million years, the Verde Valley was formed and portions of the Supai formation were eroded and redeposited as the Verde Alluvium Formation. Arsenopyrite was deposited in the alluvium which now forms the aquifer of the Big Chino and Verde Valley.



The Grand View Mine near the Grand Canyon is associated with a distinctive geologic phenomenon called solution-collapse 'breccia' pipes. This Figure (Kenny, 2003) shows the layers of rock that have collapsed into a cave formed in the Redwall Limestone, and the location where arsenic is concentrated.

### **Chemistry Rules!**

Arsenic may be geologically present, but the geochemical environment of the ground water determines whether arsenic will dissolve and be mobilized. For example, in the geology section above, arsenic was precipitated in the oxygen-poor environment of the ancient breccia pipes. Parts of this (Supai) formation were later eroded and transported, and eventually redeposited in what is now the Big Chino and Verde Valleys. The authors of the Verde study reported that during the drought of the late 1990s, water table elevations dropped, exposing arsenic-rich minerals to atmospheric oxygen. Oxygen-rich aquifer conditions in turn induced a chemical change in the arsenic mineral form, allowing it to dissolve into ground water.

Similarly, changes in ground water to high (alkaline) pH can induce desorption of arsenic from some types of arsenic-bearing minerals. This in turn can raise the levels of arsenic above drinking water standards (USGS, 1999). The authors of the Verde study also suggested that the elevated concentrations of dissolved arsenic in Montezuma's well may be due to the presence of calcium carbonate (limestone) that buffers acidity, increasing arsenic mobility. In addition, research has shown that naturally occurring soil bacteria will increase the rate of arsenic solution into ground water in low oxygen environments (Afkar, et al., 2003).

Arsenic mobility is a function of water pH and oxygen content. Therefore, any change in the geochemistry of an aquifer may elevate arsenic concentrations. The reverse is also true in that arsenic concentrations can be lowered by changing water pH and oxygen content. Several water treatment technologies are available to well owners. These technologies usually take advantage of favorable changes in oxygen and/or pH conditions and precipitate, absorb, and/or filter arsenic out of water. More information about arsenic and treatment options available to the private well owner can be downloaded from EPA's website at www.epa. gov/safewater/arsenic. For a list of home water treatment technologies used to reduce arsenic and other water contaminants in drinking water, obtain a copy of Arizona: Know your Water (Artiola et al., 2006).

Well owners may want to check for the presence of arsenic in their water by purchasing arsenic testing kits. If elevated levels of arsenic are detected, the testing kit results should be verified by an Arizona state certified laboratory. Well water samples can be analyzed for arsenic for \$20.00 to \$45.00, and sample collection bottles are usually provided by the laboratory. Well owners should follow the sample collection procedures and storage and sample transport methods recommended by the laboratory to produce unbiased results. The University of Arizona Cooperative Extension offices have a list of state certified testing laboratories and this listing can also be found at www.ag.arizona.edu/pubs/ garden/az1111.pdf. Another source of information about certified testing laboratories can by found at www.AZdhs. gov/Lab/License/index.htm.

## Reference

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Descriptions, locations, dates, and photos of samples found by Agent or brought to the Yavapai County Cooperative Extension Offices by clientele

http://ag.arizona.edu/yavapai/diagnostics/index.html

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