

# Fluoride in Ohio's Ground Water



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### The Technical Series on Ground Water Quality:

This series of reports provides information to the professional/technical community about ground water quality in Ohio's aquifers. These reports use data from:

- the ambient ground water quality monitoring program; and
- the public water system compliance programs.

These data, representative of raw water, are used to characterize the distribution of selected parameters in ground water across Ohio. The goal is to provide water quality information from the major aquifers, exhibit areas with elevated concentrations, and identify geologic and geochemical controls. This information is useful for assessing local ground water quality, water resource planning, and evaluating areas where specific water treatment may be necessary.

A series of parallel fact sheets, targeted for the general public, provide basic information on the distribution of the selected parameters in ground water. The information in the fact sheets is presented in a less technical format, addresses health effects, outlines treatment options and provides links to additional information.

#### Disclaimer

The Ohio EPA, Division of Drinking and Ground Waters (DDAGW) is providing information in this technical series as a public service. While Ohio EPA believes this information to be reliable and accurate, some data may be subject to human, mechanical or analytical error. Therefore, Ohio EPA does not warrant or guarantee the accuracy of these data. Because of the variability inherent in ground water data, caution must be taken in extrapolating point-data beyond the collection site. The accuracy, completeness, suitability and conclusions drawn from the information presented here are the sole responsibility of the user.

# Fluoride in Ohio's Ground Water

## Abstract

Fluoride concentrations in raw water across Ohio range from non-detect (<0.2 mg/L) to 3.58 mg/L. The primary control of fluoride distribution is geology. The Silurian and Devonian carbonate aquifers in western Ohio have the highest ground water fluoride concentrations. Much of the fluorite (CaF<sub>2</sub>) dissolved from the carbonates is secondary, low temperature mineralization (fluorite-sphalerite-galena). The carbonates exhibit a broad anticlinal structure that plunges slightly to the north-northeast and the fluoride distribution mimics this structure. The carbonate formations in the western half of Ohio contain more fluoride-bearing minerals than the sandstones of eastern Ohio or the widely distributed sand and gravel deposits. The second control on fluoride concentrations is contact time allowing for more dissolution of the rocks and minerals in the aquifer. Generally, deeper wells exhibit longer resident times and thus, slightly higher fluoride concentrations. The last control is local water quality. In areas where calcium concentrations are elevated due to dissolution of gypsum, the elevated calcium concentrations limits the dissolution of fluorite.

#### **Properties of Fluoride**

Fluoride (F<sup>-</sup>) is a charged atom (or "ion") that is the stable form of the gaseous element fluorine. Fluorine is a natural component of most water resources, and is among the top fifteen most common elements of the Earth's crust. Fluorine belongs to an element group called the halogens, which also includes chlorine, bromine and iodine. Fluorine tends to form monovalent (-1 charged) ions that are generally unaffected by changes in oxidation-reduction potential. Fluorine is extremely reactive due to its high electro-negativity. Consequently, it does not occur freely in nature, but rather aggressively combines with other elements (commonly calcium and phosphorous) into compounds known as fluorides.

#### Typical Concentrations and Sources of Fluoride in Water

Most natural waters contain less than 1 mg/L fluoride, and the concentration in the oceans is about 1.3 mg/L (Hem, 1985). Surface waters in the United States have low fluoride concentrations, usually in the range of 0.05 mg/L to 1 mg/L. Lake Erie has an average concentration of about 0.14 mg/L and Ohio streams and rivers typically have fluoride concentrations that are much less than 1.0 mg/L. Generally, surface water with concentrations close to 1 mg/L appear to be influenced by anthropogenic sources of fluoride. Inorganic fluorides are naturally released to Ohio's ground water through leaching from rocks and minerals as they weather.

A number of human activities can increase the load of fluorides to the air, land and water, including glass, steel, and phosphate fertilizer production. In addition, agricultural run-off, infiltration of fertilizers, and discharges from septic or sewage treatment facilities that process fluoridated water can all add inorganic fluorides to the environment. The most common inorganic fluorides are fluorite (calcium fluoride, CaF<sub>2</sub>, also known as fluorspar) and apatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,Cl,OH)). If fluoride dominates the mineralogy of apatite, it is known as fluoroapatite.

Outfall from wastewater treatment plants into streams and rivers is also a potential source of fluoride. This pathway has been studied and shown to increase downstream concentrations by less than 0.01 mg/L (Pollick, 2004). Fluoride levels have been shown to decline as water

travels from the surface through the soil zone and into ground water. Pescod (1994) found that 40-50% of the fluoride in water infiltrating to the ground water table is removed. Thus, a significant percentage of fluoride input from the surface tends to become incorporated within the soil zone, and is not transported to ground water.

#### Safe Drinking Water Levels

In 1986, the U.S. Environmental Protection Agency established the maximum contaminant level (MCL) and maximum contaminant level goal (MCLG) for fluoride as 4 mg/L and a secondary MCL (SMCL), or aesthetic, standard as 2 mg/L (U.S. Environmental Protection Agency, 1996). The Ohio Department of Health has adopted the federal drinking water standards as a health based standard for private water systems serving homes that do not receive water from a public water system. Although MCLs apply to drinking water distributed to the public and not to raw ground water, they are used in this paper as useful benchmarks for fluoride concentrations.

#### **Distribution of Fluoride in Ohio Ground Waters**

Since the early 1970s, Ohio EPA has managed the Ambient Ground Water Quality Monitoring Program (AGWQMP) to monitor and evaluate changes in the quality of ground water used as source water for public water systems across Ohio. The AGWQMP database consists of more than 4,000 individual fluoride measurements gathered at 258 wells over the last 35 years. Fluoride concentrations range from non-detect (0.2 mg/L) to 3.58 mg/L. Additional data from Ohio EPA public water system compliance databases yielded results from 389 wells (only raw water results and/or results from public water systems that do not add fluoride were used).

The distribution of fluoride in ground water from these two sources is summarized in a contour map of fluoride concentrations in Figure 1. This contour map was generated from empirical data. The contouring program does not extrapolate beyond the data points; consequently, the contoured areas do not extend to the state boundary where wells are not close to the boundary. However, the fluoride contours can be visually projected to the state boundary. The contoured fluoride data is not continuous data since data points are from several aquifer types. It is possible that a well located in an area of high fluoride concentration does not produce water with elevated fluoride because the well does not intercept fractures with fluorite mineralization. This is not a big surprise, it simply reflects the heterogeneity of the local geology and its control on water quality.

The Silurian and Devonian carbonate aquifers in western Ohio have the highest ground water fluoride concentrations. The distribution of these carbonate aquifers is controlled by the Findlay Arch, a structural high between the Appalachian basin to the southeast and Michigan basin to the north. The carbonates exhibit a broad anticlinal structure that plunges slightly to the north-northeast and the fluoride distribution crudely mimics this structure. In eastern Ohio, two samples approach fluoride concentrations of 1 mg/L to produce small localized areas of elevated fluoride concentration (0.7-1.2 mg/L) in Figure 1. These small areas are markedly different from the regional distribution of elevated fluoride in western Ohio.



Figure 1. Fluoride contour map for Ohio's ground water.

#### Controls of Fluoride Distribution

The dominant controls on fluoride concentrations in Ohio's ground water are:

- i. Geology;
- ii. Ground water contact time with fluoride minerals; and
- iii. Ground water chemical composition.

The most important control is geology. The carbonate formations in the western half of Ohio contain more fluoride-bearing minerals than the sandstones of eastern Ohio or the widely distributed sand and gravel deposits. Much of the fluorite in the Findlay Arch area is secondary, low temperature mineralization consisting of non-economic fluorite -sphalerite -galena deposits. These mineral concentrations were precipitated from Late Paleozoic brines expelled from the Appalachian Basin (Carlson, 1994; Deering, Mohr, Sypniewski and & Carlson, 1983). Because Ohio's sand and gravel aquifers may contain significant amounts of fluorite- bearing carbonate material, the fluoride concentrations in some sand and gravel aquifers are intermediate between those found in the carbonates and sandstone aquifers.

This relationship is illustrated in box plots in Figure 2. Most of the data points for the sand and gravel aquifers exhibit low fluoride concentrations, but the outliers (values greater than the upper whisker on the sand and gravel box plot) overlap with the fluoride concentrations of the carbonate aquifers. These sand and gravel aquifers with fluoride greater than 1 mg/L all occur in the western half of the state associated with the area of carbonate bedrock.



Figure 2. Box plots of fluoride concentrations in Ohio's major aquifer types.

The second control on fluoride is the overall contact time, or interaction time between minerals in the rocks and sediments and ground water. Longer residence times allow for more complete leaching and dissolution of aquifer materials. Contact time is also proportional to well depth. Broadly speaking, surface water and shallow ground water tend to be young (days to months after infiltration), while the oldest ground waters (decades to millennia after infiltration) reside in the deeper flow regimes. This suggests that fluoride concentrations should roughly correlate with sample depth. This relationship is illustrated in Figure 3.

Like Figure 2, Figure 3 clearly shows the dominance of elevated fluoride in Ohio's carbonate ground waters (blue squares) as compared to sand and gravel (green diamonds) and sandstone (red crosses) aquifers. A moderate increase of fluoride concentration with depth is exhibited in Figure 3 for the carbonate waters. In addition, multiple sand and gravel aquifer samples with elevated fluoride (outliers in Figure 2; > 1.0 mg/L) also exhibit increasing fluoride values with increased well depth. Sandstone aquifers consistently exhibit low fluoride concentrations (below 1 mg/L), most likely due to the lack of fluoride minerals.



# Fluoride as a function of Well Depth and Aquifer Type

Figure 3. Relationship of fluoride concentration to well depth and aquifer

The third control of fluoride concentration is ground water chemical composition. Since ground water fluoride concentration in Ohio is controlled by the dissolution of fluorite ( $CaF_2$ ), elevated concentrations of Ca can limit the dissolution of fluorite. Figure 4 is a plot of fluoride versus calcium concentrations in Ohio carbonate wells. The symbol size is proportional to the sulfate concentration for these data.



Fluoride vs. Calcium in Ambient GW Wells

Figure 4. Relationship of fluoride to calcium and sulfate.

Focusing on the carbonate samples with elevated fluoride and calcium, it is clear that as the calcium concentration increases, the fluoride concentration decreases. In addition, calcium and sulfate concentrations rise simultaneously. One of the primary carbonate units, the Salina Formation, contains gypsum; consequently, calcium concentrations are elevated from dissolution of calcite/dolomite and gypsum. The parallel increase of calcium and sulfate may be explained by the dissolution of gypsum.

Figure 5 illustrates the relationships between magnesium and calcium in carbonate aquifers, with symbol size again indicating relative sulfate concentration. Much of the carbonate section includes dolomite so we expect significant concentrations of magnesium in these waters. The interesting point in Figure 5 is the presence of a subset of wells in which the magnesium concentrations increase more rapidly than calcium increases. The samples with the highest Mg/Ca ratio also have elevated sulfate. Two wells with calcium greater than 250 mg/L also have elevated sulfate, but do not exhibit the elevated Mg/Ca ratios. These two data points fall along the general trend of the carbonate aquifer data excluding the data with elevated Mg/Ca ratios (data circled in figure 5). Thus, the process producing the elevated Mg/Ca ratios does not appear to affect all of the wells in this regional data set.



Calcium vs Magnesium in Ambient GW Carbonate Wells

Figure 5. Relationships of magnesium, calcium and sulfate.

These relationships suggest dissolution of gypsum is elevating the calcium concentrations resulting in de-dolomitization controlled by the following equation (Saunders and Toran 1994).

 $CaMg(CO_3)_2 + Ca^{2+} \rightarrow 2CaCO_3 (calcite) + Mg^{2+}$ 

The calcium released from the dissolution of gypsum results in precipitation of calcite and the release of magnesium into solution, which is the opposite of diagenic dolomitization. The saturation of calcium leading to calcite precipitation and the increased concentration of magnesium can inhibit the dissolution of calcium bearing minerals, like fluorite (CaF<sub>2</sub>), resulting in lower fluoride concentrations in waters with elevated calcium (as exhibited in Figure 4). These chemical reactions are not occurring at all carbonate wells as exhibited by the two data points with high calcium concentrations in Figure 5, so saturation of calcium is a localized condition. However, these relationships identify processes that may be occurring in the wells with abundant gypsum in local aquifers. Water samples from public water system production wells in bedrock are mixed samples in the sense that they collect water from multiple production zones. This mixed nature means that these are not the best samples to conduct precise geochemical studies. In spite of this limitation, however, Figures 4 and 5 illustrate geochemical trends resulting from de-dolomitization reactions that can limit dissolution of fluorite within the carbonate aquifers.

#### Conclusions

In Ohio, the Silurian and Devonian carbonate aquifers exhibit regional areas of elevated fluoride. The maximum concentrations found in raw water do not exceed the primary fluoride MCL, but some areas do exceed the secondary MCL. The primary source of the fluoride is secondary, low temperature mineralization, including fluorite, which was deposited in voids and fractures in the carbonate rocks. Depending on local geochemistry, ground water can dissolve fluorite present in the aquifer along ground water flow paths, resulting in elevated fluoride concentrations where fluorite is more abundant. Locally, the saturation of calcium can inhibit the dissolution of calcium bearing minerals, like fluorite (CaF<sub>2</sub>), resulting in lower fluoride concentrations.

#### For more information

For more information on fluoride in Ohio's ground water, contact the Ohio Environmental Protection Agency, Division of Drinking and Ground Waters at (614) 644-2752.

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