

# THE IRON FROM LANDFILLS CONUNDRUM

There is a growing awareness among landfill managers that their facility may be causing naturally occurring iron to be released from soil into groundwater. This geochemical process is not fully understood. In addition, the iron in groundwater criterion driving groundwater remediation at these sites is inappropriate. Furthermore, the regulatory environment is confounded by a general lack of understanding on how to evaluate the impact of "naturally occurring contaminants." These three key factors are briefly reviewed in this article.

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## Iron Release Geochemistry

Iron is a naturally occurring metal in the surficial soils of Florida. In some areas of Florida, such as in the Panhandle, it is readily obvious that the soils contain significant iron concentrations because of the orange-red color. However, soils lacking orange-red color may also contain abundant iron. In fact, a soil matrix may have a low saturation *in situ* because of chemically reduced, mineral-bound, iron Fe II<sup>1</sup>, even when the soil contains substantial iron. Once the soils or groundwater are exposed to air, the reduced iron may oxidize and convert to Fe III. It is in the Fe III state that the iron more readily precipitates, leaving the visual orange-red staining.

Expanding on this concept, the moisture content in the subsurface soils varies depending upon factors such as rainfall and groundwater elevation change. During periods of rainfall, stormwater will percolate through the soils at varying degrees and displace the available air in the pore space of the soils, which may chemically reduce the iron in the soils to the more soluble Fe II. Similarly, rising groundwater elevations can have the same effect. This may be the case, understanding that there is dissolved oxygen in rain and stormwater that minimize the reducing effect. Conversely, during extended periods of drought and lower groundwater elevation, the soils may convert to Fe III when air is introduced into the soil-pore space.

There is an anthropogenic condition that appears to mimic drought. The condition may be created by a relatively large cap on the surface from the construction of a lined landfill, parking lot, building, airport, etc. Assuming there is no significant reduction in groundwater levels, the groundwater flowing beneath the structures no longer has the opportunity for unfettered air and stormwater exchange. A state is therefore created that yields a reducing environment in the

saturated zone where iron converts into the more soluble Fe II. If the groundwater moves far enough downgradient to a location where the exchange of air and infiltrating precipitation resumes, the iron may convert to the less soluble Fe III and precipitate out of the formation.

In other words, these anthropogenic structures may be liberating naturally occurring iron from the soil and into the groundwater. This soluble form of iron would be expected to remain in solution until the groundwater receives an oxygen infusion via infiltrating precipitation, or when the groundwater discharges into an open surface water body. The oxygen infusion causes the iron to precipitate. This chemical exchange currently is being observed and studied at sites in areas with low permeability soils.

## Iron Groundwater Criterion

The health effects information on iron, listed in Table I of Chapter 62-777 of the Florida Administrative Code (F.A.C.), implies that gastrointestinal effects are associated with consuming water that has a concentration greater than the groundwater cleanup target level (GCTL) of 0.3 milligram per liter (mg/L). This is an easy interpretation to make; given the manner in which the information is presented in this table. Unfortunately, this interpretation is not correct. The noticeable effects<sup>2</sup> associated with iron in groundwater at concentrations above 0.3 mg/L are rusty color, sediment in tanks, a metallic taste and reddish or orange staining on surfaces.

Traditionally, when developing a GCTL, a chemical is viewed as a xenobiotic which, by definition, is a "foreign chemical."<sup>3</sup> Sometimes factors, like elevated xenobiotic concentrations, are associated with unacceptable health effects. Thus the goal is to develop a threshold concentration of the xenobiotic that when presented in a medium, like groundwater, it does not cause the unacceptable health effects.

Iron is an essential nutrient for humans as it is a constituent of hemoglobin, and a number of enzymes. The adequate intake of iron for infants from birth to 6 months is estimated to be 0.27 milligram per day (mg/day). This value was based upon the average iron concentration in human milk of 0.35 mg/L.<sup>4</sup> The iron recommended daily allowance (RDA) ranges from a low of 7 mg/day for children age 1 through 3 years to a high of 27 mg/day for pregnant women.<sup>5</sup> The RDA range is the reason that over-the-counter multimineral supplements (e.g., Advanced Formula Centrum<sup>®</sup>) show that each tablet has 18 mg of iron and note that this value represents 100 percent of the "Daily Value." The iron concentration in the empty human adult stomach after taking one multimineral tablet with one 8-ounce glass of water is therefore 75 mg/L. This concentration is 250 times the GCTL in Chapter 62-777 F.A.C. of 0.3 mg/L.

Clearly the iron GCTL of 0.3 mg/L is not health based and does not consider the fact that this compound is an essential nutrient. A more appropriate approach, for essential nutrients, is to develop GCTLs that take into consideration the "risk of inadequacy" and the "risk of adverse effects." Unfortunately, the equations used in Chapter 62-777 F.A.C. are not appropriate if the compound is an essential nutrient; therefore, an alternate approach is needed.

There is a problem when a GCTL must be developed for an essential nutrient like iron. Simply put, the conventional approach used to develop the GCTL does not consider the adverse health effects of being exposed to too small an amount of an essential nutrient. The conventional equations used to generate GCTLs do address the "risk of adverse effects," but do not address what is known as the "risk of inadequacy." This matter is a current concern to the U.S. Environmental Protection Agency (EPA) and new guidance was released last year.<sup>6</sup>

The more appropriate method is to use the iron Tolerable Upper Intake Level (UL) to derive a health-based GCTL. The UL is the highest level of daily nutrient intake that is likely to

pose no risk of adverse health effects for almost all individuals in the general population. The iron UL is 45 mg/day.<sup>7</sup> This UL was developed by dividing the lowest-observed-adverse-effects level (LOAEL) by an uncertainty factor (UF) of 1.5. The LOAEL was associated with gastrointestinal (GI) effects, which are primarily observed in individuals who consumed a high dose of supplemental iron on an empty stomach.

The alternate health-based groundwater iron GCTL is calculated to be 22.5 mg/L. This value was derived by dividing the iron UL of 45 mg/day by the typical amount of water consumed per day by adults (2 liters per day).

### Naturally Occurring Contaminant Regulation

The state of Florida recognizes that some aquifers will not be used to supply drinking water because the groundwater contains elevated levels of naturally occurring compounds. Based on this understanding, the state of Florida developed adjusted GCTLs using what is known as "Groundwater of Low Yield/Poor Quality Criteria." These adjusted GCTLs are ten times higher than the typical GCTL (e.g., the adjusted GCTL for iron is 3.0 mg/L not 0.3 mg/L). Unfortunately, most people do not understand how to determine if their site has groundwater of low yield or poor quality.

The process to determine if a site's groundwater may naturally be of poor quality is remarkably simple. It appears difficult because the procedures are scattered throughout the regulations and are often misinterpreted. All that is required is to determine if groundwater from a background location contains "naturally occurring contaminants" in excess of their respective GCTL. It is not necessary to reclassify the aquifer. The applicable regulations are found in Chapter 62-780.200(5) F.A.C., Chapter 62-780.200(35) F.A.C. and Chapter 62-780.680(2)(c)(1) F.A.C.

### Conclusions

The geochemical factors thought to release iron into the groundwater are not unique to landfills. Any facility with a large footprint, like a parking lot, may generate conditions that could cause the iron GCTL of 0.3 mg/L to be exceeded. At the moment the

state of Florida is not requiring the owners of shopping malls to monitor groundwater for iron.

Currently, a GCTL of 0.3 mg/L is being used to determine if groundwater must be remediated through actions like pump and treat. This GCTL is not health based and ignores the possibility that the groundwater at the site is unacceptable for consumption because of the presence of "naturally occurring contaminants."

The State of Florida needs to reconsider how naturally occurring iron is to be managed at sites with large footprints. A state-wide approach is needed that considers how the groundwater resource at these sites is to be protected given its intended use. This state-wide approach should be flexible and consider health issues, economic consequences and the natural state of the impacted groundwater. ■

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