

Identifying the Dominant Controls on Mn Concentrations in Springs and Groundwater Wells Across the Shenandoah Valley, VA USA

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Manganese (Mn) is an essential micronutrient but also a contaminant at elevated concentrations. With Mn solubility increasing under reducing conditions, drinking water from groundwater wells and springs is of particular concern. With 20-80% of people in Shenandoah Valley, VA counties relying on wells and springs for drinking water, and recent research finding Mn contamination in drinking water wells in adjacent regions, the potential for Mn contamination from low level chronic exposure via drinking water is of concern.

Here we examine the geochemistry of 1,966 groundwater well samples sourced from the National Water Quality Assessment (NAWQA), the Virginia Household Water Quality Project (VAHWQP), and the National Water Information System (NWIS). Additionally, field work collecting soil, rock, and water samples was conducted at 13 springs across the Shenandoah Valley. Spring samples were characterized by field and lab analyses, including pH, dissolved oxygen, alkalinity, major ions, and 22 major and trace element concentrations. Soils were analyzed via scanning electron microscopy paired with energy dispersive X-ray spectroscopy (SEM-EDS) and X-ray fluorescence (XRF). Soil samples of interest were analyzed with Mn K-edge X-ray absorption near-edge structure (XANES) spectroscopy to determine average Mn oxidation states. We find Mn concentrations are substantially lower in valleys underlain by dolostone and near soils with low Mn(II) but higher relative Mn(III/IV) content. In contrast, soils with higher Mn(II) content, as well as aquifers with sulfur-bearing black shales or unconsolidated lithologies, are associated with higher aqueous Mn concentrations, consistent with reducing conditions increasing Mn contamination risk. The geochemistry of waters in black shale aquifers are distinct from those in carbonate bearing aquifers, particularly in terms of correlated element concentrations. These results indicate that Mn concentrations within this region are largely controlled by Mn redox cycling in soils and aquifer lithologic influences on aqueous geochemistry.