Groundwater Research Report
WR14R004

EFFECT OF SOURCE CHEMISTRY ON MN-BEARING SOLID DISSOLUTION AND REACTVITY IN MUNICIPAL WATER SYSTEMS

Matthew Ginder-Vogel
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2016

Project Number WR14R004

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2016

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This project was also supported, in part, by General Purpose Revenue funds of the State of Wisconsin to the University of Wisconsin System for the performance of research on groundwater quality and quantity. Selection of projects was conducted on a competitive basis through a joint solicitation from the University and the Wisconsin Departments of Natural Resources; Agriculture, Trade and Consumer Protection; Commerce; and advice of the Wisconsin Groundwater Research Advisory Council and with the concurrence of the Wisconsin Groundwater Coordinating Council.

Final Report for "Effect of Source Chemistry on Mn-Bearing Solid Dissolution and Reactivity in Municipal Water Systems"

PI: Matthew Ginder-Vogel – University of Wisconsin – Madison

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Project Summary

Title: Effect of Source Chemistry on Mn-Bearing Solid Dissolution and Reactivity in Municipal Water Systems

Project I.D.: WR14R004

Investigators:
Principle Investigator: Matthew Ginder-Vogel, Assistant Professor, Dept. of Civil and Environmental Engineering, University of Wisconsin – Madison

Co-Principle Investigatory: Christina Remucal, Assistant Professor, Dept. of Civil and Environmental Engineering, University of Wisconsin – Madison

Research Assistant: Sarah Balgooyen, Doctoral Candidate, Environmental Chemistry and Technology Program, University of Wisconsin – Madison

Period of Contract: March 1, 2015, through February 29, 2016

Background/Need:
Flushing of sediments from the water mains may result in elevated manganese (Mn) concentrations in the drinking water distribution system. For example, during 2006, 17 of 1,119 sampled properties in Madison, WI had Mn levels that exceeded the lifetime health advisory value of 300 µg/L.[1] In response to public concerns, the City of Madison conducted extensive testing of the wellheads and found that only four of the 24 wells produced water near or above the Secondary Maximum Contaminant Level.[2, 3] The city initiated uni-directional flushing of the water mains and installed a treatment facility at Well 29, which had Mn levels of 124 µg/L.[1] These approaches have been largely successful at limiting Mn concentrations in drinking water, yet the Mt. Simon aquifer continues to be a long-term source of dissolved manganese in municipal water systems Madison and throughout southern Wisconsin. Additionally, fundamental information concerning the solubility and reactivity of Mn-bearing solid phases in municipal water distribution systems remains sparse. The proposed research project is designed to address this gap in knowledge by developing a quantitative relationship between source chemistry and Mn-bearing solid dissolution potential and reactivity.

Objectives:
Objective 1. Identify Mn bearing minerals in Mt. Simon Aquifer materials.
Objective 2. Quantify mineralogy and dissolution potential of Mn-bearing solids
Objective 3. Determine oxidative reactivity of Mn-bearing solids.

Methods:
In order to achieve the objectives described above, we examined Mn chemistry from its potential sources in the Mt. Simon Aquifer to its ultimate fate as oxidized solids in the MWU distribution system. Initially, we identified potential dissolved Mn sources in cuttings from the Mt. Simon Aquifer by utilizing wet chemical (e.g., extractions) techniques. We then collected oxidized Mn-bearing solids from the MWU distribution system and characterized the reactivity of these phases by reaction with organic contaminants.

We worked with the Wisconsin Geological and Natural History Survey to collect fresh sediment samples from Mt. Simon Formation. Additionally, we collected solid samples from the Madison water distribution system during water main flushing during the summer of 2014 and the Well 29 Mn removal system during the summers of 2014 and 2105.

Results and Discussion:

Our experiments demonstrate that the poorly crystalline solids collected from the Mn removal system in Madison, WI are capable of oxidizing BPA with a half-life of 2.3 hours (Figure 6). The loss of BPA in the presence of Well 29 Mn(III/IV) oxides was pseudo-first order over 12 hours. As we expected, the reaction rate was 30 times slower than that of δ-MnO_2 under the same conditions. However, our data demonstrates that the ability of the environmentally relevant Mn oxides to oxidize a range of target contaminants warrants further investigation. The solids collected from Well 29 are currently disposed of in a landfill, and therefore serve as an inexpensive oxidant that could be applied in passive drinking water treatment systems to treat urban stormwater or leachate from manure lagoons or landfills.

Conclusions/Implications/Recommendations:

The specific goals of the proposed project are to (1) investigate potential mineral sources of Mn(II) in deep aquifer materials, (2) quantify the mineralogy and dissolution potential of Mn-bearing solids from the Madison Water Utility (MWU) distribution system, and (3) determine the potential of these solids to oxidize organic and inorganic pollutants. A summary of the outcomes for each of these points follows below.

1) From our data, sediment from the upper portion of the Mt. Simon aquifer is much richer in Fe and Mn than sediment from deeper portions. The reasons for this variation are not readily apparent from the data collected as part of this project. It is possible that screening wells below the zone of highest sediment Fe and Mn could limit Fe/Mn in the groundwater.

2) Unfortunately for our project, but not the residents of Madison, the directional water main flushing implemented by the Madison Water Utility has severely limited solids accumulation in the water distribution system. The limited amount of solid we were able to collect is largely comprised of Fe, Mn, and Al and will likely oxidize organic contaminants. However, as sample size was quite small, we were not able to further characterize these solids.

3) Our data demonstrates that the ability of the environmentally relevant Mn oxides to oxidize a range of target contaminants warrants further investigation. We are currently investigating the ability of the solids collected from the Mn removal to oxidize additional organic and inorganic contaminants.

Related Publications:

Balgooyen, S.; Remucal, C.K.; Ginder-Vogel, M. Oxidation of Bisphenol A by delta-MnO_2. In preparation for *Environmental Science and Technology*

Balgooyen, S.; Remucal, C.K.; Ginder-Vogel, M. Characterization of Solid and Aqueous Products of Bisphenol-A Degradation by delta MnO2. In preparation for *Journal of Visual Experiments*

Key Words: Groundwater, BPA, Manganese Oxides,

Funding: University of Wisconsin System

Introduction:

Manganese in drinking water. Manganese (Mn) is ubiquitous in air, soil, and water and is considered to be an essential nutrient for humans and animals. Although manganese is an essential nutrient at low doses, chronic exposure to high doses may potentially lead to neurological effects. As a result, the US Environmental Protection Agency (EPA) recommends a lifetime health advisory value of 300 µg/L for healthy adults. Ten-day advisory levels of 300 and 1,000 µg/L are recommended for infants younger than six months and for healthy adults, respectively. In order to address consumer complaints about staining and taste issues, the EPA established a Secondary Maximum Contaminant Level (SMCL) of 50 µg/L for Mn in drinking water in 2004.[1] The health advisories and SMCL are not federally enforceable regulations and are intended as guidelines for the States.[1]

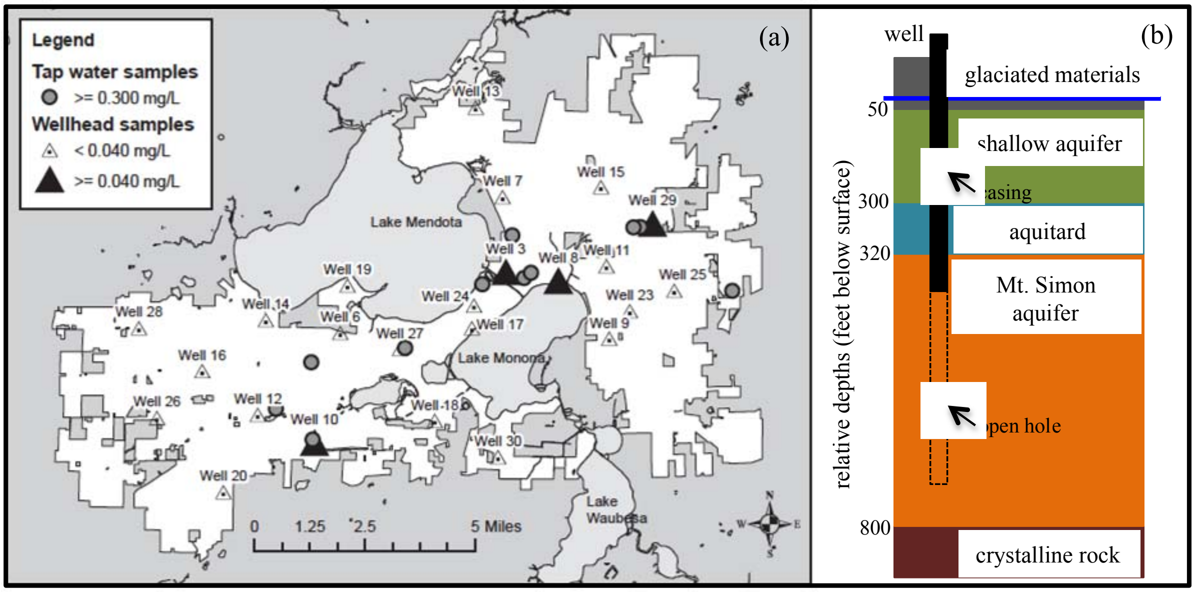

Figure 1. (a) Wells by Mn concentration and tap water samples with excess Mn in Madison, Wisconsin (after Schlenker) and (b) typical construction of Madison high capacity wells.

Flushing of sediments from the water mains may result in elevated Mn concentrations in the distribution system. During 2006, 17 of 1,119 sampled properties in Madison, WI had Mn levels that exceeded the lifetime health advisory value.[2] In response to public concerns, the City of Madison conducted extensive testing of the wellheads and found that only four of the 24 wells produced water near or above the SMCL (Figure 1). The city initiated uni-directional flushing of the water mains and installed a treatment facility at Well 29, which had Mn levels of 124 µg/L. These approaches have been largely successful at limiting Mn concentrations in drinking water, yet the Mt. Simon Aquifer continues to be a long-term source of Mn. Additionally, fundamental information concerning the solubility and reactivity of Mn-bearing solid phases in MWU's distribution systems remains sparse. **Our research project addresses this gap in knowledge by developing a quantitative relationship between source chemistry and Mn-bearing solid dissolution potential and reactivity.** The objectives of this proposal are to (1) identify Mn-bearing solid phases from well cuttings obtained from the Mt. Simon aquifer and (2) characterize the dissolution potential and (3) the reactivity of Mn-bearing solid-phases formed in MWU's water distribution system and Mn removal system located at MWU's well 29.

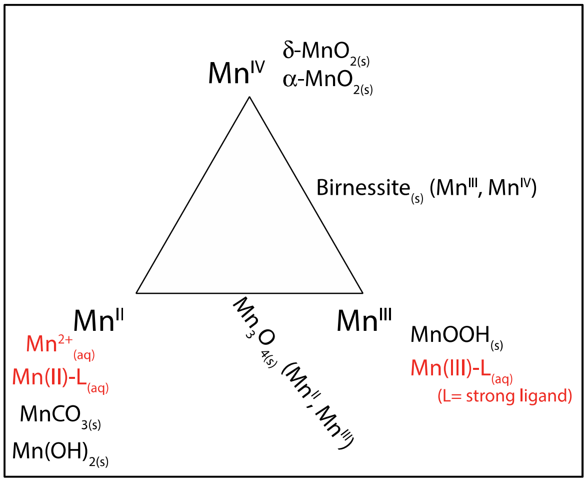

Figure 2. Common dissolved (red) and precipitated manganese species in several oxidation states

Mechanisms of Mn oxide formation. Manganese is the third most abundant transition metal in the Earth's crust (9.5 x 10^2 ppm, respectively).[3] The precipitation and dissolution of and Mn- bearing solid phases is strongly influenced by reduction and oxidation (redox) chemistry (Figure 2).[4] Significant concentrations of dissolved Mn(II) in natural waters generally only occur in the absence of oxygen (O_2). In the presence of O_2 insoluble Mn(III/IV) oxides form and limit the dissolved concentration of Mn.

Although the interconversion among redox and physical states is thermodynamically favorable in many environmental settings, it is generally kinetically limited in the absence of catalysis. For example, oxidation of aqueous Mn(II) by O_2 is thermodynamically favorable at pH 8.4, yet the reaction proceeds across years in the absence of catalysts.[5] The rate and pathway of Mn(II) oxidation and precipitation is influenced by a variety of factors including ligands, foreign surfaces, surface-active ions, and pH. Similarly, dissolution of Mn(III/IV) solids exposed to undersaturated conditions is a thermodynamically favorable, but the uncatalyzed rates are exceedingly slow.[6]

Once formed, **Mn-oxides are considered to be the strongest, naturally occurring oxidants** and oxidize a large variety of organic and inorganic substrates, as described in more detail below. In addition, the mobility and bioavailability of environmental contaminants, such as heavy metals and toxic organic molecules, are strongly regulated by manganese oxides. Precipitation of Mn oxide minerals in municipal water distribution systems may serve as a reservoir of Mn. The Mn may be released back into solution through dissolution due to changing geochemical conditions (e.g., flushing of water mains). Mn oxide mineral dissolution will also release any bound heavy metal contaminants into solution.

Mn oxide dissolution mechanisms. Dissolution rates of Mn oxide solids are dependent on many factors including surface area, pH and ligand concentration. For example, dissolution rates increase under acidic conditions. The rates of the parallel dissolution pathways vary over several orders of magnitude (Figure 3). The dissolution pathways include, from slowest to fastest, proton-promoted, ligand-promoted, reductive, and synergistic (Figure 3). Further, the rates depend on the crystallinity and degree of Fe(III) substitution of the Mn oxide minerals.[5] For example, nanocrystalline Mn(IV)O_2 (δ-MnO_2) dissolves at least 10 times faster than birnessite, its more crystalline equivalent.[7] Dissolution rates are also temporally dependent and often pass through periods of rapid dissolution, which are at least 10 times faster than steady state dissolution rates, after minor geochemical changes (e.g., change in pH, introduction of reducing agents and/or ligands).[4] Thus, in order to understand processes controlling the dissolution of Mn bearing minerals in the MWU supply system it is essential to develop an understanding of their chemical composition, crystallinity, and susceptibility to the four dissolution mechanisms described in Figure 3.

Slowest

↓

Manganese (III/IV) Oxide Dissolution

Proton-Promoted

$$\delta\text{–}\,\mathrm{MnO_2} + 4\,\mathrm{H^+} \longrightarrow \mathrm{Mn^{IV}_{(aq)}} + 2\mathrm{H_2O}$$

Ligand Promoted

$$(\delta\text{–}\,\mathrm{MnO_2}) \equiv \mathrm{Mn^{IV}}\text{–}\,\mathrm{OH} + \mathrm{L^-} + \mathrm{H^+} \longrightarrow (\delta\text{–}\,\mathrm{MnO_2}) \equiv \mathrm{Mn^{IV}}\text{–}\,\mathrm{L} + \mathrm{H_2O} \longrightarrow \delta\text{–}\,\mathrm{MnO_2} + \mathrm{Mn^{IV}}\text{–}\,\mathrm{L}_{(aq)}$$

Examples: L^- = oxalate, malonate, citrate

Reductive

$$\delta\text{–}\,\mathrm{MnO_2} + 2\mathrm{e^-} + 4\mathrm{H^+} \longrightarrow \mathrm{Mn}^{II}_{(\mathrm{aq})} + 2\mathrm{H_2O}$$

$$\mathrm{MnOOH} + \mathrm{e^-} + 3\mathrm{H^+} \longrightarrow \mathrm{Mn}^{II}_{(\mathrm{aq})} + 2\mathrm{H_2O}$$

Examples: e^- = ascorbate, hydroquinone, dithionite ($S_2O_4^{2-}$), Fe^{II}, Mn^{II}, H_2S

Synergistic

$$(\delta\text{–}\,\mathrm{MnO_2}) \equiv \mathrm{Mn^{IV}}\text{–}\,\mathrm{L} + 2\mathrm{e^-} \longrightarrow \delta\text{–}\,\mathrm{MnO_2} + \mathrm{Mn^{II}_{(aq)}} + \mathrm{L^-}$$

Examples: L^- = oxalate, malonate, citrate; e^- = ascorbate or Mn^{II}

Fastest

Figure 3. Stoichiometry and relative dissolution rates of proton promoted, ligand-promoted, reductive, and synergistic pathways of Mn(III/IV) oxide dissolution. Photoreductive pathways are omitted.

Procedures and Methods:

Figure 4. Collection of Mn oxide slurry from Well 29 Mn removal system.

In order to achieve the objectives described above, we examined Mn chemistry from its potential sources in the Mt. Simon Aquifer to its ultimate fate as oxidized solids in the MWU distribution system. Initially, we identified potential dissolved Mn sources in cuttings from the Mt. Simon Aquifer by utilizing wet chemical (e.g., extractions) techniques. We then collected oxidized Mn-bearing solids from the MWU distribution system and characterized the reactivity of these phases by reaction with organic contaminants.

We worked with the Wisconsin Geological and Natural History Survey to collect fresh sediment samples from Mt. Simon Formation. Additionally, we collected solid samples from the Madison water distribution system during water main flushing during the summer of 2014 and the Well 29 Mn removal system during the summers of 2014 and 2105 (Figure 4).

Solid-Phase Characterization

X-ray diffraction patterns were collected using a Rigaku D/Max Rapid II diffractometer equipped with a Mo X-ray tube, operating at 50 kV and 50 mA. Dried solids were prepared in sealed silica capillary tubes.

Solid-phase elemental composition was determined by complete dissolution of all collected solids in concentrated hydrochloric acid and analysis of Fe and Mn content via inductively coupled plasmas – optical emission spectrometry (ICP-OES).

Reactivity with organic contaminants

The ability of solids collected from the Well 29 Mn removal system to oxidize organic contaminants was investigated by reaction of a solution containing 80 μM BPA to 0.33 g/L filter solid. The pH of the solution was buffered at 7. The reaction was sampled at regular intervals and analyzed to determine the concentration of dissolve Mn and BPA in solution at each time point. BPA concentration was determined using high performance liquid chromatography (HPLC) and dissolved Mn concentration was determined using ICP-OES.

Results and Discussion:

Aquifer Material Characterization

Table 1: Total manganese and iron (micrograms/gram sediment) measured in aquifer materials collected from wells drilled in Dane County.

Well Location	**Interval (feet BGS)**	**Mn (ug/g)**	**±**	**Fe (ug/g)**	**±**
Madison, WI	185-230	221.8	12.5	1896	118
Madison, WI	230-275	112.8	6.5	2385	150
Madison, WI	310-315	126.2	7.3	3671	230
Madison, WI	325-350	149.8	8.3	2636	165
Madison, WI	350-370	73.0	4.2	592	38
Madison, WI	370-418	12.2	0.7	162	13
Verona, WI	260-300	853.4	47.1	4408	287
Verona, WI	380-385	162.2	9.0	1432	91
Verona, WI	430-435	8.5	0.6	194	13
Verona, WI	750-760	6.1	0.5	254	16
Verona, WI	950-960	7.9	0.5	800	50
Verona, WI	1160	130.0	7.3	9794	613

Total iron and manganese vary greatly as a function of depth in Mount Simon aquifer materials collected from a wells bored in Madison and Verona, Wisconsin (Table 1). Generally, the concentration of Fe and Mn decreases with depth. Additionally, the concentration of Fe and Mn is much higher in the sediments obtained from the Verona, WI well. The exact reasons for this trend are not clear; however, it's clear that to avoid the highest concentration of Mn and Fe, wells should be screened deeper in the Mt. Simon Aquifer.

Madison Water Utility (MWU) Water Distribution Sediments

Solids collected during water main flushing operations over the summer of 2014 are predominantly composed of iron, manganese, and aluminum, with iron being the most abundant element and aluminum being the least abundant (data not shown). Unfortunately, we were not able to collect enough of these solids for further characterization of their reactivity with respect to organic contaminants.

Solids from MWU Well 29 Mn Removal System

Solids collected from the Mn removal system located at Well #29 (Figure 1) in Madison, WI (Figure 4) are composed of ~42% Fe and 8% Mn. X-ray diffraction analysis of the solids reveals that the solid-phase is X-ray amorphous, with no crystalline phases detected (Figure 5). This basic geochemical characterization indicates that the solids from this facility are candidates for reuse in organic contaminant removal systems.

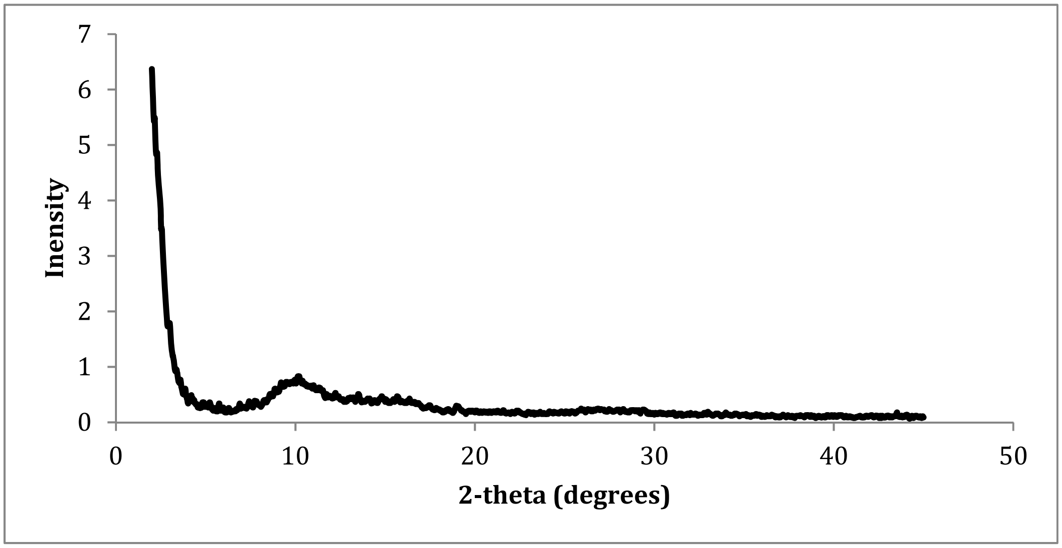

Figure 5. X-ray diffraction pattern of Fe/Mn oxide solids collected well # 29 Mn removal system in Madison, WI. Note the lack of distinct peaks in the pattern indicating that there are no crystalline mineral phases present in this sample.

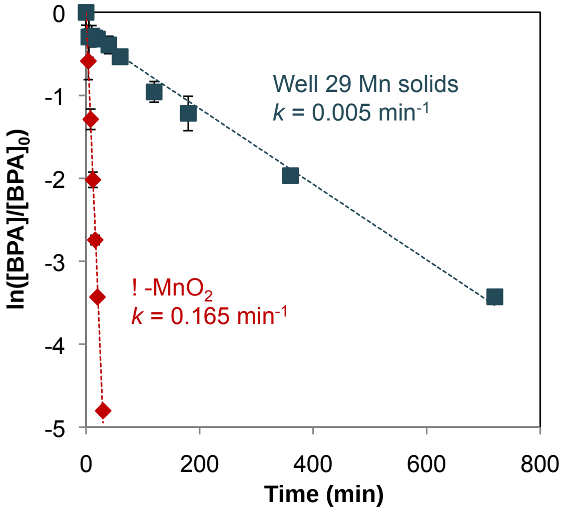

Figure 6. Degradation of 5 μM BPA by δ-MnO_2 and solids isolated from Well 29 (8.5% Mn by mass) at pH 5. The initial concentration of both solids was 400 μM as Mn.

Our experiments demonstrate that *the poorly crystalline solids collected from the Mn removal system in Madison, WI are capable of oxidizing BPA* with a half-life of 2.3 hours (Figure 6). The loss of BPA in the presence of Well 29 Mn(III/IV) oxides was pseudo-first order over 12 hours. As we expected, the reaction rate was 30 times slower than that of δ-MnO_2 under the same conditions. However, our data demonstrates that the ability of the environmentally relevant Mn oxides to oxidize a range of target contaminants warrants further investigation. The solids collected from Well 29 are currently disposed of in a landfill, and therefore serve as an inexpensive oxidant that could be applied in passive drinking water treatment systems to treat urban stormwater or leachate from manure lagoons or landfills.

Conclusions and Recommendations:

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Appendix A: Awards, Publications, Reports, Patents, Presentations, Students, Impact

Publications, Reports and Patents:

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Presentations:

Balgooyen, S.; Remucal, C.K.; Ginder-Vogel, M. 2016 Oxidation of Bisphenol A by delta-MnO_2. American Chemical Society National Meeting, Spring 2016 – 50 attendees

Balgooyen, S.; Remucal, C.K.; Ginder-Vogel, M. 2015 Mineral Surface Modification of delta-MnO_2 Decreases Bisphenol A Oxidation Rate. Soil Science Society of America Meeting, Minneapolis, MN. Fall 2015 – 50 attendees

Ginder-Vogel, M. 2015 Organic Contaminant Degradation by Mn(IV)oxides, Goldschmidt Geochemistry Conference, Prague, Czech Republic – 50 attendees

Ginder-Vogel, M. 2015 Contaminant Transformation at Transition Metal Oxide Mineral Surfaces, Wisconsin Natural History and Geologic Survey, Madison, WI - 10 attendees

Ginder-Vogel, M. 2015 Mechanisms and kinetics of contaminant transformation by Mn(IV) oxides. American Chemical Society National Meeting, Denver, CO. Spring 2015 - 100 attendees

Awards:
The initial results of this research were leveraged to write a successful proposal to the National Science Foundation to continue these studies.

Students:

Sarah Balgooyen – Doctoral Candidate in the Environmental Chemistry and Technology program at UW Madison
balgooyen@wisc.edu, 660 N. Park St., Madison, WI 53706

Impact of Work:

Our experiments demonstrate that *the poorly crystalline solids collected from the Mn removal system in Madison, WI are capable of oxidizing BPA* with a half-life of 2.3 hours (Figure 6). The loss of BPA in the presence of Well 29 Mn(III/IV) oxides was pseudo-first order over 12 hours. As we expected, the reaction rate was 30 times slower than that of δ-MnO_2 under the same conditions. However, our data demonstrates that the ability of the environmentally relevant Mn oxides to oxidize a range of target contaminants warrants further investigation. The solids collected from Well 29 are currently disposed of in a landfill, and therefore serve as an inexpensive oxidant that could be applied in passive drinking water treatment systems to treat urban stormwater or leachate from manure lagoons or landfills.