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**Rate of Manganese Release from Soil Components Interacting with  
Rainwater and Litter Leachate**

A Senior Thesis in Geosciences

by

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## **Rate of Manganese Release from Soil Components Interacting with Rainwater and Litter Leachate**

Erika L. Frey

### **Abstract**

*Manganese bearing solids such as the Rose Hill shale, Mn-oxides, and organic matter contribute a significant amount of Mn to soils at the Shale Hills Observatory in central Pennsylvania. Industrial inputs have contributed to the Mn enrichment at Shale Hills; however the Rose Hill shale, organic matter, and Mn-oxides are also natural sources that contribute Mn. The Mn-enrichment could lead to an overall decline in tree and plant health. In this study, we will analyze rainwater and litter leachate contact with particles of the Rose Hill shale, Mn-oxides, and organic matter in laboratory batch experiments. The objectives of this study are: 1) compare and contrast how rainwater and litter leachate affect the amount of Mn released from Mn-bearing solids, 2) compare and contrast the amount of dissolved Mn leached from Rose Hill shale, Mn-oxides, and organic matter, and 3) calculate rates of Mn release from each solid phase and predict dominant sources of dissolved Mn in soils at the Susquehanna Shale Hills Observatory. It was concluded that litter leachate increases Mn release from solid phases of the Rose Hill shale, organic matter, and Mn-oxides relative to rainwater, possibly due to lower pH and the presence of organic ligands. Additionally, Mn-oxides have the highest rate of Mn release in both the litter leachate (1.330  $\mu\text{mol/hr}$ ) and rainwater (0.9794  $\mu\text{mol/hr}$ ) solutions compared to organic matter and Rose Hill shale. This could be due to the abundance of Mn in the oxide. Finally, by applying calculated rate constants to a model soil profile, it was determined that the Rose Hill shale contributes the most Mn to soil solution at Susquehanna Shale Hills Observatory.*

## I. Introduction

Many soils in Pennsylvania and throughout the United States have been enriched in manganese from industrial inputs (Herndon *et al.*, 2011). Manganese, a vital micronutrient for trees, can become toxic and harmful to the overall health of the tree in such environments (Kogelmann and Sharpe, 2006). A study by Horsley *et al.* (2000) observed a decline in Mn-sensitive tree species in Eastern North America, like the sugar maple (*Acer saccharum*). St. Clair and Lynch (2005) suggest that the excess uptake of Mn is a contributing factor to the decline of forests in Eastern North America because Mn-enrichment has caused an imbalance within the nutrient cycle, which ultimately deteriorates the health of the tree. Observations of the health decline in sugar maples, as well as other sensitive deciduous tree species, include symptoms of growth reduction, leaf chlorosis, canopy deterioration, tree mortality, and low seedling regeneration rates (St. Clair and Lynch, 2005). There have been numerous studies of Mn toxicity in trees; however, more studies are needed to determine the major sources of bioavailable Mn in the soil. Here, we research the rate of Mn release from common soil components into solution, where manganese becomes available for tree uptake. This study will examine the rates at which Mn is released from interactions of rainwater and litter leachate with weathered shale particles, Mn-oxides, and organic matter.

Soil acidity is a major factor contributing to the amount of Mn available to the trees (Kogelmann and Sharpe, 2006), because Mn becomes mobile under acidic conditions. Acidic soils are considered to have a pH of 5.5 or lower in the surface layers (Marschner, 1995). Acidic soils are typically found in forested regions throughout the eastern United States and Europe due to acid rain (Marschner, 1995). As the soil

becomes acidic from the acid rain, the solids containing manganese dissolve more rapidly, causing an increase in Mn concentration in soil water (Marschner, 1995). Additionally, organic acids from leaf litter can lower pH and contribute to micronutrient toxicity within soils (Marschner, 1995).

Mn contamination from industrial sources like steel and ferroalloy manufacturing (U.S. Environmental Protection Agency, 1984) and soil acidity have been observed in the Susquehanna Shale Hills Observatory (SSHO) watershed in central PA (Herndon *et al.*, 2011). According to the National Atmospheric Deposition Program, rainwater in Huntingdon County, Pennsylvania has a pH of approximately 4.35 (annual precipitation  $\approx$  105 cm/yr). The study area at SSHO is vegetated primarily by oak and some hickory, maple, hemlock, and pines. SSHO soils along the ridges are well-drained, thin Inceptisols and the valley has thicker Ultisols (Lin *et al.*, 2006). The soil is derived from the organic-poor, Silurian-aged Rose Hill shale (Lynch, 1976). Mn is present in SSHO soils in weathered shale minerals, Mn-oxides, and organic matter. The soil particles can interact by both organic-poor (rainwater) and organic-rich (litter leachate) solutions.

In this study, we analyze rainwater and litter leachate contact with particles of Rose Hill shale, Mn-oxides, and organic matter in laboratory batch experiments. The objectives of this study are to: 1) compare and contrast how rainwater and litter leachate affect the amount of Mn released from Mn-bearing solids, 2) compare and contrast the amount of dissolved Mn leached from Rose Hill shale, Mn-oxides, and organic matter, and 3) calculate rates of Mn release from each solid phase and predict dominant sources of dissolved Mn in soils at Susquehanna Shale Hills Observatory. The purpose of this

study is to analyze the rates of Mn release from the interaction of Mn-bearing solids with rainwater and litter leachate.

## II. Methods

### 2.1. Preparation of Rainwater and Litter Leachate

#### *Preparing Rainwater Solution (100x)*

We prepared a solution similar to the rainwater chemistry for Huntingdon, PA as reported by the National Atmospheric Deposition Program (2012) (table 1). Salts containing the compounds found in rainwater were dissolved in 1 L milliQ water (table 1) to obtain a rainwater solution 100x more concentrated than reported rainwater. Then, 124  $\mu\text{L}$  of 70% nitric acid and 74.0  $\mu\text{L}$  of 96% sulfuric acid were pipetted into the rainwater solution. For all experiments, 10 mL of the stock 100x rainwater solution were added to 990 mL milliQ water to prepare a 1x rainwater solution. The pH of the rainwater solution was adjusted to 4.52 by adding 1 mL of 0.01 N NaOH, 3 drops of 1 M NaOH, and 1 drop HCl.

**Table 1:** Prepared according to average rainwater chemistry at PA42- Leading Ridge (1979-2008), <http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=PA42>

Compound	NADP Rainwater (1x) (mg/L)	NADP Rainwater (100x) (g/L)	Prepared Rainwater (100x) (g)
$(\text{NH}_4)_2\text{SO}_4$	1.057	0.106	0.11
NaCl	0.175	0.018	0.02
KCl	0.075	0.007	0.01
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0.517	0.0517	0.05
$\text{MgSO}_4$	0.120	0.012	0.01
$\text{H}_2\text{SO}_4$ , conc.	1.471		79.96 $\mu\text{L}$
$\text{HNO}_3$ , conc.	1.827		130.51 $\mu\text{L}$

### ***Preparing Litter Leachate Solution***

To prepare the litter leachate solution, leaf litter with a mass of 49.96 g was added to 1 L rainwater solution. The solution was placed in a shaker incubator and set to 100 RPM at 45° C.

The litter leachate solution was removed from the shaker incubator after six days. The litter leachate was a darker brown color than the starting rainwater solution, and the litter particles were floating on top of solution. The liquid portion of solution was transferred to another bottle using a syringe, removing as much litter as possible. The measured pH was 3.96. The solution was flushed for 10 minutes with N<sub>2</sub> to remove oxygen in the bottle, and then placed in the refrigerator at 4°C.

### ***Solid-phase particles***

The Rose Hill shale particles used in this experiment had been previously prepared. The particles were taken from Rose Hill shale core drilled at Shale Hills. The preparation of the Rose Hill shale particles is described in Liermann *et al.* (2011). Shale pieces had been ground to particle size 150 µm – 250 µm (60 to 100 mesh) and analyzed (14.56 µmol Mn g<sup>-1</sup>) (Liermann *et al.*, 2011).

The Mn-oxide was prepared according to methods for birnessite synthesis in Golden *et al.* (1986) and particles were sieved to 100 to 200 mesh (Herndon, personal communication). Birnessite contains approximately 9,282 µmol Mn g<sup>-1</sup>.

The organic matter used in experiments was collected by hand from the surface soil at Shale Hills. The organic matter was air-dried and sieved to obtain a 150 µm-200µm particle size (Herndon, personal communication). Mn concentrations in the organic matter (=101 µmol g<sup>-1</sup>) were determined by Li-metaborate fusion and inductively

coupled plasma atomic emission spectrophotometer analysis at Penn State's Materials Research Institute.

## 2.2 RAINWATER BATCH EXPERIMENTS (LONG-TERM)

### *Weighing and Autoclaving Solids*

Rose Hill shale, organic matter, and Mn-oxide particles were weighed into 250 mL Erlenmeyer flasks (tables 2 & 3) for long-term experiments. Experiments with shale were labeled RHS1,2,3 while those with Mn-oxides were labeled Mn-ox1,2,3. Samples with organic matter were labeled (OM1,2,3) and summarized in Table 3.

**Table 2:** Weighed solid phase of Rose Hill shale and Mn-oxide for RW-long term

Flasks	Solid Phase Mass (g)	Total Mn in solid ( $\mu\text{mol}$ )
RHS1	0.25315	3.69
RHS2	0.25268	3.68
RHS3	0.25045	3.65
Mn-ox1	0.25171	2337
Mn-ox2	0.25171	2337
Mn-ox3	0.25123	2332

\*RHS (Rose Hill shale) and Mn-oxide (manganese oxide)

Erlenmeyer flasks (with dry solids) with the cap on loosely, diluted rainwater solution, and a graduated cylinder were placed in the autoclave twice at 250°F for 45 minutes to prevent contamination from bacteria. Flasks containing organic matter were weighed before and after autoclaving to ensure that no loss of material to combustion occurred (Table 3).

**Table 3:** Weighed solid phase organic matter for RW-long-term

Flask	Flask Mass (g)	Solid Phase Mass (g)	Post- Autoclaved Mass (Flask and OM) (g)	Total Mn in solid ( $\mu\text{mol}$ )
OM1	56.72258	0.25620	57.06414	26.0
OM2	57.74836	0.25384	58.00826	25.8
OM3	55.89212	0.25305	56.16180	25.7

\*OM (organic matter)

### *Sampling of Rainwater Batch (long-term)*

Ninety milliliters of post-autoclaved rainwater (1x) were transferred into the Erlenmeyer flasks containing solids, and then stirred for several seconds. The Erlenmeyer flasks were tightly capped with a lid, when they were not in use. A sterile pipette was used to abrade the Mn-oxide solids, because Mn-oxides adhered to the bottom of the flasks during autoclaving. Five milliliters aliquots from each flask were transferred into 15 mL centrifuge tubes using a 5 mL pipette. The centrifuge tubes were metal-free polypropylene tubes obtained from VWR, International. Additionally, gloves were worn to prevent contamination.

The organic matter and Rose Hill shale aliquots were visually observed to be particle free. However, Mn-oxides aliquots contained particles: we therefore filtered those samples. A 0.45  $\mu\text{m}$  filter and a syringe were used to transfer and filter aliquots into a new centrifuge tube. All aliquots were acidified with one drop of nitric acid. All Erlenmeyer flasks were placed on the bench top shaker at 180 RPM. Over the course of three weeks, aliquots were periodically sampled using a 5 mL pipette and transferred into a 15 mL centrifuge tube. The Mn-oxides samples were filtered at each sample period acidified. Sampling occurred in the laminar flow hood. Sampling occurred on:

- 1.) 9/14/11 at 11 AM
- 2.) 9/14/11 at 2:30 PM
- 3.) 9/16/11 at 11 AM
- 4.) 9/19/11 at 11 AM
- 5.) 9/21/11 at 11 AM
- 6.) 9/23/11 at 11 AM
- 7.) 9/30/11 at 11 AM
- 8.) 10/7/11 at 11 AM



### 2.3. LITTER LEACHATE BATCH EXPERIMENTS (LONG-TERM)

#### *Weighing Rose Hill Shale, Mn-oxide, and Organic Matter for Litter Leachate Batch*

For these experiments, the Mn-bearing solids were weighed and transferred into 250 mL Erlenmeyer flasks (table 4).

**Table 4:** Weighed solid phase Rose Hill shale (RHS), manganese oxide (Mn-oxide), and organic matter (OM) for LL (long-term).

<b>Flask</b>	<b>Solid Phase Mass (g)</b>	<b>Total Mn in solid (μmol)</b>
RHS1	0.25322	3.69
RHS2	0.25520	3.71
RHS3	0.25096	3.65
Mn-oxide1	0.25705	2386
Mn-oxide2	0.25473	2365
Mn-oxide3	0.25171	2337
OM1	0.25211	25.6
OM2	0.25136	25.5
OM3	0.25718	26.1

#### *Sampling of Litter Leachate Batch*

Precisely 70 mL of post-autoclaved distilled water and 20 mL of litter leachate were added to each Erlenmeyer flask with the weighed solids. The Erlenmeyer flasks were tightly capped with a lid, when they were not in use. Instead of autoclaving the solids, 1 mL of 0.45% weight by volume sodium azide was added to each flask to prevent bacterial contamination. The final concentration of the sodium azide in solution was 0.05% w/v. Then, the flasks were stirred, and a sterile 5 mL pipette was used to transfer 5 mL into a 15 mL centrifuge tube. All Erlenmeyer flasks were placed on a benchtop shaker at 180 RPM.

Aliquots from flasks containing solutions with Rose Hill shale, Mn-oxides, and organic matter were filtered using a 0.45 μm filter and syringe and transferred into a new

centrifuge tube. Then, one drop of concentrated nitric acid was added to all samples. Over six weeks, additional aliquots were sampled from the flasks: 5 mL was transferred using 5 mL pipette and placed into a 15 mL centrifuge tube. All aliquots were filtered and acidified. All of the sampling occurred in the laminar flow hood, which occurred on:

- |                        |                        |
|------------------------|------------------------|
| 1.) 10/5/11 at 11 AM   | 7.) 10/17/11 at 11 AM  |
| 2.) 10/5/11 at 3:30 PM | 8.) 10/19/11 at 11 AM  |
| 3.) 10/7/11 at 11 AM   | 9.) 10/21/11 at 11 AM  |
| 4.) 10/10/11 at 11 AM  | 10.) 11/4/11 at 11 AM  |
| 5.) 10/12/11 at 11 AM  | 11.) 11/18/11 at 11 AM |
| 6.) 10/14/11 at 11 AM  |                        |

### *Preparing Samples for Chemical Analysis*

For aliquots taken between 10/05/11 and 10/17/11, brown precipitate formed within the litter leachate aliquots. In order to properly run the samples for chemical analysis, 1 mL of each aliquot from the litter leachate samples was transferred into 4 mL of 2% nitric acid. For aliquots after 10/17/2011, 3 additional drops of concentrated nitric acid were added to each aliquot from the rainwater batch and the litter leachate batch. The total amount of nitric acid added to each aliquot was 4 drops.

## **2.4 LITTER LEACHATE AND RAINWATER BATCH EXPERIMENTS (SHORT-TERM)**

A second batch of experiments was conducted to examine Mn release over a shorter time frame. Unlike the long-term experiments, which had three replicates, only one replicate was used for each experiment. The Erlenmeyer flasks were tightly capped using aluminum foil, when they were not in use. Organic matter, Rose Hill shale, and

Mn-oxide particles were weighed into 250 mL Erlenmeyer flasks for each the rainwater and litter leachate batch (table 5).

For the litter leachate batch, 70 mL distilled water, 20 mL litter leachate, and 1 mL 0.45% weight/volume sodium azide were added to each Erlenmeyer flask with the weighed organic matter, Rose Hill shale, and Mn-oxides. The flasks were stirred, and then a sterile 5 mL pipette was used to transfer 5 mL aliquots into a 15 mL centrifuge tube. The Rose Hill shale, Mn-oxides, and organic matter aliquot samples were filtered into a new centrifuge tube using a 0.45  $\mu\text{m}$  filter and syringe. After transferring into a new centrifuge tube, four drops of concentrated nitric acid were added to all aliquots to maintain consistency with the long-term batches.

For the rainwater batch, precisely 90 mL of rainwater (1x) were transferred into Erlenmeyer flasks with the weighed solids, and then stirred for several seconds. Five mL aliquots were transferred using a 5 mL pipette into a 15 mL centrifuge tube. The centrifuge tubes were metal free and gloves were worn to prevent any contamination. A 0.45  $\mu\text{m}$  filter and a syringe were used to filter and transfer aliquots into a new centrifuge tube for all samples. After transferring into a new centrifuge tube, four drops of concentrated nitric acid were added to all aliquots to maintain consistency with the long-term batches.

After aliquots of the rainwater and litter leachate batch were taken, the Erlenmeyer flasks were placed on the benchtop shaker at 180 RPM. The sampling occurred within a 24 hour period on: 12/18/11 at 10:10 AM, 12:00 PM, 2:00 PM, and 4:00 PM, and on 12/19/11 at 9:00 AM.

**Table 5:** Weighed organic matter (OM), Rose Hill shale (RHS), and Mn-oxides (MnOx) for rainwater (RW) and litter leachate (LL) batch.

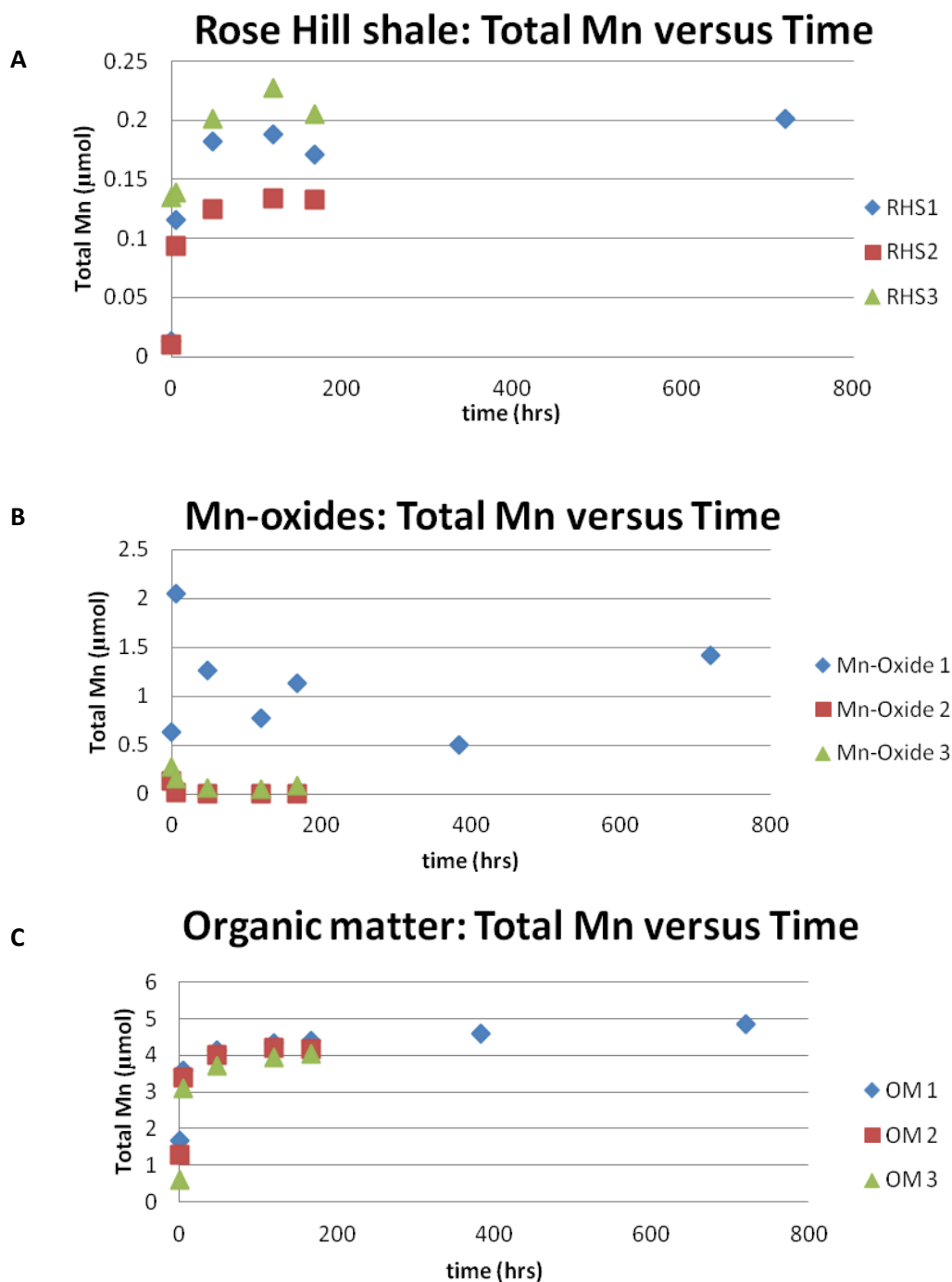
<b>Flask</b>	<b>Solid Phase Mass (g)</b>	<b>Total Mn in solid (<math>\mu\text{mol}</math>)</b>
RW-OM	0.25900	26.3
RW-RHS	0.25626	3.73
RW-MnOx	0.25532	2370
LL-OM	0.25873	26.3
LL-RHS	0.25593	3.73
LL-MnOx	0.25789	2394

## 2.5 Chemical analysis

Samples from the long-term rainwater, short-term rainwater, and short-term litter leachate experiments were analyzed on the inductively coupled plasma mass spectrometer (ICP-MS), and samples from the long-term litter leachate experiments were analyzed on the ICP-AES. The chemical analysis of the ICP-MS and ICP-AES were completed at the Penn State Materials Characterization Laboratory.

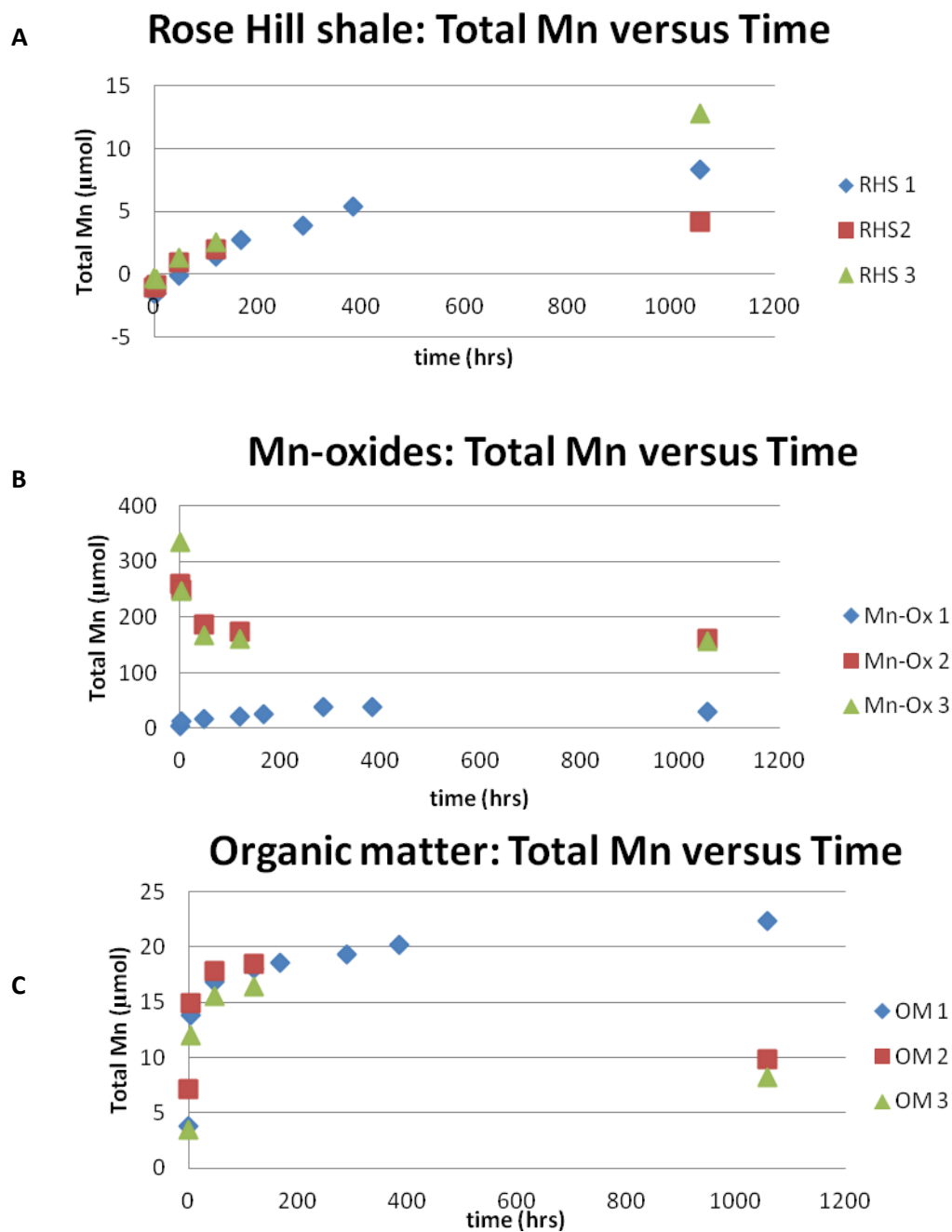
### III. Results

#### Long-Term Rainwater Batch



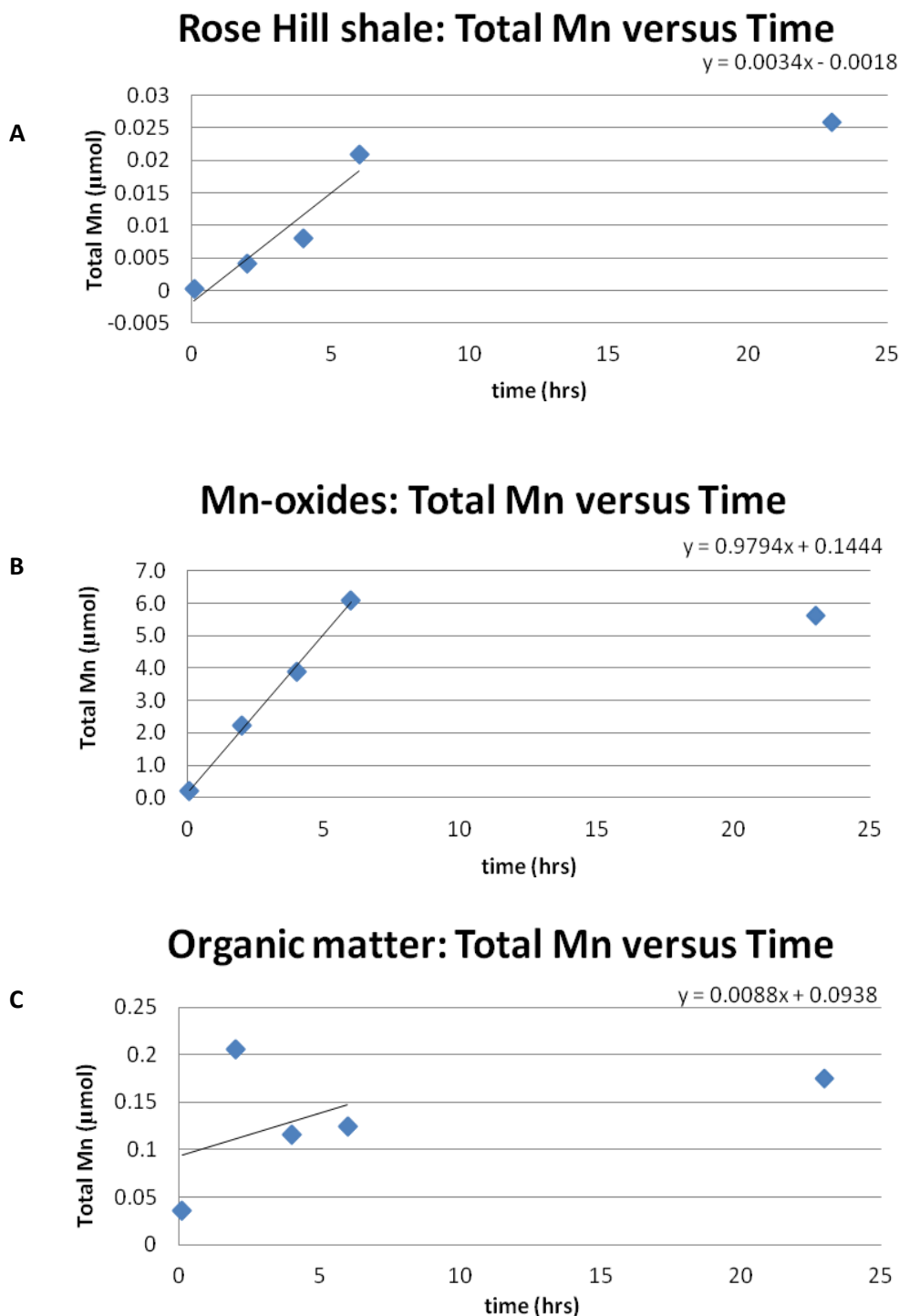
**Fig. 1:** A) Mn release from Rose Hill shale into solution exhibits a rapid increase followed by a slight decrease over time and replicates display a consistent trend, B) Mn-oxide does not display a consistent trend, and C) Mn release from organic matter exhibits an initial rapid increase followed by a gradual increase over time and replicates display a consistent trend.

## Long-Term Litter Leachate Batch



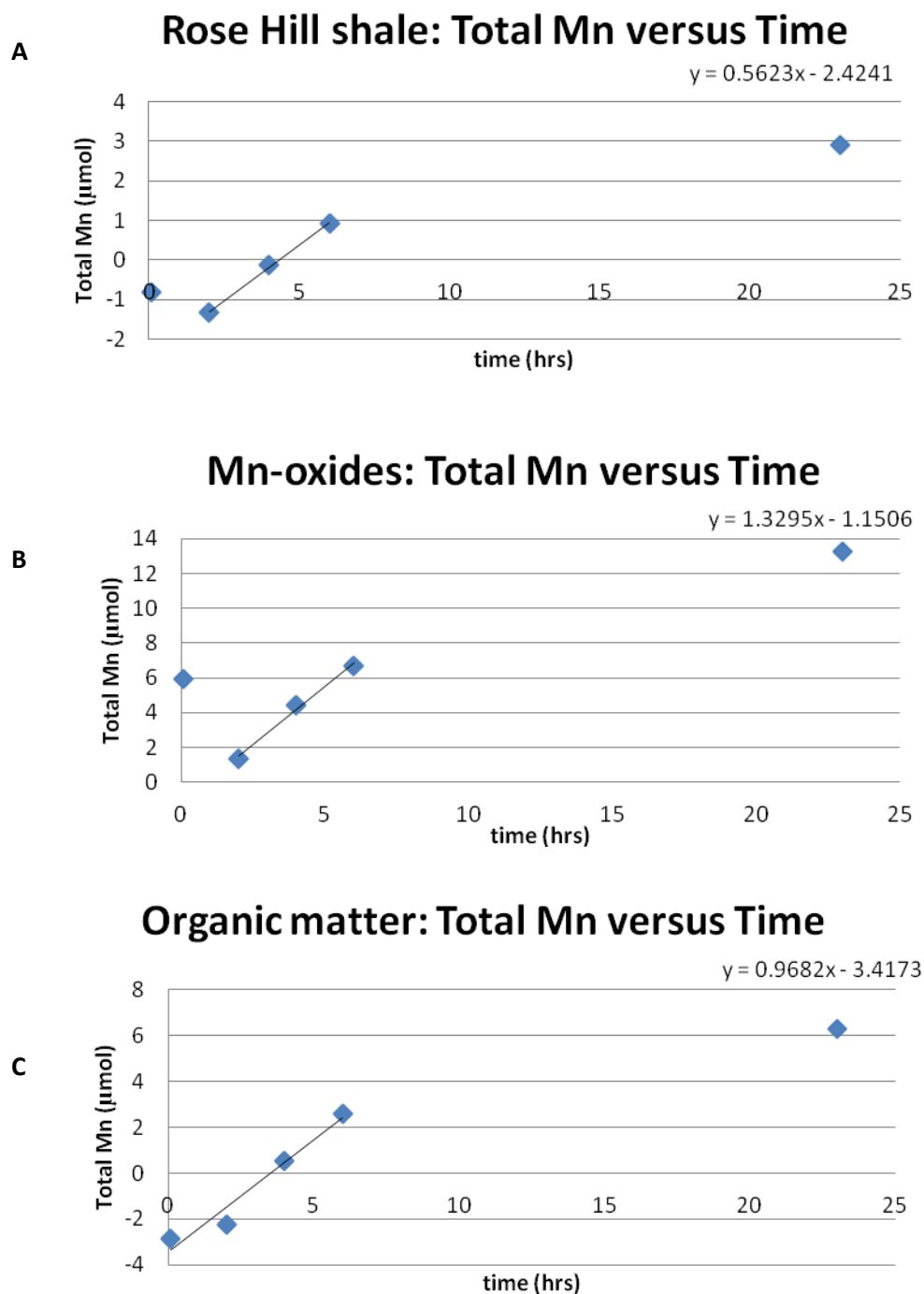
**Fig. 2:** A) Mn release from Rose Hill shale exhibits a steady increasing trend over time and replicates display a consistent trend, B) The Mn-oxide replicates displays an opposing trend, and C) Mn release from organic matter exhibits an initial rapid increase followed by a gradual increase (OM 1) or slight decrease (OM 2 and OM 3) over time and replicates display a consistent trend.

### Short-Term Rainwater Batch



**Fig. 3:** A) Rose Hill Shale exhibits a steady increasing trend with Mn leaching from the Rose Hill shale at a linear rate of  $0.0034 \mu\text{mol hr}^{-1}$ . B) Mn-oxide exhibits an increasing trend with Mn leaching from the Mn-oxides at a linear rate of  $0.9794 \mu\text{mol hr}^{-1}$ , and C) organic matter exhibits a general increasing trend with Mn leaching from the organic matter at a linear rate of  $0.0088 \mu\text{mol hr}^{-1}$ . The linear trendline was constrained to the first 10 hours on all short-term rainwater graphs.

## Short-Term Litter Leachate Batch



**Fig. 4:** A) Rose Hill shale exhibits a generally increasing trend with Mn leaching from the Rose Hill shale at a linear rate of  $0.5623 \mu\text{mol hr}^{-1}$ . B) Mn-oxide exhibits an increasing trend with Mn leaching from the Mn-oxide at a linear rate of  $1.3295 \mu\text{mol hr}^{-1}$ , and C) organic matter exhibits a general increasing trend with Mn leaching from the organic matter at a linear rate of  $0.9682 \mu\text{mol hr}^{-1}$ . The linear trendline was constrained to the first 10 hours on all short-term litter leachate graphs to analyze initial release only, not when the reaction reaches equilibrium. For graphs A and B, the first data point was not included to avoid effects from adsorption of Mn onto the solid.



**Table 6:** Long-term rainwater batch

<b>Sample</b>	<b>Time (hrs)</b>	<b>Mn concentration (<math>\mu\text{mol/L}</math>)</b>	<b>Volume (mL)</b>	<b>Total Mn (<math>\mu\text{mol}</math>)</b>
Rose Hill shale 1	0.083	1.46E-04	90	0.013
	5	0.00136	85	0.115
	48	0.00228	80	0.182
	120	0.00251	75	0.188
	168	0.00244	70	0.171
	720	0.00366	55	0.201
	Rose Hill shale 2	0.083	0.00011	90
5		0.00109	85	0.093
48		0.00157	80	0.125
120		0.00178	75	0.134
168		1.82E-04	70	0.132
Rose Hill shale 3		0.083	0.00149	90
	5	0.00164	85	0.139
	48	0.00251	80	0.201
	120	0.00304	75	0.228
	168	0.00293	70	0.205
	Mn-oxide 1	0.083	0.00697	90
5		0.02415	85	2.05
48		0.01581	80	1.26
120		0.01041	75	0.78
168		0.01625	70	1.14
384		0.00839	60	0.50
720		0.02586	55	1.42
Mn-oxide 2		0.083	0.00149	90
	5	1.47E-04	85	1.25E-02
	48	5.26E-05	80	4.20E-03
	120	3.24E-05	75	2.43E-03
	168	3.55E-05	70	2.48E-03
Mn-oxide 3	0.083	0.00306	90	0.275
	5	0.00181	85	0.154
	48	8.01E-04	80	0.064
	120	6.04E-04	75	0.045
	168	0.00120	70	0.084

Sample	Time (hrs)	Mn concentration ( $\mu\text{mol/L}$ )	Volume (mL)	Total Mn ( $\mu\text{mol}$ )
Organic matter 1	0.083	0.01875	90	1.68
	5	0.04223	85	3.59
	48	0.05187	80	4.15
	120	0.05752	75	4.32
	168	0.06261	70	4.38
	384	0.07663	65	4.60
	720	0.08810	60	4.85
Organic matter 2	0.083	0.01402	90	1.27
	5	0.03986	85	3.39
	48	0.05024	80	4.02
	120	0.05588	75	4.20
	168	0.05952	70	4.16
Organic matter 3	0.083	0.00673	90	0.60
	5	0.03659	85	3.11
	48	0.04641	80	3.72
	120	0.05260	75	3.95
	168	0.05788	70	4.05

**Table 7:** Long-term litter leachate batch

Sample	Time (hrs)	Mn concentration ( $\mu\text{mol/mL}$ )	Volume (mL)	Total Mn ( $\mu\text{mol}$ )	Mn from Litter Leachate ( $\mu\text{mol}$ )	Mn leached from solid ( $\mu\text{mol}$ )
Rose Hill shale 1	0.083	0.20	90	18.4	19.9	-1.53
	4	0.19	85	17.2	18.8	-1.55
	48	0.19	80	17.6	17.7	-0.11
	120	0.20	75	18.0	16.6	1.41
	168	0.20	70	18.2	15.5	2.77
	288	0.20	65	18.2	14.4	3.84
	384	0.21	60	18.6	13.3	5.34
	1056	0.24	55	20.4	12.2	8.28
Rose Hill shale 2	0.083	0.21	90	18.8	19.9	-1.08
	4	0.20	85	18.0	18.8	-0.84
	48	0.21	80	18.6	17.7	0.90
	120	0.21	75	18.5	16.6	1.95
	1056	0.30	55	16.3	12.2	4.17
Rose Hill shale 3	0.083	0.22	90	19.6	19.9	-0.29
	4	0.20	85	18.4	18.8	-0.38
	48	0.21	80	19.0	17.7	1.28
	120	0.21	75	19.1	16.6	2.56
	1056	0.45	55	25.0	12.2	12.81

Sample	Time (hrs)	Mn Concentration ( $\mu\text{mol/mL}$ )	Volume (mL)	Total Mn ( $\mu\text{mol}$ )	Mn from Litter Leachate ( $\mu\text{mol}$ )	Mn leached from solid ( $\mu\text{mol}$ )
Mn-oxide 1	0.083	0.26	90	23.4	19.9	3.48
	4	0.36	85	31.7	18.8	12.96
	48	0.39	80	34.0	17.7	16.30
	120	0.43	75	37.0	16.6	20.43
	168	0.48	70	40.4	15.5	24.95
	288	0.67	65	52.8	14.4	38.39
	384	0.66	60	52.4	13.3	39.11
	1056	0.48	55	42.7	12.2	30.50
Mn-oxide 2	0.083	3.10	90	279.3	19.9	259.38
	4	3.15	85	267.8	18.8	249.01
	48	2.55	80	204.0	17.7	186.36
	120	2.53	75	189.5	16.6	173.00
	1056	3.16	55	173.6	12.2	161.44
Mn-oxide 3	0.083	3.95	90	355.5	19.9	335.63
	4	3.14	85	266.6	18.8	247.79
	48	2.30	80	184.3	17.7	166.65
	120	2.38	75	178.3	16.6	161.72
	1056	3.08	55	169.4	12.2	157.23
Organic matter 1	0.083	0.26	90	23.7	19.9	3.48
	4	0.36	85	32.7	18.8	12.96
	48	0.39	80	34.6	17.7	16.30
	120	0.39	75	34.6	16.6	20.43
	168	0.38	70	34.1	15.5	24.95
	288	0.37	65	33.7	14.4	38.39
	384	0.37	60	33.4	13.3	39.11
	1056	0.39	55	34.5	12.2	30.50
Organic matter 2	0.083	0.30	90	27.0	19.9	7.11
	4	0.38	85	33.7	18.8	14.94
	48	0.40	80	35.5	17.7	17.82
	120	0.40	75	35.1	16.6	18.48
	1056	0.40	55	22.0	12.2	9.87
Organic matter 3	0.083	0.26	90	23.3	19.9	3.43
	4	0.35	85	30.8	18.8	12.02
	48	0.38	80	33.3	17.7	15.60
	120	0.38	75	33.1	16.6	16.48
	1056	0.37	55	20.4	12.2	8.21

**Table 8:** Short-term rainwater batch

Sample	Time (hrs)	Mn Concentration ( $\mu\text{mol/mL}$ )	Volume (mL)	Total Mn ( $\mu\text{mol}$ )
Rose Hill shale	0.083	2.00E-06	90	1.80E-04
	2	4.87E-05	85	4.15E-03
	4	9.75E-05	80	8.05E-03
	6	2.69E-04	75	2.09E-02
	23	3.39E-04	70	2.58E-02
Mn-oxide	0.083	2.18E-03	90	0.20
	2	2.62E-02	85	2.24
	4	4.67E-02	80	3.88
	6	7.63E-02	75	6.10
	23	6.93E-02	70	5.61
Organic matter	0.083	0.0217	90	0.036
	2	0.131	85	0.205
	4	0.0699	80	0.116
	6	0.0768	75	0.125
	23	0.116	70	0.175

**Table 9:** Short-term litter leachate batch

Sample	Time (hrs)	Mn Concentration ( $\mu\text{mol/mL}$ )	Volume (mL)	Total Mn ( $\mu\text{mol}$ )	Mn from Litter Leachate ( $\mu\text{mol}$ )	Mn leached from solid ( $\mu\text{mol}$ )
Rose Hill shale	0.083	0.212	90	19.1	19.9	-0.82
	2	0.193	85	17.5	18.8	-1.32
	4	0.194	80	17.6	17.7	-0.13
	6	0.193	75	17.5	16.6	0.93
	23	0.206	70	18.4	15.5	2.91
Mn-oxide	0.083	0.287	90	25.9	19.9	5.96
	2	0.220	85	20.2	18.8	1.37
	4	0.245	80	22.1	17.7	4.44
	6	0.260	75	23.3	16.6	6.69
	23	0.339	70	28.8	15.5	13.29
Organic Matter	0.083	0.190	90	17.1	19.9	-2.837
	2	0.195	85	16.5	18.8	-2.248
	4	0.227	80	18.2	17.7	0.510
	6	0.256	75	19.2	16.6	2.605
	23	0.311	70	21.8	15.5	6.305

**Table 10:** The rate of Mn release based on the short term experiments of the rainwater batch (RW) and litter leachate batch (LL).

Sample	Solution	Rate ( $\mu\text{mol/hr}$ )	Rate constant $k$ ( $\text{hr}^{-1}$ )
Rose Hill shale	RW	0.0034	0.000911
Organic matter	RW	0.0088	0.000335
Mn-oxide	RW	0.9794	0.000413
Rose Hill shale	LL	0.5623	0.151
Organic matter	LL	0.9682	0.0369
Mn-oxide	LL	1.3295	0.000555

**Table 11:** The rate constant and soil composition based on soil profile at Shale Hills.

Sample	Solution	Rate constant, $k$ , ( $\text{hr}^{-1}$ )	Mn Mass in solid ( $\mu\text{mol Mn cm}^{-2}$ )	Total Rate ( $\mu\text{mol/hr}$ )
Rose Hill shale	RW	0.000911	770	0.701
Organic matter	RW	0.000335	142	0.050
Mn-oxide	RW	0.000413	850	0.351
Total Rate=				1.10
Rose Hill shale	LL	0.151	770	116
Organic matter	LL	0.0369	142	5.24
Mn-oxide	LL	0.000555	850	0.472
Total Rate=				122.0

### 3.1 Calculations

#### 1. *Converting from Mn concentration in the flask to Total Mn ( $\mu\text{mol}$ ) at each time step:*

$$T(x) (\mu\text{mol}) = T(x-1) + (C' - C) * V$$

The total Mn in solution at time  $x$  ( $T(x)$ ;  $\mu\text{mol}$ ) is equal to the total Mn from the previous time step ( $T(x-1)$ ;  $\mu\text{mol}$ ) plus the difference between the Mn concentration at time  $x$  ( $C'$ ;  $\mu\text{mol/mL}$ ) and the Mn concentration at the previous time step ( $C$ ;

$\mu\text{mol/mL}$ ), multiplied by the volume in the flask at time  $x$  ( $V$ ; mL).. This equation is from Brantley and Conrad (2008).

*Example calculation:*

Total Mn for short-term litter leachate batch, Rose Hill shale at 2 hours

$$\begin{aligned} \text{Total Mn at 2 hours} &= 19.07 \mu\text{mol/mL} + (0.193 \mu\text{mol mL}^{-1} - 0.212 \mu\text{mol mL}^{-1}) * 85 \\ &\text{mL} \\ &= 17.5 \mu\text{mol} \end{aligned}$$

## **2. Subtracting litter leachate Mn from total Mn in litter leachate experiments:**

In the litter leachate experiments, the Mn present in the initial litter leachate must be subtracted from the total Mn in solution to determine the amount of Mn leached from the solid phase:

$$T_s(x) = T(x) - C_L * V$$

Here, the total Mn released from the solid at time  $x$  ( $T_s(x)$ ;  $\mu\text{mol}$ ) is equal to the total Mn in solution ( $T(x)$ ;  $\mu\text{mol}$ ; Eqn.1) subtracted by the concentration of the Mn in litter leachate ( $C_L = 12.14 \mu\text{mol/mL}$ ) multiplied by the volume at time  $x$  ( $V$ ; mL). Negative values imply adsorption of litter leachate Mn to the solid particles, and positive values indicate release of Mn. In the rainwater experiments,  $T = T_s$ .

*Example calculation:*

$$\begin{aligned} \text{Total Mn with Litter Leachate subtracted} &= 17.5 \mu\text{mol} - ((12.14 \mu\text{mol}/54.94) * 85) \\ &= -1.3 \mu\text{mol} \end{aligned}$$

### 3. *Calculating the rate constant, k:*

$$k = m / (M * C)$$

The rate constant ( $k$ ;  $\text{hr}^{-1}$ ) was determined by dividing the rate of Mn release, which was the slope of the linear trendline ( $m$ ;  $\mu\text{mol/hr}$ ) (Figs.3&4), by the mass of the solid ( $M$ ; grams), multiplied by the concentration of Mn in solid ( $C$ ;  $\mu\text{mol/g}$ ). The rate constant indicates the fraction of total Mn lost from each Mn-bearing solid per unit time.

#### *Example Calculation:*

Short-term Rose Hill shale litter leachate batch

$$k = 0.4284 \mu\text{mol/hr} / (0.25 \text{ g}) (800 \mu\text{g/g})$$

$$= 0.115 \text{ hr}^{-1}$$

### 3.2 *Long-Term Rainwater Batch*

Total Mn in solution in the long term rainwater batch rapidly increased for the Rose Hill shale and organic matter over the first 50 hours followed by a slower increase over the next 150 hours (Figure 1). The organic matter increased more rapidly within the first 50 hours, compared to the Rose Hill shale. The Mn-oxides showed two different trends with time depending upon the replicate: either a decrease with time (with significant variability) or an increase with time. The inconsistency amongst replicates could be due to the fact that the Mn-oxides adhered to the sides of the flasks after autoclaving. This may have affected the amount Mn-oxide surface area exposed to solution within each Mn-oxide flask, ultimately affecting the rate of Mn release. Furthermore, the fine nature of the Mn oxides probably promoted clumping, and it is

possible that fine particles passed the filters during sampling, causing the variability in Mn concentration.

### ***3.3. Long-Term Litter Leachate Batch***

Total Mn in solution in the long term litter leachate batch (Figure 2) rapidly increased for Rose Hill shale and organic matter over the first 50 hours, followed by a more gradual increase over the next 150 hours. The total Mn released from organic matter was higher within the first 100 hours than Mn released from the Rose Hill shale. Again, Mn release from the Mn-oxide did not show a trend within this experiment.

### ***3.4 Short-Term Rainwater Batch***

In the short-term rainwater experiments, the total Mn released into solution was approximately linear with respect to time. The rates, from highest to lowest for the short-term rainwater batch were Mn-oxide, organic matter, and Rose Hill shale (table 10). The rate for Rose Hill shale, organic matter, and Mn-oxides were  $0.0034 \mu\text{mol hr}^{-1}$ ,  $0.0088 \mu\text{mol hr}^{-1}$ , and  $0.9794 \mu\text{mol hr}^{-1}$ , respectively. The rate constants,  $k$ , for Rose Hill shale, organic matter, and Mn-oxides were similar within an order of magnitude. Organic matter had a rate of  $0.000335 \text{ hr}^{-1}$ , Mn-oxides had a rate constant of  $0.000413 \text{ hr}^{-1}$ , and Rose Hill shale had a rate constant of  $0.000911 \text{ hr}^{-1}$ . Mn-oxide had a slightly higher rate constant than the organic matter, and the Rose Hill shale had the highest rate constant.



### ***3.5 Short-term Litter Leachate Batch***

In the short-term litter leachate experiments, the total Mn released into solution was approximately linear with respect to time. The rates of release from highest to lowest for the litter leachate batch were Mn-oxide, organic matter, and Rose Hill shale. Mn-oxide had a rate of  $1.3295 \mu\text{mol hr}^{-1}$ , organic matter had a rate of  $0.9682 \mu\text{mol hr}^{-1}$ , and the Rose Hill shale had a rate of  $0.5623 \mu\text{mol hr}^{-1}$ . Rose Hill shale had the highest rate constant ( $0.151 \text{ hr}^{-1}$ ), followed by the organic matter ( $0.0369 \text{ hr}^{-1}$ ) then Mn-oxides ( $0.000555 \text{ hr}^{-1}$ ).

Rose Hill shale and organic matter exhibit an order of magnitude increase in Mn release into solution in the litter leachate experiments relative to the rainwater experiments. Whereas, the Mn-oxides have only a slight increase from the rainwater batch experiments to the litter leachate batch experiments.

## **IV. Discussion**

### **4.1 Mn release in organic-poor rainwater versus organic-rich litter leachate**

In the long term rainwater experiments, the total Mn released from the Rose Hill shale and organic matter particles increased over time. The replicates of the Rose Hill shale and the organic matter were similar. The long term litter leachate batch also shows an increase in total Mn from the Rose Hill shale and organic matter over time. The total amount of Mn released from the organic matter and the Rose Hill shale into litter leachate was higher than into rainwater. There could be two factors that affect the higher amounts of total Mn in the litter leachate batch experiments compared to the rainwater batch experiments: 1) pH and 2) organic ligands. The pH may have been a contributing factor

to the total amount of Mn leached between the litter leachate and rainwater batches. Acidic pH is known to increase Mn leaching from solids (Marschner, 1995). The litter leachate pH before the experiments commenced was measured at 3.96, which is more acidic than the rainwater batch. The rainwater had an initial pH of 4.52. The lower pH in the litter leachate could have broken more bonds, which resulted in more total Mn in solution compared to the rainwater batch.

The higher amounts of organics in litter leachate compared to the organic-poor rainwater could have contributed to the increased rate of Mn release in the litter leachate experiments. Litter leachate contains dissolved organic matter, which will complex with Mn in the solid. The Mn could attach to the carboxylic acid groups on the organic matter. The dissolved organic matter can dissolve oxides more quickly by pulling Mn ions out of the solid structure. This would explain the higher release of Mn in the litter leachate batch experiments than in the rainwater batch experiments.

#### **4.2 Long-term batch experiments**

The Mn-oxides in the long term rainwater and litter leachate batches did not exhibit a consistent trend. Autoclaving the rainwater batch may have affected the amount of Mn available for reaction with solution, since some Mn adhered to the sides of the flasks. A significant amount of Mn was bound to the sides of the three Mn-oxide flasks. A pipette was used to scrape off the Mn-oxide particles, but some particles remained stuck on the sides of the flask. MnO<sub>x1</sub> had the most Mn scraped off into solution, whereas most of the Mn in MnO<sub>x2</sub> and MnO<sub>x3</sub> could not be removed from the sides of the flask.

In all the Rose Hill shale and organic matter long-term rainwater and litter leachate batch experiments, the total Mn in solution increases more slowly over the course of the

experiment. The rate of Mn release could slow down over time due to Mn in the solid reaching equilibrium with Mn in solution.

As more Mn is released into solution and the reaction gets closer to equilibrium, back reactions will increase. In the forward reaction, Mn from solid is released into the solution, after which the Mn in solution can react back into solid form. An increase in back reactions as equilibrium is reached could ultimately slow the observed rate of Mn release until the total Mn in solution does not change.

### **4.3 Rates and rate constants**

The short-term batch experiments were used to calculate the rates of Mn release from solids in both rainwater and litter leachate. The rate of Mn release equals the linear slope of total Mn in solution versus time. The Mn-oxides had the highest rate for the rainwater batch and the litter leachate batch. The Rose Hill shale had the slowest rate in the rainwater batch and litter leachate batch.

The rate of Mn release for Mn-oxide, both in rainwater and litter leachate batch, is higher than the organic matter and Rose Hill shale. This could be due to the high amounts of Mn already present in the solid, meaning that more Mn is available to be leached. Rose Hill shale and organic matter have lower Mn concentrations. The organic matter has a higher rate and Mn concentration than the Rose Hill shale. The organic matter could have higher Mn concentration in the solid than the Rose Hill shale.

The rate constant,  $k$ , is defined as the fraction of Mn from the Mn-bearing solids that is lost over time. Although the Mn-oxides had the highest release rate in the rainwater and litter leachate batches, it also had the smallest fraction of Mn loss over time in the litter leachate experiments. The highest rate constant in the rainwater batch and

litter leachate batch was calculated for the Rose Hill shale. The Rose Hill shale does not contain as much Mn in solid, so the higher rate constant implies that the Mn would be used up the fastest. However, this data also is consistent with the conclusion that the phases that contain Mn in the shale are more reactive than either Mn oxides or Mn in organic matter.

A factor that could determine values for rate constants in the various Mn-bearing solids could be the bond strengths of the Mn-bearing solids. Mn-oxides may be more tightly bound because of their strong covalent bonds with oxygen. This could be a contributing factor to the reason why the Mn-oxides have the lowest rate constant in the rainwater and litter leachate batch. Mn in the organic matter may be bound more loosely by electrostatic forces compared to the Mn-oxides. The rate constant for the organic matter in the litter leachate and rainwater is higher than for the Mn-oxides. Mn in the Rose Hill shale could be loosely bound, contributing to a high rate constant; however, the specific Mn-bearing phase in the shale is unknown.

#### **4.4 Rate constants and soil composition**

We use the calculated rate constants to predict Mn leaching from a ridgetop soil profile at SSHO. The SSHO soil modeled here is an average composition of previously characterized ridge soil profiles with 770  $\mu\text{mol Mn cm}^{-2}$  Rose Hill shale, 850  $\mu\text{mol Mn cm}^{-2}$ , and 142  $\mu\text{mol Mn cm}^{-2}$  (table 11). The total rate of Mn leaching from the soil profile is equal to:

$$\text{Rate } (\mu\text{mol hr}^{-1}) = k_1M_1 + k_2M_2 + k_3M_3$$

The total rate is equal to the sum of rates for each Mn-bearing solid (subscripts 1,2,3), which is the rate constant ( $k$ ;  $\text{hr}^{-1}$ ) multiplied by the mass of the Mn in each solid in soil

profile normalize to land surface area ( $M$ ;  $\mu\text{mol Mn cm}^{-2}$ ). The Rose Hill shale contributed the most to the total rate, both in the litter leachate and rainwater experiments. Mn-oxides contributed the least in the litter leachate. The organic matter contributed the least in the rainwater experiment. The total rate of Mn release associated with the rainwater was  $1.10 \mu\text{mol hr}^{-1} \text{cm}^{-2}$  and the total Mn release rate associated with the litter leachate was  $122.0 \mu\text{mol hr}^{-1} \text{cm}^{-2}$ . The litter leachate greatly affects the total Mn in the soil water.

#### **IV. Conclusion**

After analyzing the total amount of Mn and the rates of Mn release from the interaction of Mn-bearing solids with rainwater and litter leachate, it was concluded that the litter leachate increases Mn release from solid phases of the Rose Hill shale, organic matter, and Mn-oxides relative to rainwater. The effect of litter leachate was more pronounced for the Rose Hill shale and organic matter than for the Mn-oxides. The pH and the presence of organic ligands could be factors that contribute to higher total Mn in the litter leachate batch, compared to the rainwater batch.

In the short-term experiments, we find that the Mn-oxides had the highest rate ( $\mu\text{mol hr}^{-1}$ ) for the rainwater batch and the litter leachate batch, but smallest rate constant ( $k$ ;  $\text{hr}^{-1}$ ). This could be due to the large amount of Mn present in the solid and the Mn being tightly bound by covalent bonds. The Rose Hill shale and the organic matter contain less Mn, which could contribute to the lower amount of Mn released. The rate constants of the Rose Hill shale and organic matter are higher, possibly due to the Mn being more loosely bound than in the Mn-oxides.

This experiment suggests that the Mn-oxides release Mn quickly, since it had a faster rate than the other Mn-bearing solids. However, the Mn-oxides release only a small fraction of the total Mn, since it had a lower rate constant. This implies that the rate of Mn release could last a long time, since there is an abundance of Mn present. The organic matter and Rose Hill shale release Mn more slowly than the Mn-oxide. However, less Mn is present in the organic matter and Rose Hill shale compared to the Mn-oxides, suggesting that Rose Hill shale and organic matter may have a shorter amount of time that Mn can be released before the Mn is depleted.

The long term rainwater batch and litter leachate batch experiments for the Rose Hill shale and organic matter display an initial rapid increase, followed by a gradual slow increase. Factors that could contribute to the total Mn leveling off over time include back reactions and a decrease in particle surface area. For future long term batch experiments, the Mn-oxides should not be autoclaved due to a loss of Mn that adhered to the sides of the flasks.

In this experiment, litter leachate had a higher rate of Mn release compared to rainwater; however both are effective in mobilizing Mn from soil components, which make them available for uptake by trees. Mn-oxides, Rose Hill shale, and organic matter are sources that can contribute to plant available Mn in soil solution. The Mn-oxide in this experiment seems to be the primary contributor to total Mn; however, the SSHO soils indicate the Rose Hill shale is a major contributor of soil solution Mn in the field due to the abundant amount of Rose Hill shale. Trees at SSHO may be greatly affected by the litter leachate and rainwater contact with the Rose Hill shale and organic matter. The contact between Mn-bearing solids and rainwater or litter leachate can greatly affect the

health of the tree. The more available Mn, the higher amount of Mn uptake within the trees, which could lead to manganese toxicity.

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### **References**

- Brantley S.L. & Conrad C.F. (2008) "Analysis of rates of geochemical reactions" in *Kinetics of Water-Rock Interaction* (ed. S.L. Brantley, J.D. Kubicki, and A.F. White). New York, New York.
- Herndon, E. M., Jin, L., and Brantley S. L. (2011) Soils reveal widespread manganese enrichment from industrial inputs. *Environ. Sci. Technol.*, **45**, 241-247.
- Kogelmann, W. J.; Sharpe, W. E. Soil acidity and manganese in declining and nondeclining sugar maple stands in Pennsylvania. *J. Environ. Qual.* **2006**, *35*, 433–441.
- Liermann L. J., Mathur R., Wasylenki L. E., Nuester J., Anbar A. D., and Brantley S. L. (2011) Extent and isotopic composition of Fe and Mo release from two Pennsylvania shales in the presence of organic ligands and bacteria. *Chemical Geology* **281**, 167- 180.
- Lin H., Kogelmann W., Walker C., and Bruns M.A. (2006) Soil moisture patterns in a forested catchment: a hydrogeological perspective. *Geoderma* **131**, 345-368.
- Lynch J.A. (1976) Effects of antecedent soil moisture on storm hydrographs. PhD Dissertation. Pennsylvania State University, University Park, PA.
- Marschner, H. 1995. Mineral nutrition of higher plants. 2nd ed. Academic Press, New York.

National Atmospheric Deposition Program. <http://nadp.sws.uiuc.edu/> (accessed April 1, 2012).

St. Clair, S. B., Lynch, J. P. (2005) Element accumulation patterns of deciduous and evergreen tree seedlings on acid soils: implications for sensitivity to manganese toxicity. *Tree Physiology*, **25**, 85-92.

U.S. Environmental Protection Agency. *Health Assessment Document for Manganese: Final Report*; Report No. EPA-600/ 8-83-013F; Cincinnati, OH, 1984.