ABSTRACT

LAUBSCHER, SYDNEY, M.S. DECEMBER 2019 GEOLOGY

MANGANESE UPTAKE IN RED MAPLE TREES IN RESPONSE TO MINERAL DISSOLUTION RATES IN SOIL

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Manganese (Mn), an essential nutrient critical for photosynthesis in plants but a toxic element in excess, impacts the fate and transport of other nutrients and toxins, forest metabolism, carbon storage, and ecosystem productivity. Given the significant role Mn can play in ecosystems, it is important to understand how soil geochemistry controls Mn uptake by vegetation. The purpose of this research was to explore how Mn uptake by plants is related to Mn supply to plants through mineral dissolution. We conducted a greenhouse pot experiment to quantify Mn uptake by plants based on controlled geochemical constraints. Specifically, we investigated whether Mn uptake was limited by the supply of Mn to soil solution or by biological controls within the plants. Greenhouse soil pots (quartz sand + peat) that were non-vegetated or vegetated with red maple saplings were supplied with either no added Mn, dissolved Mn, Mn-oxides, or crushed shale containing Mn-bearing pyrite. We analyzed the chemical composition of plant tissue to quantify Mn uptake and soil leachate to quantify Mn losses. From these values, we constructed a mass balance model and calculated pseudo-first order rate constants to compare Mn mobilization between treatments. Mn uptake was higher in systems with dissolved Mn because it was not limited by mineral weathering. Mn uptake was also higher in systems supplied with fast-weathering substrates (pyrite in the shale) than slow-weathering substrates (Mn-oxides). There were not significant differences in Mn leaching and total Mn loss between vegetated and non-vegetated pots in the Mn-oxide or shale treatments. We conclude that Mn uptake is controlled by dissolution rates of Mn-minerals in soil.

MANGANESE UPTAKE IN RED MAPLE TREES IN RESPONSE TO MINERAL DISSOLUTION RATES IN SOIL

A thesis submitted
To Kent State University in partial
Fulfillment of the requirements for the
Degree of Master of Sciences

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December, 2019

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Acknowledgments

First, I would like to thank Dr. Elizabeth Herndon for her constant help, support, and expertise. Dr. Herndon is a role model as a leader and scientist. She not only helped me gain a better understanding of environmental issues and their global significance, but also encouraged me to think more deeply about research problems and how to solve them. Without her research and knowledge, I would not have been able to complete this project. Thank you to my committee members, Dr. David Singer and Dr. Chris Blackwood, for answering my questions and being available for advice. Thank you to the Herndon, Singer, and Blackwood lab groups for their help with my experiment. I would like to also acknowledge the seminars hosted by Dr. Herndon and Dr. Singer, and how useful they were regarding research discussions, collaboration, and presentation opportunities. Thank you to Dr. Carla Rosenfeld for taxonomically describing the microbial communities in this work, Dr. Christie Bahlai for her statistical expertise, and Nick Johnson for his assistance with the ICP. Lastly, I would also like to thank the funding sources; this work was supported by grants from the National Science Foundation (CAREER: Manganese biogeochemistry and impacts on carbon storage in plant-soil systems), the Kent State University Research Council, and the Geological Society of America.

1. Introduction

1.1 Manganese in soil

Manganese (Mn), an essential micronutrient in all organisms, is the tenth most abundant element in the Earth's crust (0.1%) and the second most abundant heavy metal behind iron (Fe) (Kabata-Pendias and Pendias, 2001; Turkian and Wedopohl, 1961). Manganese in rocks typically ranges from 350-2000 mg kg^{-1} (~6,300-36,400 μmol kg^{-1}), while the global average of Mn in soil is 437 mg kg^{-1} (~8,000 μmol kg^{-1}) and ranging from 150-1500 mg kg^{-1} (~2,700-27,300 μmol kg^{-1}) in United States forest soils (Kabata-Pendias and Pendias, 2001). Common lithological sources of Mn include sedimentary rocks (clay sediments, limestone, and shale) and most igneous rocks (felsic and mafic) (Kabata-Pendias and Pendias, 2001). Through anthropogenic activities such as iron ore smelting, coal combustion, and mining, soils can become enriched in Mn (and other heavy metals) from atmospheric deposition and enhanced mineral dissolution and accumulation (Cole et al., 1988; Pacyna and Pacyna, 2001; Herndon et al., 2011).

Rock and mineral weathering release soluble Mn(II) into soil pore water, where its mobility is highly influenced by redox potential (Eh) and pH. In oxidizing and/or basic environments, aqueous Mn(II) is oxidized to immobile Mn(III/IV) oxide/hydroxide minerals that occur as fine-grained aggregates with large surface areas (Post, 1999). In reducing or acidic soils, such as those developed on mine waste or affected by acid rain, Mn-oxides are reduced to aqueous Mn(II) (Schemel et al., 2000; Post, 1999). Mn(II) is highly mobile under anoxic conditions and can be transported within the soil column or through the watershed. Dissolution rates of Mn-bearing minerals are affected by pH, redox potential, mineral crystallinity, and reduced species concentration (Mn(II)) (Martin, 2005).

Oxidation of aqueous Mn(II) can be slow without a catalyst, with some reactions taking years to complete (Diem and Stumm, 1984; Martin, 2005). Microorganisms often greatly accelerate the reaction (Tebo et al., 2005) and generate some of the most abundant (and reactive) Mn(III/IV)-oxides in nature, even in acidic conditions (Mayanna et al., 2015). Bacteria and fungi have been shown to directly oxidize Mn through enzymatic catalyzation (Webb et al., 2005), or indirectly accelerate Mn-oxidation by either modifying regional Eh-pH conditions, releasing Mn-oxidizing metabolic end products, or by releasing reactive oxygen species (Richardson et al., 1988; Hullo et al., 2001; Hansel et al., 2012; Li et al., 2014; Barboza et al., 2017). Microorganisms are known to play an important role in Mn(II) oxidation in soils, although the physiological function of this reaction is not understood. Bacterial and fungal species impact Mn-oxide structure, size, and morphology, and therefore ultimately impact Mn-oxide reactivity (Santelli et al., 2011).

More than 30 known Mn-oxides occur in nature, some of the most common being birnessite $(Na,Ca,K)_x(Mn^{4+},Mn^{3+})_2O_4 \bullet 1.5(H_2O)$, lithiophorite $(Al,Li)Mn^{4+}O_2(OH)_2$, and hollandite $Ba(Mn^{4+},Mn^{3+})_8O_{16}$. Mn-oxides can greatly influence soil and water chemistry due to their affinity to adsorb other elements. Many of these sorbed elements are trace metal(oid)s that can act as nutrients or contaminants (Fe, Co, Ni, Cu, Zn, Mo, As, Se, and Cr), and sorption to Mn-oxides can control their transport and bioavailability (Post, 1999; Kabata-Pendias and Pendias, 2001; Tebo et al., 2005). This process has been utilized as a remediation technique to immobilize contaminants in wastewater, drinking water, and soil water (Tebo et al., 2005).

Manganese can also exist in the soil as exchangeable Mn^{2+} on soil exchange sites, while often replacing elements with similar valences and ionic radii, such as Ca^{2+}, Fe^{2+}, and Mg^{2+} (Kogelmann and Sharpe, 2006). Exchangeable Mn is loosely adsorbed to soil, and is more bioavailable than mineral Mn, but less bioavailable than dissolved Mn.

1.2 Manganese as a nutrient

Manganese plays a key role in oxygenic photosynthesis and is therefore an essential nutrient for plants, algae, and cyanobacteria. As electrons are transferred from water to carbon dioxide (CO_2) to produce carbohydrates during photosynthesis, water is split and oxidized to form oxygen gas (O_2). Manganese is a key component of the oxygen-evolving complex (OEC) that catalyzes water oxidation (Saur, 1980; Umena et al., 2011). Manganese is also structurally important for enzymes and proteins (Lagoutte and Duranton, 1975; Millaleo et al., 2010). In plants, deficiency is detrimental, reducing photosystem units per unit leaf area, and subsequently reducing the plant's ability to produce chemical energy to live (Millaleo et al., 2010; Socha and Guerinot, 2014; Tebo et al., 2005).

Despite small quantities being essential to plants (deficiency being < 25 mg kg^{-1} in total dry weight), Mn in excess can be highly toxic (Clarkson, 1988; Loneragan, 1988; Migocka and Klobus, 2007). As plants are exposed to higher levels of bioavailable Mn in the soil, plant uptake increases to toxic levels, although toxic concentrations vary by species. For example, 500 mg kg^{-1} is considered to be toxic in most plants, although more resistant species, such as red maple trees, may tolerate up to 1000 mg kg^{-1}. Physiological responses to Mn toxicity include chlorosis, leaf puckering, necrotic brown spots, browning roots, dry leaf tips, and uneven distribution of chlorophyll (Kabata-Pendias and Pendias, 2001). Just like cation exchange in soils, Mn can replace other cations of similar size and valence in plants (Ca^{2+}, Fe^{2+}, and Mg^{2+}), where Mn-toxicity in this case may be expressed as deficiency in the replaced cations.

1.3 Impact on forest ecosystems

Manganese that is leached from minerals in forest soils can be retained in the ecosystem through vegetative uptake and storage (Herndon, et al., 2015; Kraepiel et al., 2015, Herndon, et al., 2019), redistributing Mn from mineral soil to biomass and the organic horizon (Li et al., 2008; Jobbagy and Jackson, 2004). Excess Mn(II) in soil pore water or leaf litter has been proposed to increase litter decomposition rates by forming reactive Mn(III) compounds that break down lignin (Hofrichter, 2002; Jobbagy and Jackson, 2004; Keiluweit et al., 2015). Mn(II) contained in leaf litter can eventually be leached or oxidized to form these Mn(III) compounds, or ultimately form Mn(IV) oxides (Herndon et al., 2014; Herndon et al., 2015; Keiluweit et al., 2015). Manganese-oxide accumulation could also impact carbon storage by oxidizing (Stone and Morgan, 1984) or stabilizing organic matter through adsorption (Estes et al., 2016).

Manganese supply and retention in an ecosystem may therefore impact forest metabolism, leaf litter decomposition rates, and organic matter in soils. These effects can lead to changes in carbon storage, which plays an important role in maintaining soil health and supporting ecosystem productivity (Jurgensen et al., 1997). Carbon is a vital source of energy for nutrient cycling (Attiwill and Adams, 1993) and thus impacts water and energy budgets (Raich and Schlesinger, 1992).

1.4 Research goal

Although Mn cycling and uptake in soils is well researched, it is unclear to what extent geochemical mineral weathering and biological factors influence these processes. Here, we use a greenhouse pot experiment to investigate the question “Does geochemistry constrain the ability of vegetation to recycle Mn through soil?” Our hypothesis is that the rate of Mn uptake by plants is limited by the rate of mineral dissolution, with three sub-hypotheses: 1) Mn uptake will be higher in systems supplied with dissolved Mn than Mn minerals because it will not be limited by mineral weathering; 2) Manganese uptake will be higher in systems supplied with fast-weathering substrates, such as Mn-bearing pyrite, than slow weathering substrates, such as Mn-oxides; and 3) Element release rates will be higher in vegetated systems than non-vegetated systems due to biological enhanced weathering, but solute loss will be lower due to plant uptake.

2. Methods

2.1 Greenhouse set-up

Red maple saplings were grown in 2.83 L plastic plots (one per pot, 10.2 x 10.2 x 35.6 cm, Stuewe & Sons, Inc.) in the Herrick Conservatory greenhouse at Kent State University for 13 weeks (May through August 2018). Bare root red maple saplings were purchased from Cold Stream Farms, Free Soil, Michigan. Prior to planting, saplings were stored at 4°C to prevent premature budding. Each pot was lined with a plastic bag that funneled into tubes attached to 250 mL amber plastic bottles for leachate collection. Cotton was placed at the bottom of each pot inside the plastic bag to prevent sediment from leaking into the bottles. Prepared soil media, described in section 2.2, was poured into all pots (excluding a pot blank for reference) and saplings were planted in the vegetated systems. Non-vegetated systems were set-up on 16 May, 2018 and vegetated systems were planted on 17 May, 2018. "Week one" refers to 21 May, 2018, and the following six days. Subsequent weeks are referred to similarly, until week 13 where plant harvest and soil drying occurs mid-week on 15 August, 2018.

Pots were statistically randomized in eight 3 x 3 pot boxes (with 7-8 pots placed in each box) in the greenhouse (Figure 1). The boxes were elevated with cinder blocks and wooden planks to allow water to drain from the bottom of each pot and collect in the amber plastic bottle. All pots were watered twice a week with 200-250 mL greenhouse tap water at each watering event using a pressurized drip irrigation system. An additional pot blank was installed containing an empty plastic bag with the cotton base to monitor drainage and leachate chemistry unaltered by soil. Nutrient solution (10 mL of 10 mmol L^{-1} monopotassium phosphate, 10 mmol L^{-1}

calcium nitrate, and 1 mmol L^{-1} magnesium chloride) was added to all pots (vegetated, non-vegetated, and the pot blank) once a week starting week two of the experiment. Each week, the nutrient solution was applied to the base of the sapling (or the middle of the pot for non-vegetated pots) after watering with greenhouse tap water. Greenhouse temperature ranged from ~20-50 °C and light intensity ranged from ~0-35,000 lux (Figure 2); temperature and light intensity data were collected using a HOBOware data logger.

2.2 Treatment groups

The experiment consisted of a 2 x 4 factorial design for vegetation (with or without a sapling) and Mn treatment (dissolved Mn, Mn-oxide, shale, or no added Mn (control)) to yield eight different groups. Each treatment consisted of 10 vegetated pots and five non-vegetated pots, and each pot contained 2.5 kg of soil media. The soil in each treatment group was a mixture of sand, organic matter, and the Mn source; the weight percentages of soil constituents varied between treatments to allow for the various sources of Mn. The soil media for the control group (referred to as CP for “control plant” or CS for “control soil-only”) was 90% wt. quartz sand (Quikrete Premium Play Sand) and 10% wt. organic matter (Espoma Organic Sphagnum Peat Moss). The control was not supplied with an additional source of Mn, while the three treatments were supplied with either dissolved Mn, Mn-oxides, or crushed Mn-bearing shale.

In the dissolved Mn treatment (referred to as DMP for “dissolved Mn plant” or DMS for “dissolved Mn soil-only”), the weight percentages of quartz sand and organic matter were the same as the control. 10 mL of a 190 mmol L^{-1} Mn solution was added to each pot once per week starting in week three and continuing for the duration of the experiment. The solution was made by dissolving $MnCl_2 \cdot 4H_2O$ in ultrapure deionized water. In total, 20.9 mmol dissolved Mn were added to each pot over the course of the experiment. The dissolved Mn solution was applied to the base of the sapling after watering and after the application of the nutrient solution.

In the Mn-oxide treatment (referred to as MOP for "Mn-oxide plant" or MOS for "Mn-oxide soil-only"), the soil medium consisted of 85% wt. sand, 5% wt. Mn-oxide coated sand, and 10% wt. organic matter. The Mn-oxide coated sand was lab-synthesized using a previously reported method of producing birnessite (δ-MnO_2, Händel et al, 2013). To synthesize the δ-MnO_2, 70 mL of sodium lactate and ~600 g of sand were added simultaneously while stirring to a 1 L 63.3 mM potassium permanganate ($KMnO_4$) solution that was prepared with ultrapure deionized water. The mixture was stirred until a dark brown sludge fully replaced the purple solution (Figure 3). After a dwell time of > 2 hrs, the mixture was sieved to remove particles < 75 µm, washed with tap water until the runoff was clear, and then rinsed with ultrapure deionized water. The coated sand was dried in a drying oven for ~24 hours at 60°C before being weighed and mixed with the un-amended sand and organic matter.

The shale treatment (referred to as SP for "shale plant" or SS for "shale soil-only") contained 70% wt. sand, 10% wt. organic matter, and 20% wt. crushed black shale per pot. The shale was collected from abandoned coal mine waste located in the HR-25 subwatershed of the Huff Run Watershed in Mineral City, Ohio. Runoff from these waste piles have produced acid mine drainage enriched in Mn (Kinney, 2013; Frederick, 2017). The shale was ground with mortar and pestle until all particles passed through a 2 mm sieve and was then homogenized before mixing with sand and organic matter. The Mn-bearing minerals in the shale were investigated using scanning electron microscopy (see below).

2.3 Soil geochemistry

Pre-experiment (n = 1) and post-experiment (n = 5 for non-vegetated, n = 10 for vegetated) soil media were analyzed for geochemical characterization and/or element concentration. Initial soil media were air-dried at room temperature in the laboratory, while final soil-media were air-dried in the greenhouse. The dried samples were split into representative subsamples using a Riffle-type sample splitter, and a subsample was ground into a fine powder using a Spex 8000 Ball Mill. The subsequent powder (11 g of each medium) was mixed with 1.6 g of SPEX SamplePrep PrepAid 3642 Cellulose Binder and pressed into a pellet using a Carver Press System. The pellet was then analyzed using Epsilion 3 XLE Benchtop Energy Dispersion X-Ray Fluorescence. Manganese concentrations in the soil media were quantified by comparison to calibration standards. One set of standards was prepared by mixing varying amounts of laboratory-grade Mn-oxide (MnO_2) powder with control soil media to yield 0 to 10,000 mg kg^{-1} Mn concentrations. A second set of standards was prepared by diluting USGS GXR-2 reference soil with pure quartz to yield 9.6 to 960 mg kg^{-1} Mn concentrations (Gladney and Roelandts, 1990). Known prepared standard concentrations were compared with instrument-reported values and USGS GXR-2 calibration curves to determine the most appropriate linear equation to apply to samples (Figure 4). Measured values between 1-300 mg kg^{-1} were corrected using the low end of the GXR-2 Mn curve (GXR-2 actual range: 52.2 – 415.5 mg kg^{-1}), measured values between 400-700 mg kg^{-1} were corrected using the mid-level curve (GXR-2 actual range: 236.8 – 1,760 mg kg^{-1}), and measured values between 800-3000 mg kg^{-1} were corrected using the high curve (GXR-2 actual range: 598.9 - 3,170 mg kg^{-1}). Error is reported as the highest of the analytical error or standard error of the average of experimental replicates.

Major mineral phases in the pre-experiment unaltered sand, lab-synthesized Mn-oxides, and shale were identified with qualitative X-Ray Powder Diffraction (Rigaku DMaxB with MDI Datascan controlling software, copper source) on milled powders. Diffraction peaks were identified by comparison with a reference library using MDI Jade 6.0 and Qual S/M analysis software. Peaks associated with Mn oxides were identified by comparison with reported 2θ (Händel et al., 2013). The Mn-bearing minerals in the crushed shale were determined using a Hitachi Benchtop Scanning Electron Microscope TM3030.

Initial soil pH was determined by creating a 10 mL slurry with 1.0 g of soil and 0.01 M $CaCl_2$ and measuring the pH of the slurry. Additionally, these soil pH values were compared with a 10 mL slurry of soil and ultrapure deionized water (18 MΩ). Soil pH from the method using $CaCl_2$ was used to calculate exchangeable H^+ concentrations (mmol $kg\text{-}soil^{-1}$). To determine the cation exchange capacity (CEC) and concentrations of exchangeable cations in the pre-experiment soil media, representative subsamples (n = 3) were generated using a Riffle-type sample splitter and dried at 60°C for 24 hours. 1 g of each sample was weighed and added to a 50 mL centrifuge tube. A 10 mL solution containing 0.1M $BaCl_2$ and 0.1M NH_4Cl was added to the weighed soil (1:10 ratio of soil to solution) (Amacher et al., 1990; Jin et al., 2010). Tubes were vortexed to homogenize and mixed on an end-over-end rotator for 1 hour. Tubes were then centrifuged at 4,000 rcf for 30 minutes to separate the solid pellet from the solution. The supernatant was filtered through a 0.45 µm polyethersulfone membrane syringe filter into a new 50 mL tube. The pellet was rinsed with 10 mL of ultrapure deionized water, vortexed, and centrifuged at 4,000 rcf for 30 minutes. The rinse was added to the previously separated supernatant, acidified with two drops of ultrapure concentrated nitric acid, and analyzed on a Perkin-Elmer ICP-OES 8000 for major cations (Al^{3+}, Ca^{2+}, Fe^{2+}, K^+, Mg^{2+}, Mn^{2+}, and Na^+).

Cation exchange capacity (meq kg^{-1}) was calculated as the sum of all exchangeable cations (mmol kg^{-1}) converted to milliequivalents. Error is reported as the standard error of replicate averages.

2.4 Plant tissue

Leaf counts were completed weekly for each sapling throughout the experiment. Two saplings never produced leaves (CP5 and CP7) and were considered dead upon planting. CP5 and CP7 are considered non-vegetated pots for leachate and soil concentrations, and are not considered vegetated pots for foliar concentrations, foliar biomass, or non-foliar biomass calculations. Due to homogenization of non-foliar tissue after weighing, CP5 and CP7 were included with the vegetated pots for non-foliar tissue element concentrations. Foliar and non-foliar weights were tested for significant differences between treatments using a one-way ANOVA and a Tukey post-hoc test ($\alpha = 0.05$).

After harvest at 13 weeks, leaves and rinsed non-foliar biomass (stem + roots) were dried at 60°C for > 24 hours separately, weighed, and ground using a Spex 8000 Ball Mill (10 minutes). Leaf mass for each sapling was too low for individual analysis; therefore, all the leaves from all plants within each treatment group were combined and homogenized before being analyzed. Non-foliar tissue was also homogenized before being analyzed. Powdered leaves and non-foliar tissue were analyzed separately along with replicate NIST 1570a spinach leaf standards at the Agricultural Analytical Services Laboratory in the College of Agricultural Sciences at The Pennsylvania State University using hot block acid digestion for ICP emission spectroscopy (see Huang and Schilte, 1985 for method) for major and minor elements (P, K, Ca, Mg, Mn, Fe, Cu, B, Al, Zn, Na). Error is reported as highest between the standard error of the average and the analytical error from the NIST 1570a replicates.

2.5 Leachate sampling and analysis

The volume of leached water in the collection bottles was recorded twice per week ~24 hours after watering events so that the total volume of leached water was quantified. Water samples for chemical analysis were collected once per week, ~24 hours after watering events that included the addition of the dissolved Mn and nutrient solutions. Pairwise comparisons were used on replicate leachate data to determine significant differences in volume of leached water. Data was not normally distributed, so a generalized linear modal was made to produce an analysis of deviance (two-way ANOVA with chi square). To combat error, a more conservative alpha was used ($\alpha = 0.017$). The independent variables were treatment and vegetation, while the dependent variable was volume of leached water (mL).

Collected leachate samples were brought back to the lab and filtered through a 0.45 µm Supor membrane disc filter using an acid washed plastic filter tower which was rinsed between each sample. Volume was recorded before filtering, while pH and specific conductance were recorded from the filtered sample. Volume, pH, and specific conductance error is calculated as the standard error for the average values. Due to equipment malfunction, only one measurement from each treatment (vegetated and non-vegetated) apart from the control was taken in week one. Element concentrations of leachate in-between sampling events were assumed to be the average of the individual leachate concentrations collected before and after.

The filtered leachate samples were split into two subsamples for cation (Al, Ca, Fe, K, Mg, Mn, and Na) and anion (F^-, Cl^-, NO_2^-, SO_4^{2-}, Br^-, NO_3^-, and PO_4^{3-}) analysis. Cation subsamples were collected weekly, acidified with 2-3 drops of concentrated ultrapure nitric acid, and analyzed using a Perkin-Elmer ICP-OES 8000. Cation subsamples were diluted, if needed, with 2% nitric acid in ultrapure deionized water (18 MΩ). Anion subsamples were collected five times throughout the experiment (weeks 1, 2, 6, 10 and 13) and analyzed using Dionex ICS-2100 chromatography. Values below detection are reported as half of the detection limit, while values above detection (mainly Ca and Fe in the shale treatment) are reported and used for averages, they are indicated as being above detection in their respective graphs. Quality assurance standards were used for analytical error, while reported error is the higher of the analytical or standard error of replicate averages.

Pairwise comparisons were used on replicate leachate data to determine significant differences of Mn and other cations in leached water. Data was not normally distributed, so a generalized linear modal was made with gamma distribution to produce an analysis of deviance (two-way ANOVA with chi square). To combat error, a more conservative alpha was used ($\alpha = 0.017$). The independent variables were treatment and vegetation, while the dependent variables were Mn, Ca, Mg, and Fe in leached water (µmol).

3.0 Results

3.1 Soil geochemistry

3.1.1 Pre-experiment soil geochemistry

The initial quartz sand contained no mineralogical impurities detectable by XRD (low detection limit: 5 wt%) (Figure 5, Table 1). Shale diffraction patterns were dominated by quartz and pyrite with clay minerals kaolinite and illite (Figure 5, Table 2). Diffraction peaks for the lab-synthesized Mn-oxides used to coat the sand were consistent with birnessite (Figure 6**,** Table 3). Specifically, the XRD pattern exhibited two broad, low intensity peaks at 36.62 and 65.59 2θ degrees that are characteristic of nanocrystalline birnessite (< 500 nm) (Händel et al., 2013).

The treatment groups contained different Mn concentrations in their initial soil media (Figure 7**,** Table 4). The soil media in the control and dissolved Mn treatment contained 232 ± 62 μmol Mn kg^{-1} soil (= 581 ± 156 μmol Mn per pot). For the dissolved Mn treatment, an additional 20,900 μmol Mn was added during the experiment to yield 21,481 μmol total Mn per pot (initial soil + added aqueous Mn(II)). The initial soil Mn concentration in the Mn-oxide treatment was the highest at 2,641 ± 62 μmol kg^{-1} (= 6,603 ± 156 μmol Mn per pot). The initial soil Mn concentration in the shale treatment was 459 ± 62 μmol kg^{-1} (= 1,147 ± 156 μmol Mn per pot). Error was calculated as the standard error of a shale standard analyzed eight times by XRF (USGS SBC-1, Brush Creek Shale).

Initial soil pH (0.01 M $CaCl_2$) was moderately acidic for the Mn-oxide treatment (5.13) and for the control and dissolved Mn treatments (4.99), and highly acidic for the shale treatment (3.01). Using ultrapure deionized water, soil pH relationships were similar: 6.17 for the Mn-oxide treatment, 5.92 for the control and dissolved Mn treatments, and 3.22 for the shale treatment. Exchangeable H^+ was calculated using the $CaCl_2$ soil pH to yield 0.2 meq kg-soil^{-1} for the control, dissolved Mn, and Mn-oxide treatments, and 20 meq kg-soil^{-1} for the shale treatment.

Total cation exchange capacity was higher in the shale (63.5 ± 2.1 meq kg-soil^{-1}), than in the control and dissolved Mn treatment (38.3 ± 2.6 meq kg-soil^{-1}) or the Mn-oxide treatment (37.9 ± 12.5 meq kg-soil^{-1}). Exchangeable Mn^{2+} was 0.01 ± < 0.01 meq kg-soil^{-1} for the initial soil in the control and dissolved Mn treatments, 0.49 ± 0.03 meq kg-soil^{-1} for the Mn-oxide treatment, and 0.20 ± 0.01 meq kg-soil^{-1} for the shale treatment (Figure 8, Table A9). Exchangeable Ca^{2+} was the highest of the exchangeable cations, but did not vary between treatments (29.7 ± 1.6 meq kg-soil^{-1} for the control and dissolved Mn treatment, 29.5 ± 3.5 meq kg-soil^{-1} for the Mn-oxide treatment, and 28.2 ± 1.4 meq kg-soil^{-1} for the shale treatment). Exchangeable Mg was also high and similar amongst treatments (5.7 ± 0.3 meq kg-soil^{-1} for the control and dissolved Mn treatment, 5.5 ± 0.7 meq kg-soil^{-1} for the Mn-oxide treatment, and 5.7 ± 0.2 meq kg-soil^{-1}). Exchangeable Al^{3+} and Fe^{2+} were higher for the shale (3.7 ± 0.2 meq kg-soil^{-1} and 4.5 ± 0.1 meq kg-soil^{-1}, respectively) than the other treatments (< 0.2 meq kg-soil^{-1}).

Manganese in the shale was associated with minerals composed of Al, Fe, K, O, Si, and S (Figure 9). Although Mn-associations are likely to be pyrite and clay minerals, Mn quantities in the shale were too low, and SEM data were too noisy to effectively identify mineral-associations and specific Mn phases. A previous study showed that shale from Huff Run had Mn primarily associated with pyrite (Singer et al., 2019).

3.1.2 Post-experiment soil geochemistry

Soil in the dissolved Mn treatment gained Mn in both the vegetated treatment (+ 9,567 ± 368 μmol kg^{-1}; 5,000 ± 500% increase) and in the non-vegetated treatment (+ 11,688 ± 1,194 μmol kg^{-1}; 4,000 ± 160% increase), indicating that a portion of added Mn was stored in the soil (Figure 7, Table 4). In the shale treatment, Mn concentrations decreased in both the vegetated (– 275 ± 64 μmol kg^{-1}; 34 ± 19% decrease) and the non-vegetated soil (– 154 ± 84 μmol Mn kg^{-1}; 60 ± 19% decrease). There were no measurable differences between the initial and final soil Mn concentrations in the control or Mn-oxide treatment (non-vegetated or vegetated) (Table X).

Exchangeable cations were measured in the post-experiment soil from the dissolved Mn treatment (Figure 8, Table A9). The most drastic change between the initial and final soil occurred with exchangeable Mn^{2+}, where final soil exchangeable Mn^{2+} (9.4 ± 0.7 meq kg-$soil^{-1}$, 4,735 ± 347 μmol kg-$soil^{-1}$ for non-vegetated, and 8.6 ± 0.4 meq kg-$soil^{-1}$, 4,319 ± 200 μmol kg-$soil^{-1}$ for vegetated) was over 800x higher in both the non-vegetated and vegetated treatments than concentrations in the initial soil. These values, however, only account for less than half of the total stored Mn in the dissolved Mn treatment (~11,000 – 12,000 μmol kg-$soil^{-1}$, Table 4). Exchangeable Al^{3+}, Ca^{2+}, and Na^{2+} were all slightly higher in the final soil than the initial soil, however, exchangeable K^{+} was drastically lower (~10x) and exchangeable Mg^{2+} was slightly lower (~2x) in the finial soil than the initial soil.

3.2 Plant health and composition

Color variations in sapling leaves were indicators of overall plant health. By the end of week one, most saplings in each treatment group had leafed out. By week three, all saplings had leafed out besides two in the control that never leafed out and were considered dead upon planting (CP5 and CP7). All leaves in the control and the Mn-oxide treatments remained green throughout the experiment. In the dissolved Mn treatment, all leaves developed browning around the edges between weeks five and eight and looked "burned" (Figure 10). In the shale treatment, leaves began to bleach and droop as early as week four. Shale treatment plant mortality was 20% at week five and 70% at week seven. After week seven, mortality remained constant. Because leachate chemistry was not different for the saplings that died in the shale treatment, all vegetated pots are included in the analyses.

Non-foliar biomass did not differ between the Mn-oxide treatment (3.03 ± 0.32 g), the control (2.85 ± 0.41 g), and the shale treatment (2.78 ± 0.25 g) but was relatively low in the dissolved Mn treatment (2.07 ± 0.15 g) (Figure 11, Table A1). The Mn-oxide treatment and the control both had higher foliar biomass (1.03 ± 0.06 g and 0.83 ± 0.18 g, respectively) than the dissolved Mn and the shale treatments (0.60 ± 0.08 g and 0.57 ± 0.04 g, respectively).

Statistically, there was only one significant difference ($\alpha = 0.05$) in total biomass (foliar + non-foliar) between treatments where Mn-oxide treatment biomass was higher than dissolved Mn treatment biomass (overall model significance: $p = 0.038$; pair significance: $p = 0.027$, Table 5). When only comparing non-foliar biomass, there were no significant differences between treatments (overall model significance: $p = 0.087$). When only comparing foliar biomass between treatments (overall model significance: $p = 0.005$), Mn-oxide treatment biomass was higher than dissolved Mn treatment biomass ($p = 0.013$) and shale treatment biomass ($p = 0.008$).

Foliar Mn concentrations were highest in the dissolved Mn treatment (83.60 ± 0.54 mmol kg^{-1}), followed by the Mn-oxide treatment (6.75 ± 0.01 mmol kg^{-1}), the shale treatment (4.57 ± 0.01 mmol kg^{-1}), and the control (0.84 ± 0.01 mmol kg^{-1}) (Figure 12, Table 6). Total Mn stored in foliar tissue (μmol) was calculated as the product of foliar Mn concentration (mmol kg^{-1}) and leaf biomass (kg) for each tree (Figure 13, Figure 14). Total Mn stored in foliage in the dissolved Mn treatment (50.2 ± 1 μmol) was more than 7 times as much as the Mn-oxide (6.9 ± 0.1 μmol) and shale treatments (2.6 ± 0.1 μmol). The control foliage stored only 0.69 ± 0.01 μmol Mn. As a fraction of total Mn in each pot, the leaves in the shale treatment stored 0.23 ± 0.01%, the dissolved Mn treatment stored 0.23 ± < 0.01%, the control stored 0.12 ± 0.01%, and the Mn-oxide group stored 0.12 ± < 0.01%.

Similarly, Mn concentrations in non-foliar biomass were the highest in the dissolved Mn treatment (5.03 ± 0.27 mmol kg^{-1}), followed by the Mn-oxide treatment (1.70 ± 0.01 mmol kg^{-1}), the shale treatment (1.03 ± 0.01 mmol kg^{-1}) and the control (0.65 ± 0.01 mmol kg^{-1}) (Figure 12, Table 6). Total Mn storage in non-foliar biomass (μmol) is calculated as the product of Mn concentration in non-foliar tissue (mmol kg^{-1}) and non-foliar biomass (kg) for each tree (Figure 13, Figure 14). Total Mn stored in non-foliar tissue was the highest the dissolved Mn treatment (10.42 ± 0.55 μmol), followed by the Mn-oxide treatment (5.15 ± 0.04 μmol), the shale treatment (2.71 ± 0.02 μmol) and the control (1.85 ± 0.02 μmol). As a fraction of total Mn added to each pot, the non-foliar biomass in the control stored 0.32 ± 0.03%, the shale treatment stored 0.24 ± 0.01%, the Mn-oxide treatment store 0.08 ± <0.01%, and the dissolved Mn stored 0.05 ± <0.01%. However, we cannot fully distinguish Mn stored in the non-foliar tissue during the experiment from Mn present in the sapling at time zero. Therefore, these values represent maximum possible uptake from the soil and storage in non-foliar tissues during the experiment.

3.3 Leachate analyses

3.3.1 Volume

Leachate volume was consistently lower in vegetated treatments than non-vegetated treatments ($p < 0.017$, Figure 15, Table 7, Table A2), although the differences were variable between treatments; vegetated pots leached 40 ± 7 mL less than non-vegetated pots in the Mn-oxide treatment, 23 ± 8 mL less in the dissolved Mn treatment, 15 ± 8 mL in the shale treatment, and 12 ± 6 mL less in the control. Over time, leachate volume fluctuated between 50-200 mL each treatment, depending on volume of added water (200-250 mL) and vegetation (Figure 16).

3.3.2 pH and specific conductance

Effluent pH remained circumneutral in the control (7.81 ± 0.02), the dissolved Mn (7.70 ± 0.01), and the Mn-oxide (7.86 ± 0.02) treatments throughout the entire experiment, with weekly averages consistently fluctuating in each treatment by < 1 with fluctuations in greenhouse tap water pH (8.96 ± 0.07) (Figure 17, Table A3). Effluent pH in the shale treatment was extremely acidic and decreased over the course of the experiment from 3.79 ± 0.07 (week two) to 2.20 ± 0.03 (week 13). Averaged effluent pH for vegetated and non-vegetated pots in each treatment were within one pH unit of each other during each sampling event, with the exception of the shale treatment in weeks one and four (week one: vegetated = 5.56, non-vegetated = 3.82; week four: vegetated = 4.13 ± 0.36, non-vegetated = 3.03 ± 0.12).

Effluent specific conductance was highest in the shale treatment and fluctuated throughout the experiment (Figure 17, Table A4). Specific conductance for the shale treatment was lowest in week one (2,841 µS/cm for non-vegetated, 1,992 µS/cm for vegetated), peaked in week nine (11,718 ± 1,374 µS/cm for non-vegetated, 10,116 ± 751 µS/cm for vegetated), and steadily decreased to week 13 (5,644 ± 515 µS/cm for non-vegetated, 6,322 ± 224 µS/cm for vegetated). Effluent specific conductance for the dissolved Mn treatment increased by > 3x from week one (578 µS/cm for non-vegetated, 753 µS/cm for vegetated) to week 13 (2080 ± 117 µS/cm for non-vegetated, 2440 ± 134 µS/cm for vegetated). For the Mn-oxide treatment, specific conductance increased less dramatically from week one (615 µS/cm for non-vegetated and 654 µS/cm for vegetated) to week 13 (831 ± 54 µS/cm for non-vegetated, 996 ± 45 µS/cm for vegetated). Effluent specific conductance in the control similarly increased from week one (691 ± 44 µS/cm for non-vegetated, 674 ± 31 µS/cm for vegetated) to week 13 (886 ± 40 µS/cm for non-vegetated, 976 ± 32 µS/cm for vegetated) but was not different between vegetated and non-vegetated pots. In both the dissolved Mn and Mn-oxide treatments, non-vegetated and vegetated pots were similar in the beginning of the experiment but differentiated in weeks seven through 13 where vegetated pots had higher effluent specific conductance than non-vegetated pots. In the shale treatment, non-vegetated pots had higher specific conductance than vegetated pots until week nine, where thereafter average values were within error of each other.

3.3.3 Cations

All individual leachate measurements (µmol) were included in an analysis of deviance to test the effect of either vegetation (vegetated or non-vegetated) or treatment (dissolved Mn, Mn-oxide, shale, control) on leachate chemistry ($\alpha = 0.017$) (Figure 18, Table 7, Tables A5-A8). CP9, a vegetated control pot, consistently produced excessively high leachate Mn relative to the other control pots and was removed from leachate analyses due to possible Mn contamination. The effect of vegetation on Mn leaching was tested within each treatment group. The only significant difference was between the Mn-oxide non-vegetated (MOS) and vegetated (MOP) groups, where MOP leached less Mn than MOS ($p = 1.8 \times 10^{-5}$). The effect of treatment on Mn leaching was tested within vegetated or non-vegetated groups. The non-vegetated control (CS) had significantly lower Mn than the other three non-vegetated treatments (DMS, MOS, SS, $p < 2.2 \times 10^{-16}$). The non-vegetated dissolved Mn treatment (DMS) did not differ from the non-vegetated Mn-oxide (MOS) or shale (SS) treatments; however, the DMS:MOS interaction ($p = 0.019$) was barely above the $\alpha = 0.017$ cutoff. Leached Mn in the non-vegetated Mn-oxide treatment (MOS), however, was significantly lower than the non-vegetated shale treatment (SS, $p = 1.4 \times 10^{-14}$). When testing the effect of treatment within the vegetated pots, all were significantly different from one another (CP, DMP, MOP, and SP), with the exception of the dissolved Mn and Mn-oxide combination. The shale had the highest Mn leaching, followed by the Mn-oxide and dissolved Mn treatments, and then the control.

Cumulative Mn leaching was highest in the shale treatment (362 ± 11 µmol for non-vegetated and 350 ± 7 µmol for vegetated), followed by the dissolved Mn treatment (241 ± 39 µmol for non-vegetated and 151 ± 27 µmol for vegetated), the Mn-oxide treatment (131 ± 2 µmol for non-vegetated and 112 ± 2 µmol for vegetated), and the control (8.9 ± 0.2 µmol for non-vegetated and 9.3 ± 0.6 µmol for vegetated) (Figure 19, Tables A5-A8). Non-vegetated pots leached 1.5 times more Mn than the vegetated pots in the dissolved Mn treatment and 1.2 times more in the Mn-oxide treatment, although the effect of vegetation in the dissolved Mn treatment was not considered significant when analyzing weekly Mn values (Table 5). Cumulative Mn leaching from the non-vegetated pots did not differ from the vegetated pots in the shale treatment and the control.

Despite cumulative leaching being similar between vegetated and non-vegetated pots, increases in Mn leaching from vegetated pots lagged behind non-vegetated pots for the shale and dissolved Mn treatments when considering changes over time (Figure 20). In the shale treatment, Mn leaching peaked in week five for the non-vegetated group (34 ± 4 µmol) and week six for the vegetated group (30 ± 1 µmol) before declining to < 5 µmol by week 13. In the dissolved Mn treatment, Mn leaching steadily increased in the non-vegetated group and peaked in week 13 (29 ± 12 µmol). Mn leaching from the vegetated group was delayed, staying < 5 µmol until week 11, after which Mn in leachate rapidly increased to 39 ± 15 µmol. Manganese leaching from the control and Mn-oxide treatments peaked in week three at < 1 µmol and ~10 µmol, respectively, and then steadily declined, with non-vegetated pots leaching slightly more Mn by week 13.

All of the pairwise comparisons for weekly leached Ca measurements were statistically different from one another when considering treatment and holding vegetation constant (Figure 18, Table 7, Tables A5-A8), with the exception of the vegetated and non-vegetated control and Mn-oxide pairs (CS:MOS and CP:MOP). In both the vegetated and non-vegetated treatments, the shale treatment had the highest Ca in leachate, followed by the dissolved Mn treatment, and then the similar control and Mn-oxide treatments. When considering vegetation and holding treatment constant, the non-vegetated control and Mn-oxide treatments leached more Ca than their vegetated counterparts (CS:CP, $p = 1.5 \times 10^{-14}$; MOS:MOP, $p < 2.2 \times 10^{-16}$), while vegetated and non-vegetated treatments were statistically similar for the dissolved Mn and shale treatments.

When considering changes over time, in the shale treatment Ca leaching trends were very different from the other treatments, peaking week four (2,968 ± 104 µmol for non-vegetated, 2,450 ± 36 µmol for vegetated) and decreasing for the rest of the experiment (Figure 21). In the dissolved Mn treatment, calcium leaching increased throughout the experiment in both the non-vegetated and vegetated pots, although remaining below 1,250 µmol per sampling event. In the Mn-oxide treatment and the control, calcium leaching did not vary over time other than fluctuations in greenhouse tap water, although non-vegetated pots consistently had more calcium leaching than vegetated pots.

Weekly Fe leaching was drastically higher in the shale treatment than the other treatments ($p < 2.2 \times 10^{-16}$ in all cases), although there was no effect of vegetation on Fe leaching from shale (SS:SP, Figure 18, Table 7, Tables A5-A8). Iron leaching remained < 10.5 µmol per sampling event in the control, dissolved Mn treatment, and Mn-oxide treatment (Figure 22). In the shale treatment, Fe leaching increased dramatically from week four (282 ± 160 µmol for non-vegetated, 7 ± 2 µmol for vegetated) to week six (3,784 ± 707 µmol for non-vegetated, 2,027 ± 224 µmol for vegetated). Fe leaching was higher in the shale non-vegetated pots than the vegetated pots in weeks four through eight, where there was no difference between non-vegetated and vegetated pots in weeks 10 through 12.

In both the vegetated and non-vegetated treatments, Mg leaching decreased in the following order: shale > dissolved Mn > control > Mn-oxide ($p \leq 2.8 \times 10^{-12}$ for all interactions). (Figure 18, Table 7, Tables A5-A8). The vegetated Mn-oxide treatment had higher Mg leaching than the non-vegetated treatment (MOS:MOP, $p = 5.9 \times 10^{-8}$), while the effect of vegetation was not significant in the other treatments. In the shale treatment, Mg leaching peaked in week four (390 ± 10 µmol for non-vegetated, 296 ± 16 µmol for vegetated), and decreased from week four to week 13 (62 ± 28 µmol for non-vegetated, 59 ± 20 µmol for vegetated, Figure 23). In the dissolved Mn treatment, however, Mg leaching increased throughout the experiment, peaking in week 11 (66 ± 20 µmol for non-vegetated, 74 ± 18 µmol for vegetated). Magnesium leaching remained < 50 µmol per sampling event for both vegetated and non-vegetated pots in the control and the Mn-oxide treatment.

3.3.4 Anions

Chloride (Cl^-) leaching was similar between all treatments in weeks one and two, remaining below 400 µmol each sampling event (Figure 24, Table A10). By week ten, Cl^- leaching in the dissolved Mn treatment had increased by > 10x in the vegetated group (3250 ± 476 µmol) and > 6x in the non-vegetated group (2092 ± 315 µmol), due to the additional Cl^- inputs from the dissolved Mn solution. Leachate Cl^- increased gradually over time in the control, Mn-oxide, and shale treatments, although values never exceeded 800 µmol per sampling event. There were no differences between vegetated and non-vegetated Cl^- leaching in any of the treatments.

Sulfate (SO_4^{2-}) leaching was highest in the shale treatment, reaching up to > 100x higher than the other treatments (Figure 25, Table A10). Sulfate leaching peaked in week six for the non-vegetated treatment (21,805 ± 3,550 µmol) and week 10 for the vegetated group (23,207 ± 876 µmol). In the control, dissolved Mn, and Mn-oxide treatments, SO_4^{2-} leaching remained < 200 µmol, dropping from week one to week two and then steadily increasing for the remainder of the experiment. There were no consistent trends regarding differences between vegetated and non-vegetated treatments.

4.0 Discussion

4.1 Manganese mass balance model

A mass balance model was used to quantify rates of Mn weathering, Mn leaching, and plant uptake across treatments (Figure 26). Each pot was modeled as a box with inputs and outputs, where fluxes were depicted by arrows and reservoirs were depicted by boxes. At time zero, each pot contained sand, organic matter, and either Mn-oxides or crushed shale where added. The initial Mn content (µmol) included the sum total of Mn contained within these different soil components. The input fluxes included the additional greenhouse tap water and dissolved Mn (when added) and the output fluxes were plant uptake into biomass and element release into soil leachate. Pot soil and plant biomass were reservoirs. The inputs do not include the nutrient solution because it contained no Mn. “Leached” refers to element release into soil leachate, while “weathered” or “mobilized” refer to total Mn lost from the soil (leached + plant uptake).

Weekly element mass in the input water (W: µmol), which included inputs from greenhouse tap water (subscript *tap*) and the dissolved Mn solution (subscript *DMn*) where applied, was calculated as the product of the element concentration (C: µmol L^{-1}) and the volume of water (V: L) for each solution, where n refers to the sampling event and i refers to the element (here, i = Mn):

$$(1)\ W_i^n = C_{i,tap}^n V_{tap}^n + C_{i,DMn}^n V_{DMn}^n$$

Total input (µmol) was calculated as the sum of all weekly inputs:

$$(2)\ W_i = \sum W_i^n$$

Total plant uptake (U: µmol) was calculated using the sum of treatment-averaged leaf and wood concentrations ($C_{i,s}$: µmol tree^{-1}) multiplied by the mass (m: kg) of the individual sapling (subscript s):

$$(3)\ U_{i,s} = C_{i,f}m_f \ + \ C_{i,w}m_w$$

Where subscript f refers to foliar tissue and subscript w refers to non-foliar tissue.

Weekly element mass in the soil leachate ($L_{i,s}^n$; µmol week^{-1}) was calculated as the product of solute concentrations ($C_{i,s}^n$; µmol L^{-1}) and the volume of leachate ($V_s{}^n$; L) for each pot:

$$(4)\ L_{i,s}^n = \left(C_{i,s,}^n V_s{}^n\right)$$

Here, s refers to the individual pot. Once per week when volumes were recorded but chemistry was not determined, concentrations were calculated as the average between the sampling events before and after. Cumulative element leaching over the course of the experiment for each pot ($L_{i,s}$; µmol) was calculated as the sum of the weekly element mass in the leachate:

$$(5)\ L_{i,s} = \sum L_{i,s}^n$$

The change in element mass in the soil over time (ΔM: µmol) was calculated as the sum of total inputs and outputs:

$$(6)\ \Delta M = \ W_{i,s} - (L_{i,s} + U_{i,s})$$

Here, a positive value indicated increased Mn storage and a negative value indicated net Mn loss. Changes in soil Mn were also calculated from XRF analysis of initial and final soil media;

however, because of the high error associated with XRF measurements in initial and final soil compared with low ICP error for the inputs and outputs, equation *(6)* is used to represent the change in soil Mn.

The rate of element loss in leachate (R_L; µmol d^{-1}), equivalent to the leachate flux, was calculated as the cumulative mass loss of the element in leachate over time:

$$(7)\ R_L = \frac{L_{i,s}}{t}$$

Here, *t* refers to the entirety of the experiment (= 86 days). The rate of plant uptake (R_U; µmol d^{-1}) was calculated in the same manner by dividing total uptake ($U_{i,s}$) by time:

$$(8)\ R_U = \frac{U_{i,s}}{t}$$

A first-order rate constant for Mn loss in leachate (k_L: d^{-1}) was calculated for each treatment by normalizing leachate fluxes by the mass of Mn in the soil reservoir:

$$(9)\ R_L = k_L[M_{i,s}]$$

Here, *M* is the total element mass in the soil available to be leached or taken up by vegetation during the experiment, including Mn present in the starting soil plus any Mn added throughout the experiment. A first-order rate constant for Mn uptake (k_U: d^{-1}) into the plant was calculated the same way:

$$(10)\quad R_U = k_U[M_{i,s}]$$

Rate constants were used to compare uptake and leachate fluxes across treatments that had widely different total Mn concentrations. Total weathered Mn (k_T: d^{-1}) was calculated as the sum of the leached rate constant and the uptake rate constant:

$$(11)\ R_L + R_U = k_T\left[M_{i,s}\right],\ k_T = k_L + k_U$$

4.1.1 Control mass balance

Manganese in the control treatment was provided by the soil media (581 ± 156 μmol) and the minimal amount in the greenhouse tap water (cumulative: 1.4 μmol). In the non-vegetated treatment, the soil in each pot lost 7.5 ± 0.2 μmol Mn while 8.9 ± 0.2 μmol Mn was released into the soil leachate, representing k_L = 1.8 ± 0.5 x 10^{-4} d^{-1} (Figure 27). Here, the main factor controlling Mn release was mineral dissolution from trace amounts in the quartz sand and organic matter. In the vegetated treatment, 9.3 ± 0.6 μmol Mn pot^{-1} were released into the soil leachate (k_L = 1.8 ± 0.5 x 10^{-4} d^{-1}) while 2.9 ± 0.4 μmol Mn were taken up by each sapling (k_U = 0.6 ± 0.2 x 10^{-4} d^{-1}) to yield k_T = 2.4 ± 0.5 x 10^{-4} d^{-1}. The vegetated and non-vegetated treatments were similar within error in their total weathered rate constants (k_L for non-vegetated = k_T for vegetated); however, both leaching rates were more than 3x the vegetated uptake rate (Figure 30). The presence of vegetation did not change the total Mn weathering rate.

4.1.2 Dissolved Mn mass balance

The soil in the dissolved Mn treatment stored the majority of added Mn. In the non-vegetated treatment, the soil in each pot stored 20,660 ± 39 μmol Mn while 241 ± 39 μmol Mn were released into soil leachate (k_L = 1.3 ± 0.5 x 10^{-4} d^{-1}) (Figure 27**)**. In the vegetated treatment, the soil stored 20,607 ± 28 μmol Mn while only 151 ± 27 μmol Mn were released into soil leachate (k_L = 0.8 ± 0.3 x 10^{-4} d^{-1}) and 143 ± 10 μmol Mn were taken up by each sapling (k_U = 0.8 ± < 0.1 x 10^{-4} d^{-1}, k_T = 1.6 ± 0.3 x 10^{-4} d^{-1}). The rate constants for vegetated and non-vegetated leaching (k_L), uptake (k_U), and mobilization (k_T) were similar within error. Although the presence of vegetation caused the cumulative Mn in soil leachate to be lower than the non-vegetated, vegetation did not impact the overall leaching rate constants or the total Mn weathering rate constants that included uptake.

Dissolved Mn added in this treatment could have been oxidized in the soil due to the high pH of the greenhouse tap water stored as Mn-oxides. Although it is unclear whether Mn-oxidation occurred, it is likely that Mn^{2+} was loaded onto the exchange sites of the soil. The dissolved Mn treatment was the only treatment where concentrations of Ca and Mg (assumed to be Ca^{2+} and Mg^{2+}) increased in the soil leachate over time. Both Ca and Mg were shown to be highly exchangeable in the soil, indicating that the added Mn may have replaced these elements on cation exchange sites, allowing for the increases of Ca and Mg in soil leachate. Furthermore, exchangeable Mn^{2+} was higher in the final dissolved Mn soil than the initial dissolved Mn soil, indicating the soil was storing Mn on exchange sites. These exchangeable Mn^{2+} values in the final dissolved Mn soil, however, only accounted for less than half of the increase in stored Mn, indicating the possibility of the Mn oxidation occurring along with cation exchange.

Before week six, Mn was consistently low in soil leachate for both the vegetated and non-vegetated treatments. After week six, however, the non-vegetated soil leachate saw an increase in Mn. This point in time likely represents when the cation exchange sites reached capacity could not hold any more Mn. In the vegetated treatment, this did not occur until week 10, where a very rapid increase in leached Mn indicates when not only the soil, but also the vegetation could not accumulate any more Mn. This is reflected in the "burning" of dissolved Mn treatment leaves that started in week six, and by week eight, all plants had leaves that were “burned,” where the plants were experiencing Mn toxicity.

High levels of Mn may not have been the sole cause of “burning” leaves. Red maple trees have been shown to have decreased photosynthetic function when Mn accumulates near roots and light intensity is high (St. Clair and Lynch, 2004, 2005). Often in the greenhouse, light intensity exceeded 20,000 lux, although light intensity was only measured in regard to visible light and does not reflect all light available to plants.

4.1.3 Mn-oxide mass balance

A portion of the Mn-oxides added to each pot (6603 ± 156 μmol total added) dissolved over time, releasing Mn in the soil leachate. In the non-vegetated treatment, 131 ± 2 μmol were lost to soil leachate (k_L = 2.3 ± 0.1 x 10^{-4} d^{-1}), and in the vegetated treatment, 112 ± 2 μmol were lost to soil leachate (k_L = 2.0 ± 0.1 x 10^{-4} d^{-1}) while 15.8 ± 2.0 μmol was taken up by each sapling (k_U = 0.3 ± < 0.1 x 10^{-4} d^{-1}, k_T = 2.3 ± < 0.1 x 10^{-4} d^{-1}) (Figure 27). Vegetation in this treatment lowered the cumulative Mn leached from the soil, as reflected in the leaching rate constants, although the total weathering rate (leaching + plant uptake) remained unchanged with vegetation.

Manganese-oxide reductive dissolution is generally very low when pH is circumneutral or slightly basic (Kabata Pendias and Pendias, 2001), as was the case for the greenhouse tap water pH (8.96 ± 0.07); however, soil pH was mildly acidic (between 5 and 6), allowing a portion of the added Mn-oxides to be reduced and mobilized. Although a large portion of the birnessite (~ 98%) remained immobilized in the soil, a small fraction was able to weather in these conditions. Roots are typically associated with increasing Mn-oxide dissolution through by releasing acid or organic exudates that reduce Mn(III) (Rengel and Marschner, 2005), but the high pH and oxidizing conditions of this treatment may have prevented Mn mobilization that may have occurred under more acidic and reducing conditions. Microbial associations with roots can also increase Mn(III) reduction, however, depending on species, soil conditions, and nutrient availability, microorganisms can also have the opposite effect, promoting oxidation rather than reduction (Marschner, 1995). Thus, this experiment represents environmental conditions typically associated with Mn limitation rather than toxicity.

4.1.4 Shale mass balance

The shale treatment leached more Mn than the other treatments (Table 6). Starting with 1147 ± 156 µmol, the non-vegetated treatment lost 361 ± 11 µmol to soil leachate (k_L = 36 ± 5 x 10^{-4} d^{-1}) and the vegetated treatment lost 355 ± 7 µmol to soil leachate (k_L = 35 ± 5 x 10^{-4} d^{-1}) while plant uptake was only 6.0 ± 0.4 µmol (k_U = 0.6 ± 0.1 x 10^{-4} d^{-1}, k_T = 36 ± 5 x 10^{-4} d^{-1}) (Figure 27). No differences in total Mn weathering between the vegetated and non-vegetated treatments was observed.

Geochemically, the shale treatment was very different than the other treatments in that it contained various sources of Mn and other minerals that impacted the weathering and mobilization of elements, where leachate was essentially acid mine drainage high in acid and metals. Manganese in the shale was associated with pyrite and clay minerals. Pyrite dissolution contributed to Mn release and high acidity associated with sulfuric acid production. Acidity may also have contributed to the dissolution of other clay minerals, releasing more Mn. High acidity not only had potential for positive feedback on mineral dissolution, but it also had an obvious negative impact on vegetation. With final plant mortality being 70%, vegetation did not have the opportunity to alter Mn weathering or soak up much of the added Mn. Besides Mn, other cations (Al, Ca, Fe, and Mg) and SO_4^{2-} were mobilized into the soil leachate because of pyrite and clay mineral dissolution.

4.2 Treatment comparisons

The dissolved Mn treatment had the lowest combined non-foliar and leaf tissue biomass, despite mortality in the shale treatment which had the second lowest combined biomass. The Mn-oxide treatment saplings proved to be the healthiest, not only in terms of high biomass, but also because the leaves showed no discoloration, drooping, or any visible indication of stress. Slow Mn release may be better suited for healthy vegetation than fast-weathering Mn-bearing substrate or high quantities of dissolved Mn. The Mn-oxide treatment may also have provided sufficient Mn to support growth that was limited in the control treatments.

Leaching rates were much higher than plant uptake rates in all cases except for the dissolved Mn treatment, where uptake rates were as high as leaching rates. In this treatment, uptake was not limited by mineral weathering, allowing plants to take up a slightly higher fraction of added Mn than the Mn-oxide and shale treatments. In the Mn-oxide and shale treatments where bioavailable Mn concentrations depended on mineral dissolution, the plant uptake rate was lower (Figure 27). Manganese uptake in the shale treatment was higher than the Mn-oxide treatment. The shale contained fast-weathering substrate (pyrite) that released Mn while Mn-oxides were slower to weather, especially under the high pH, oxidizing conditions. Slow weathering rates decreased the rate at which bioavailable Mn could be supplied to the plant.

The control may have had a higher Mn uptake rate constant comparable with the shale treatment because the plants may have accessed the minimal amounts dissolved in the greenhouse tap water. Interestingly, despite large differences in total cumulative Mn uptake, vegetated pots accumulated a similar fraction of total added Mn. Uptake rate constants (k_U) were all on the same order magnitude, with only the slight above-mentioned differences between them.

Manganese total release rates in the vegetated treatments (uptake + leaching rate), however, were not higher than the non-vegetated treatment because uptake comprised such a small fraction of Mn loss. This indicates that vegetation did not significantly affect Mn mobilization from the soil under these conditions. In contrast to our findings, other studies have shown the impact vegetation can have on Mn mobilization. Vegetation has been shown to redistribute Mn from mineral soil to shallow, organic layers (Jobbagy and Jackson, 2004), although this occurred over the course of 50-100 years in plantations and grasslands. In our shorter, 13-week experiment, we not only did not have time to observe Mn redistribution, but we also actively removed leached Mn through sampling whereas in a natural environment, there is possibility for immobilization in deeper soils through mineralization or further Mn recycling through uptake of surrounding plants (not just one sapling).

Vegetation has also been shown to decrease Mn mobilization in leachate through accumulation in plant biomass (Herndon et al. 2015; Kraepiel et al. 2015; Herndon et al., 2019). Although our study shows vegetated pots leached less water, vegetation was not shown to lower Mn leaching rates over the entire course of the experiment; however, this changes when altering the timescale. In the dissolved Mn treatment, there was a dramatic lag time between Mn leaching in the vegetated and non-vegetated pots, where up until week 10 (Figure 20), non-vegetated Mn leaching was much higher than vegetated Mn leaching. When the mass balance model was altered to only include weeks 1-10 (Figure 28), there was a large difference between leachate rate constants in the dissolved Mn treatment (vegetated k_L = 2.5 ± 0.8 x 10^{-5} d^{-1}, non-vegetated k_L = 10.2 ± 3.7 x 10^{-5} d^{-1}). Vegetation in the dissolved Mn treatment decreased Mn leaching rates until week 10, where Mn input exceeded healthy levels. The 10-week mass balance alteration did not impact the relative k_L values between vegetated and non-vegetated pots in the other treatments, suggesting that vegetation did not impact leached Mn in the control, Mn-oxide, and shale treatments. In these treatments, vegetative-enhanced weathering may have balanced loss through plant uptake, causing leaching values to remain constant.

.

5. Conclusions

In this study, we have shown that dissolution rates impact plant uptake. Uptake rate constants were higher in systems supplied with dissolved Mn than Mn minerals (both Mn-oxides and Mn-bearing shale) because uptake was not limited by mineral weathering. Manganese uptake rates were also higher in systems supplied with fast weathering substrate (shale) than slow weathering substrate (Mn-oxides). Despite these differences between uptake rate constants, all were within one order of magnitude in all treatments. Vegetation, however, did not alter total Mn release rates in the control, dissolved Mn treatment, or the shale. In the dissolved Mn treatment, vegetation drastically reduced Mn in leachate up until week 10, where added Mn exceeded the capacity of the system to store Mn. It is possible that leaching rate constants would have followed the same trend as uptake rate constants, where Mn-oxide < shale < dissolved Mn; however, between exchangeable Mn^{2+} on soil exchange sites and possible Mn oxidation, too much Mn was stored in the soil to impact leaching in the same way as uptake.

This work quantifies the relationship between uptake and dissolution rates, contributing to the broader understanding of Mn biogeochemical cycling in soils. Manganese has unquantified impacts on carbon storage through forest health, growth, and leaf litter decomposition. Whereas the ability of plants to take up and store Mn is vital to Mn cycling and may be vital to carbon cycling, we show that dissolution rates of Mn-minerals in soils are a strong geochemical factor controlling the rate of Mn uptake, and thus, Mn-cycling. Future studies should investigate how elevated Mn in plant biomass may impact carbon cycling regarding decomposition of organic carbon in leaf litter, and the broader impacts Mn may have on carbon storage.

References

Amacher, M. C., Henderson, R. E., and Breithaupt, M. D., et. al., (1990). Unbuffered and Buffered Salt Methods for Exchangeable Cations and Effective Cation-Exchange Capacity. *Soil Sci. Soc. of Amer.* 54, 1036-1042.

Attiwill, P. M., and Adams, M. A., (1993). Review: Nutrient Cycling in Forests. *New Phytologist*. 124, 561-582.

Barboza N. R., Morais, M. M. C., and Queiroz P. S. et al., (2017). High manganese tolerance and biooxidation ability of *Serratia marcescens* isolated from manganese mine water in Minas Gerais, Brazil. *Front. Microbiol.* 8(1946) 1-11.

Chen, L., Huang, L., Méndez-García, C., and Kuang, J., et al. (2016). Microbial communities, processes and functions in acid mine drainage ecosystems. Curr. Opin. Biotechnol. 38, 150–158.

Clarkson, D.T. (1988). The uptake and translocation of manganese by plant roots. In: R.D. Graham, R. J. Hannam, N. J. Uren. (eds). *Manganese in Soil and Plants*. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 101-111.

Cole, K. L., Engstrom, D. R., and Futyma, R. P., et al., (1990). Past atmospheric deposition of metals in northern Indiana measured in a peat core from Cowles Bog, *Environ. Sci. Technol*., 24(4), 543–549.

Daims, H., Lebedeva, P., and Pjevac, P., et al., (2015). Complete nitrification by *Nitrospira* bacteria. *Nature*. 528, 504.

Diem, D., and Stumm, W., (1984). Is dissolved Mn^{2+} being oxidized by O_2 in absence of Mn-bacteria or surface catalysts? *Geochimica et Cosmo. Acta*, 48(7) 1571-1573.

Estes, E. R., Andeer, P. F., and Nordlund, D., et al., (2016). Biogenic manganese oxides as reservoirs of organic carbon and proteins in terrestrial and marine environments. *Geobiology*. 1-15.

Frederick, H., (2017). A geochemical evaluation of weathering processes and metal uptake by vegetation in coal mine spoil. Kent State University Thesis.

Gladney, E.S., and Roelandts, I., (1990). 1988 Compilation of Elemental Concentration Data for USGS Geochemical Exploration Reference Materials GXR-1 to GXR-6. *Geostandards and Geoanalytical Research*. 14, 21-118.

Händel, M., Rennert, T., and Totsche, K. U., (2013). A simple method to synthesize birnessite at ambient pressure and temperature. *Geoderma*. 193-194, 117-121.

Hansel, C. M., Zeiner, C. A., and Santelli, C. M., et al., (2012). Mn(II) oxidation by an ascomycete fungus is linked to superoxide production during asexual reproduction. *PNAS*, 109(31), 12621-12625.

Herndon, E. M., Jin, L., and Andrews, D. M., et al., (2015). Importance of vegetation for manganese cycling in temperate forested watersheds. *Global Geochemical Cycles*, 29, 160-174.

Herndon, E. M., L. Jin, and S. L. Brantley, (2011). Soils reveal widespread manganese enrichment from industrial inputs, *Environ. Sci. Technol*., 45(1), 241–7.

Herndon, E. M., Martínez, C. E., and Brantley, S. L., (2014). Spectroscopic (XANES/XRF) characterization of contaminant manganese cycling in a temperate watershed. *Biogeochemistry* 121, 505-517.

Herndon, E. M., Yargerm B., and Frederick, H., (2019). Iron and manganese biogeochemistry in forested coal mine spoil. *Soil Systems.* 3(1), 13.

Hofrichter, M. (2002). Review: Lignin conversion by manganese peroxidase (MnP). *Enzyme Microb. Technol.* 30, 454-466.

Huang, Chao-Yong Luh, and Schulte, E. E., (1985). Digestion of plant tissue for analysis by ICP emission spectrpscopy. *Comm. In Soil Sci. Plant Anal.*, 16(9), 943-958.

Hullo M. F., Moszer I., and Danchin A., et al., (2001). CotA of Bacillus subtilis is a copper-dependent laccase. *J. Bacteriol*. 183 5426–5430.

Jin, L., Ravella, R., and Ketchum, B., et al., (2010). Mineral weathering and elemental transport during hillslope evolution at the Susquehanna/Shale Hills Critical Zone Observatory. *Geochimica et Cosmochimica Acta* 74 (13):3669-3691.

Jobbagy, E. G., and R. B. Jackson, (2004). The uplift of soil nutrients by plants: Biogeochemical consequences across scales. *Ecology*, 85(9), 2380–2389.

Jurgensen, M. F., Harvey, A. E., and Graham, R. T., et al., (1997). Impacts of timber harvesting on soil organic matter, nitrogen, productivity, and health of inland northwest forests. *Forest Science*. 43(2): 234-251.

Kabata-Pendias, A., and Pendias, H., (2001). Trace Elements in Soils and Plants, 3rd ed., *CRC Press LL*, Boca Raton, Fla.

Keiluweit, M., Nico, P., and Harmon, M. E., et al., (2015). Long-term litter decomposition controlled by manganese redox cycling. *PNAS*, 112(38) E5253-E5260.

Kinney, C., (2013). Huff Run Acid Mine Drainage Abatement and Treatment Plan Addendum.

Kogelmann, W.J. and Sharpe, W.E., (2006). Soil Acidity and Manganese in Declining and Nondeclining Sugar Maple Stands in Pennsylvania. *Journal of Environmental Quality*. 35(2), 433-441.

Kraepiel, A. M. L., Dere, A. L., and Herndon, E. M., et al., (2015). Natural and anthropogenic processes contributing to metal enrichment in surface soils of central Pennsylvania. *Biogeochemistry*.

Lagoutte, B. and Duranton, J., (1975). A manganese protein complex within the chloroplast structures. *FEBS Lett*. 51, 1.

Li, H. P., Daniel, B., and Creeley, D., et al., (2014). Superoxide production by a manganese-oxidizing bacterium facilitates iodide oxidation*. Appl. Environ. Microbiol.* 80, 2693–2699.

Li, J., D. D. Richter, A. Mendoza, and P. Heine, (2008). Four-decade responses of soil trace elements to an aggrading old-field forest: B, Mn, Zn, Cu, and Fe. *Ecology*, 89(10), 2911–2923.

Li, J., Menguy, N., and Gatel, C., et al., (2015). Crystal growth of bullet-shaped magnetite in magnetotactic bacteria of the *Nitrospirae* phylum. *J. R. Soc. Interf.* 12

Loneragan, J.F., (1988) Distribution and Movement of Manganese in Plants. In: Graham R.D., Hannam R.J., Uren N.C. (eds) Manganese in Soils and Plants. *Developments in Plant and Soil Sciences*, vol 33. Springer, Dordrecht

Marschner, H., (1995). Mineral Nutrition of Higher Plants, Ed 2. Academic Press, London, p 889.

Martin, S. T., (2005). Precipitation and dissolution of iron and manganese oxides, in *Environmental Catalysis*, edited by V. H. Grassian, pp. 61–81, CRC Press, Boca Raton, Fla.

Mayanna S., Peacock C. L., and Schaffner F. et al., (2015) Biogenic precipitation of manganese oxides and enrichment of heavy metals at acidic soil pH. *Chem Geol* 402:6–17.

Migocka M. and Klobus G., (2007). The properties of the Mn, Ni and Pb transport operating at plasma membranes of cucumber roots. *Physiol. Plant*. 129, 578-587.

Millaleo R., Reyes-Diaz M., and A.G. Ivanov, et al., (2010). Manganese as essential and toxic element for plants: transport, accumulation, and resistance mechanisms. *J. Soil Sci. Plant Nutr.* 10(4): 470-481.

Pacyna, J. M., and Pacyna E. G., (2001). An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide, *Environ. Rev*., 9, 269–298.

Post, Jeffrey E., (1999). Manganese oxide minerals: Crystal structures and economic and environmental significance. *PNAS*.

Raich, J. W., and Schlesinger, W. H., (1992). The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate. *Tellus*. 44B, 81-89.

Rengel, Z., and Marschner, P., (2005). Nutrient availability and management in the rhizosphere: exploiting genotypic differences. *New Phytologist*. 168 (305-312).

Richardson L. L., Aguilar C., and Nealson K. H., (1988). Manganese oxidation in pH and O_2 microenvironments produced by phytoplankton. *Limnol. Oceanogr.* 33:352–63

Santelli, C. M., Webb, S. M., and Dohnalkova, A. C., et al., (2011). Diversity of Mn oxides produced by Mn(II)-oxidizing fungi. *Geochemica et Cosmo. Acta*. 75(10), 2762,2776.

Saur, Kenneth, (1980). A role for manganese in oxygen evolution in photosynthesis. *Accounts of Chemical Research*, 13(8), 249-256.

Schemel, L. E., Kimball, B. A., and Bencala, K. E., (2000). Colloid formation and metal transport through two mixing zones affected by acid mine drainage near Silverton, Colorado, *15*.

Singer, D., Herndon, E. M., and Cole, K., et al., (2019). Micron-scale distribution controls metal(loid) release during simulated weathering of a Pennsylvanian coal shale. (Manuscript).

Socha, A. L., and Guerinot, M. L., (2014). Mn-euvering manganese: the role of transporter gene family members in manganese uptake and mobilization in plants. *Front. Plant Sci.*

St. Clair, S.B., and Lynch J.P., (2004). Photosynthetic and antioxidative enzyme responses of sugar maple and red maple sedlings to excess manganese in contrasting light environments. *Functional Plant Biology*. 28 (874-885).

St. Clair, S.B., and 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).

Stone, A. T., and Morgan, J. J., (1984). Reduction and dissolution of manganese(III) and manganese(IV) oxides by organics. 1. Reaction with hydroquinone. *Environ. Sci. Technol.* 18, 617-624.

Tebo, B. M., Johnson, H. A., and McCarthy, J. K., et al., (2005). Geomicrobiology of manganese(II) oxidation. *Trends in Microbiology*. 13(9), 421-428.

Tebo, B. M., Bargar, J. R., and Clement, B. G., et al., (2004). Biogenic Manganese Oxides: Properties and Mechanisms of Formation, *Annu. Rev. Earth Planet Sci.* 32, 287-328.

Turekian, K. K. and Wedepohl, K. L,. (1961). Distribution of the Elements in the Earth's Crust. *Geol. Soc. Am. Bull.* 72, 175-192.

Umena Y., Kawakami K., and Shen J., et al., (2011). Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9Å. *Nature*. 473(7.45) 55-60.

Villegas-Plazas, M., Sanabria, J., and Junca, H., (2019). A composite taxonomical and functional framework or microbiomes under acid mine drainage bioremediation systems. *J. of Envir. Manag.* 251.

Webb, S. M., Dick, G. J., and Bargar, J. R., et al., (2005). Evidence for the presence of Mn(III) intermediates in the bacterial oxidation of Mn(II). *PNAS*. 102(15), 5558-5563.

Figures

Figure 1. Photographs of the experimental set-up showing boxes #1-4 immediately after planting (top), boxes #5-8 week one (middle), and boxes #5-8 week 11 (bottom).

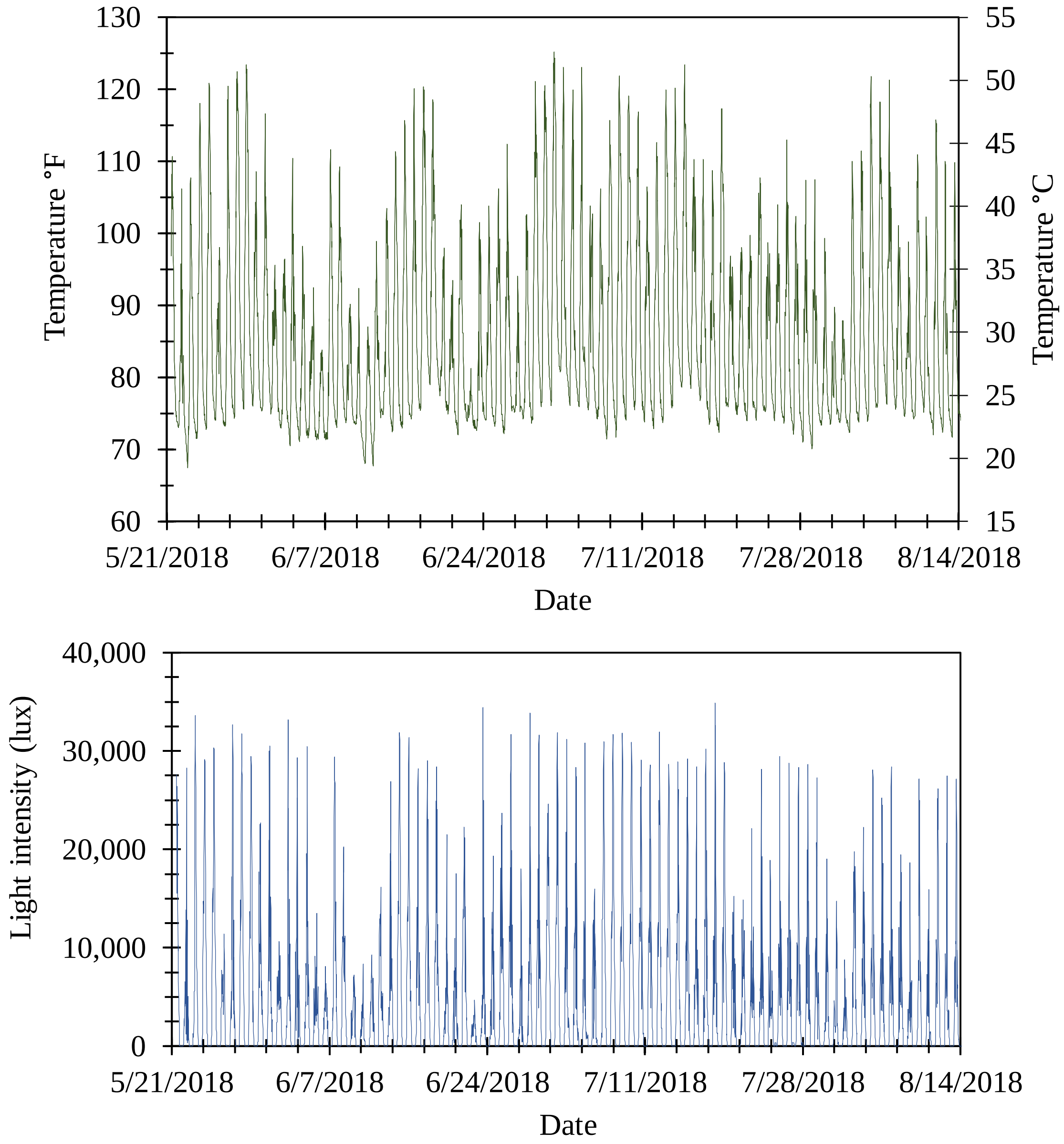

Figure 2. Greenhouse temperature (top) and light intensity (bottom) throughout the experiment as measured by a HOBOware data logger (30-min intervals).

Figure 3. Left: Manganese oxide slurry generated by mixing potassium permanganate, sodium lactate, sand, and deionized water. Right: Mn-oxide coated sand rinsed with deionized water.

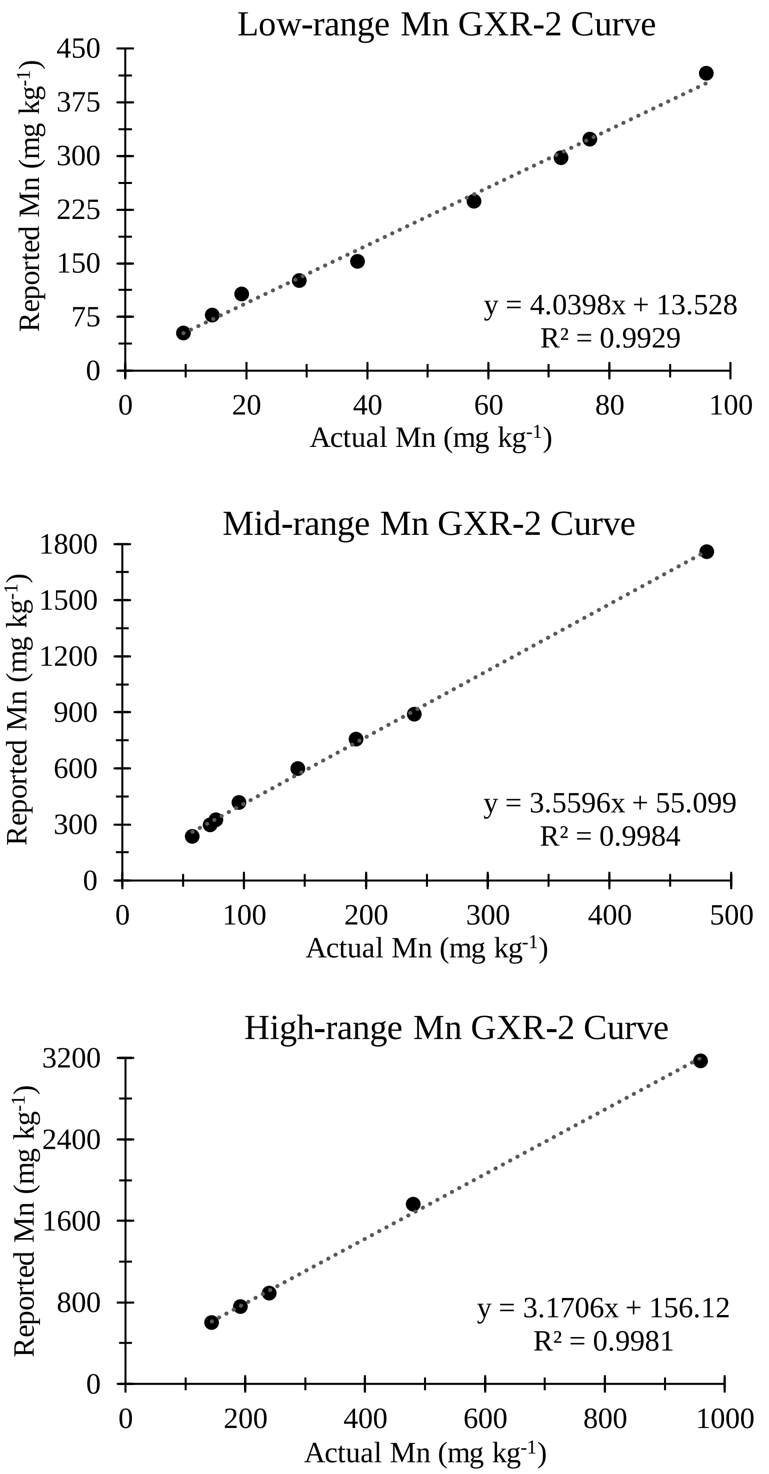

Figure 4. Low-, mid-, and high-range Mn calibration curves collected on mixtures of USGS GXR-2 soil with pure quartz sand and used to calibrate XRF measurements on soil media.

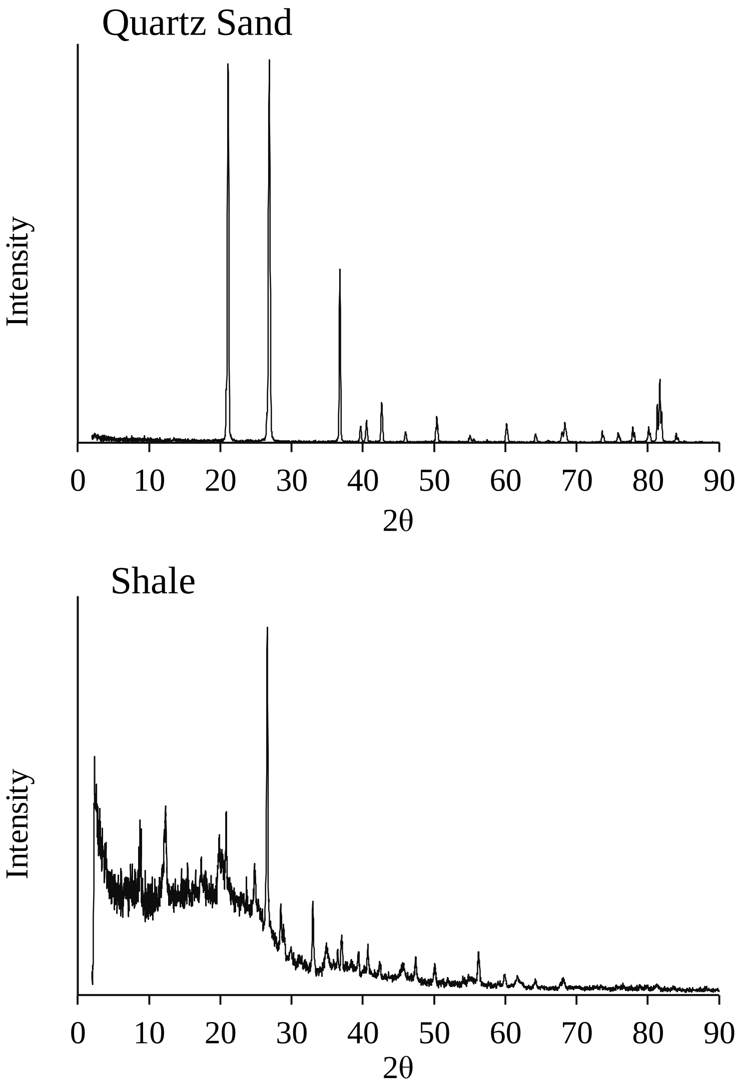

Figure 5. Diffraction patterns by XRD for the quartz sand (top) and the crushed Huff Run shale (bottom). Peaks and associated phases are listed in Table 1 (quartz sand) and Table 2 (shale).

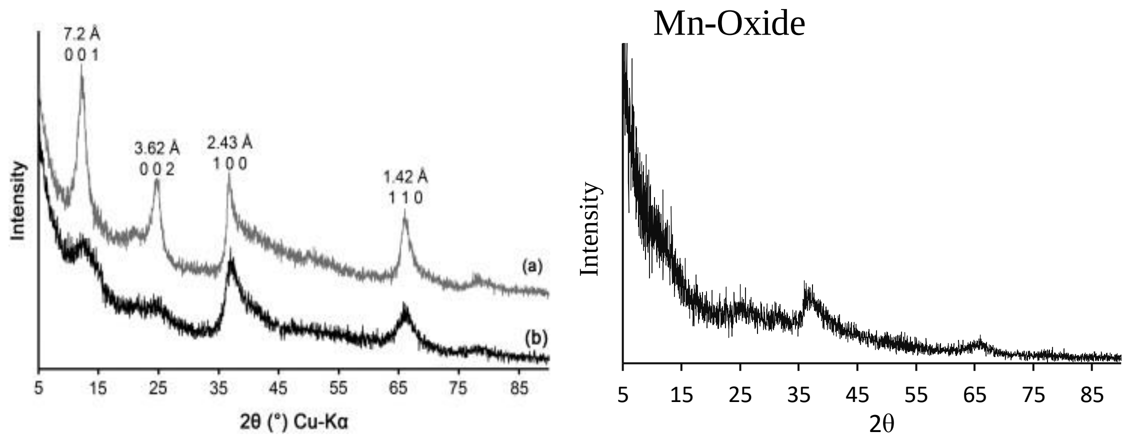

Figure 6. Left: Figure from Handel et al., 2012 showing XRD patterns of birnessite synthesized from (a) McKenzie, 1971 and (b) Handel et al., 2012. Right: Lab synthesized Mn-oxides used to coat quartz sand in Mn-oxide treatment, method based on Handel et al., 2012.

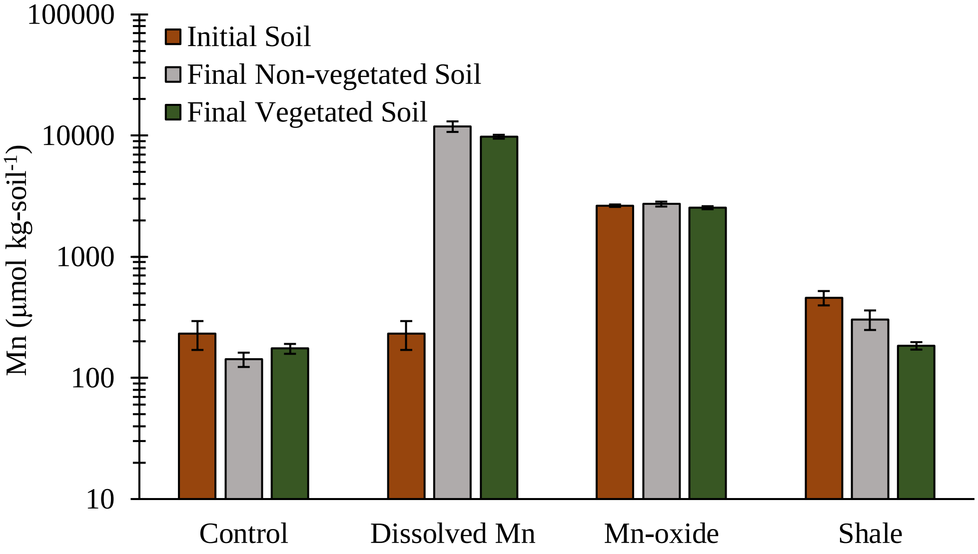

Figure 7. Initial and final Mn concentrations in soil media for each vegetated and non-vegetated treatment as measured by x-ray fluorescence. Error bars represent the highest of the analytical error and standard error of the replicate average.

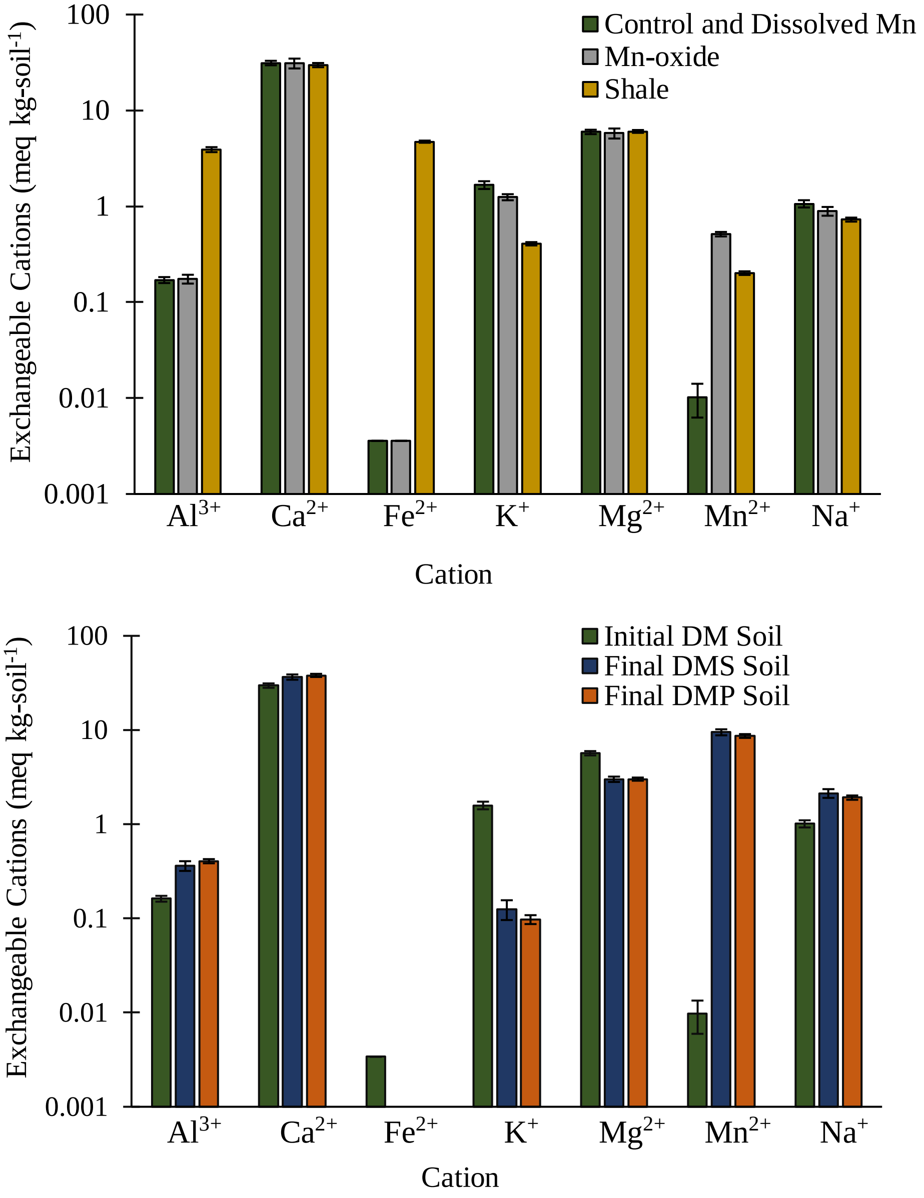

Figure 8. Top: Averaged concentrations of exchangeable cations measured for the initial soil in each treatment (top) and for the initial and final soil in the dissolved Mn treatment (bottom). DM: Dissolved Mn treatment, DMS: Dissolved Mn non-vegetated, DMP: Dissolved Mn vegetated. Error bars indicate the highest of the analytical error and standard error of the replicate average. Due to dilution differences, Fe^{2+} in the final dissolved Mn soil was below the detection of the instrument (0.07 meq kg-soil^{-1}), but not necessarily below the initial dissolved Mn soil Fe^{2+} value.

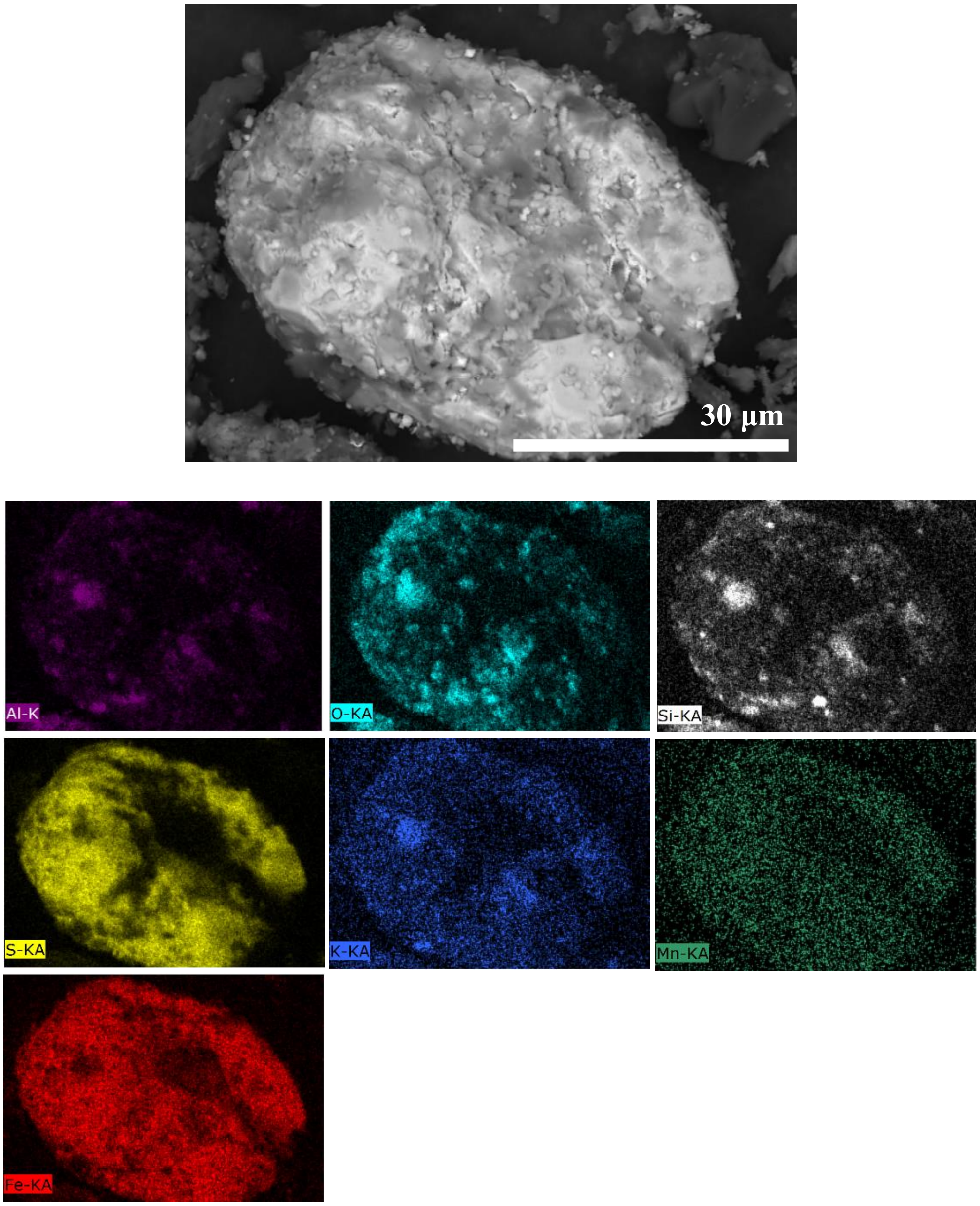

Figure 9. SEM-EDS images of Huff Run crushed shale used in the shale treatment. The top panel shows the backscattered image with aluminum (purple), oxygen (light blue), silicon (white), sulfur (yellow) potassium (dark blue), manganese (green), and iron (red) below. Element distributions show manganese association with an iron sulfide-clay mineral complex.

Figure 10. “Burned” leaves in the dissolved Mn treatment due to Mn toxicity. Left: DMP8 (week 9). Right: DMP9 (week 10).

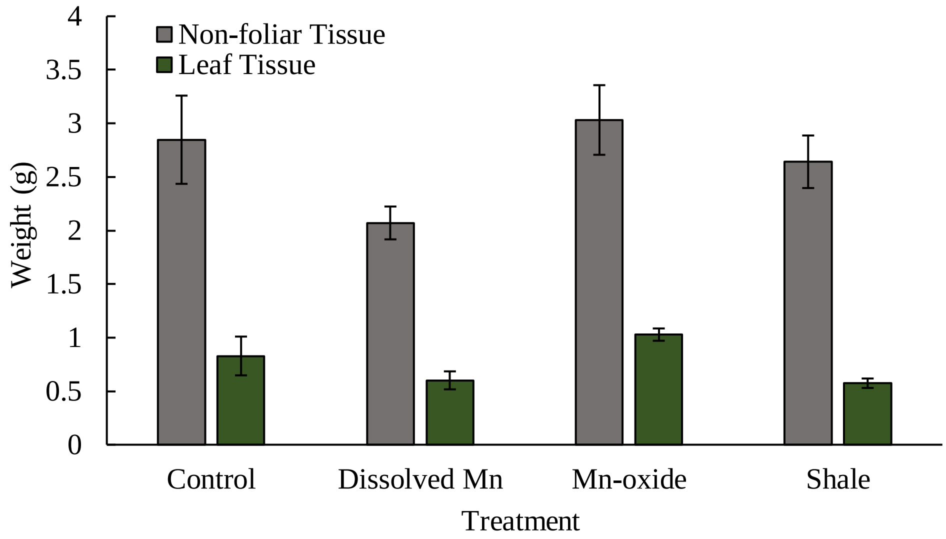

Figure 11. Foliar and non-foliar biomass. Weights were measured individually for each replicate and averaged. Error bars represent standard error of analytical replicates. Treatments with the same letters indicate statistical similarities, whereas the lack of similar letters indicate statistical differences (p-values in Table 5). While some foliar comparisons were significant and indicated by letters, non-foliar comparisons were not significant.

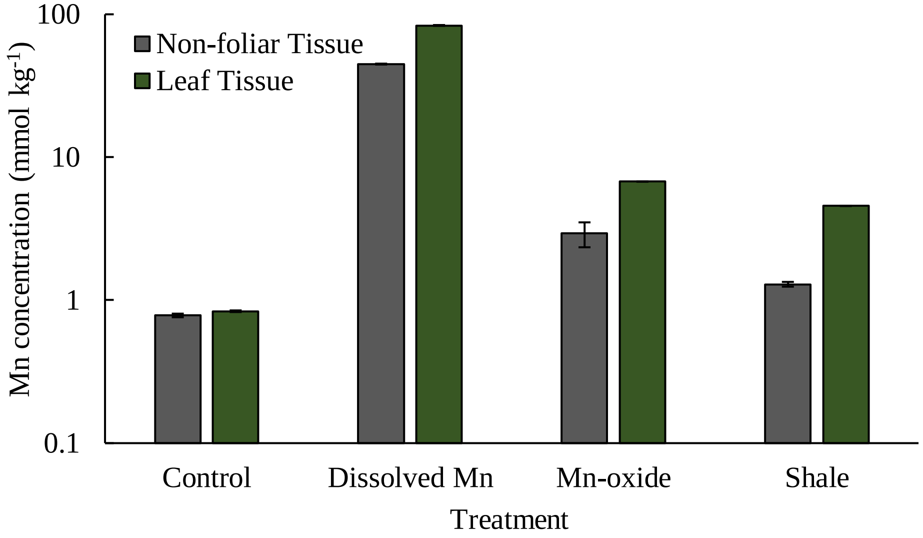

Figure 12. Manganese concentrations (mmol kg^{-1}) in non-foliar and leaf tissue homogenized across all replicates for each treatment. Error bars indicate the highest of the analytical error and the standard error of

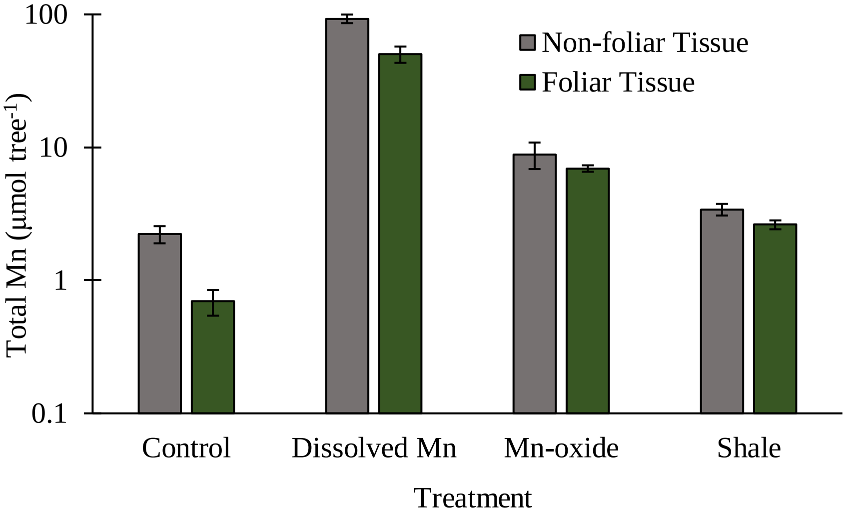

Figure 13. Total Mn (µmol tree^{-1}) in non-foliar and leaf tissue homogenized across all replicates for each treatment. Error bars indicate the highest of the analytical error and the standard error of the averaged

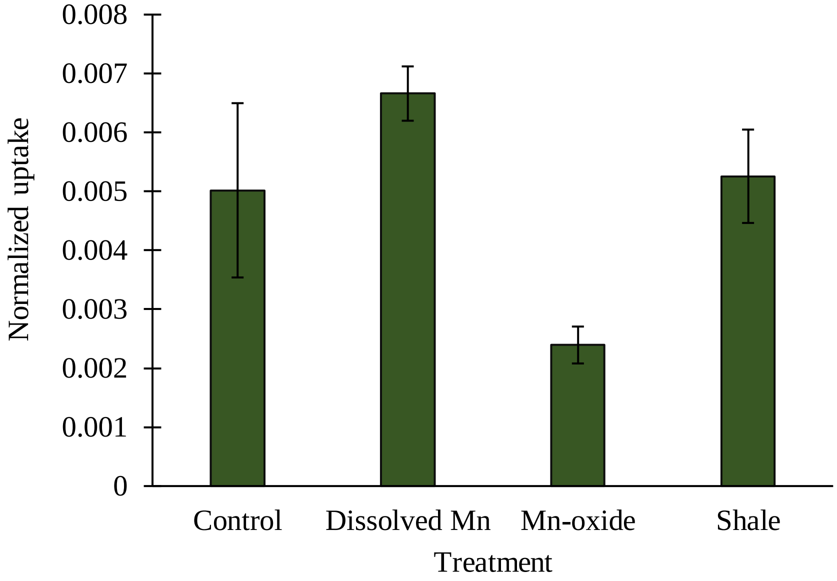

Figure 14. Combined foliar and non-foliar Mn uptake normalized to total added Mn per tree. Error bars represent the highest of the analytical error and the standard error of the averaged replicates.

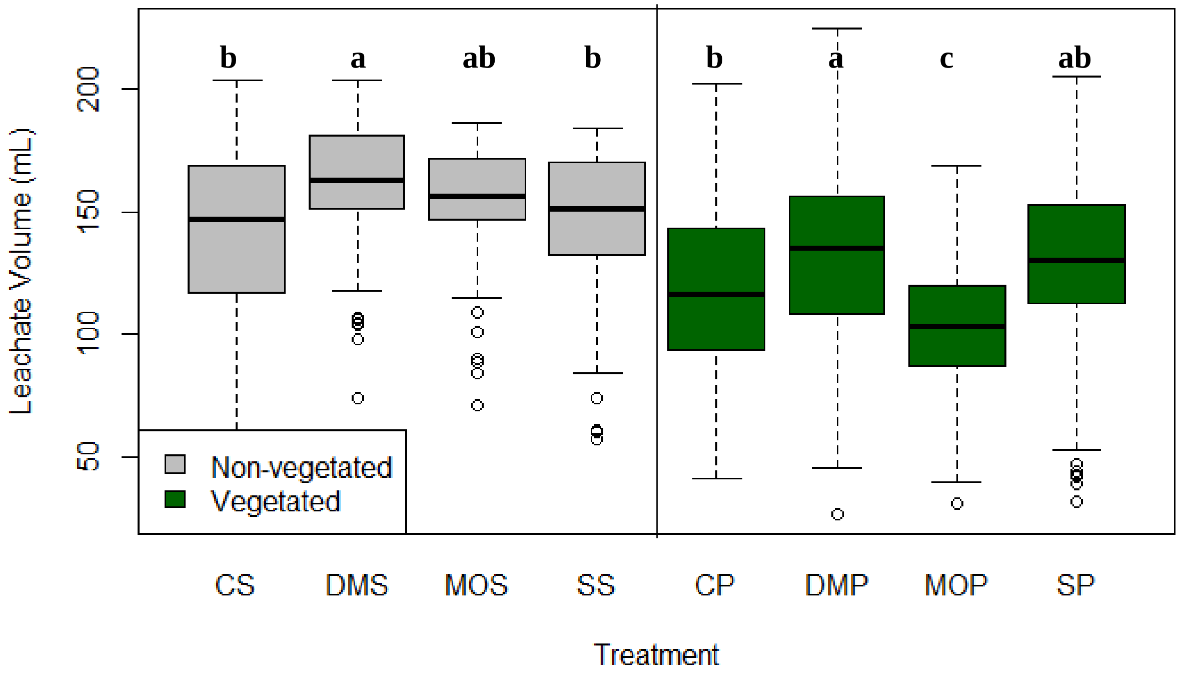

Figure 15. Boxplot of leachate volume (mL) for each treatment, non-vegetated (grey boxes; CS = control, DMS = dissolved Mn, MOS = Mn-oxide, SS = shale) and vegetated (green boxes; CP = control, DMP = dissolved Mn, MOP = Mn-oxide, SP = shale). Dashed lines lead out from the boxes to horizontal lines that represent the maximum and minimum values, while outliers are depicted by no-fill circles. The top and bottom of each box represents the upper and lower quartiles, respectively. The line in the middle of each box represents the median. Treatments with the same letters indicate statistical similarities, whereas the lack of similar letters indicate statistical differences (p-values in Table 7). Either the effect of vegetation or the effect of treatment was tested, not the interaction (i.e. CS is not compared to DMP, MOP, or SP). The effect of vegetation was significant in all treatments, and not depicted by letters in the figure.

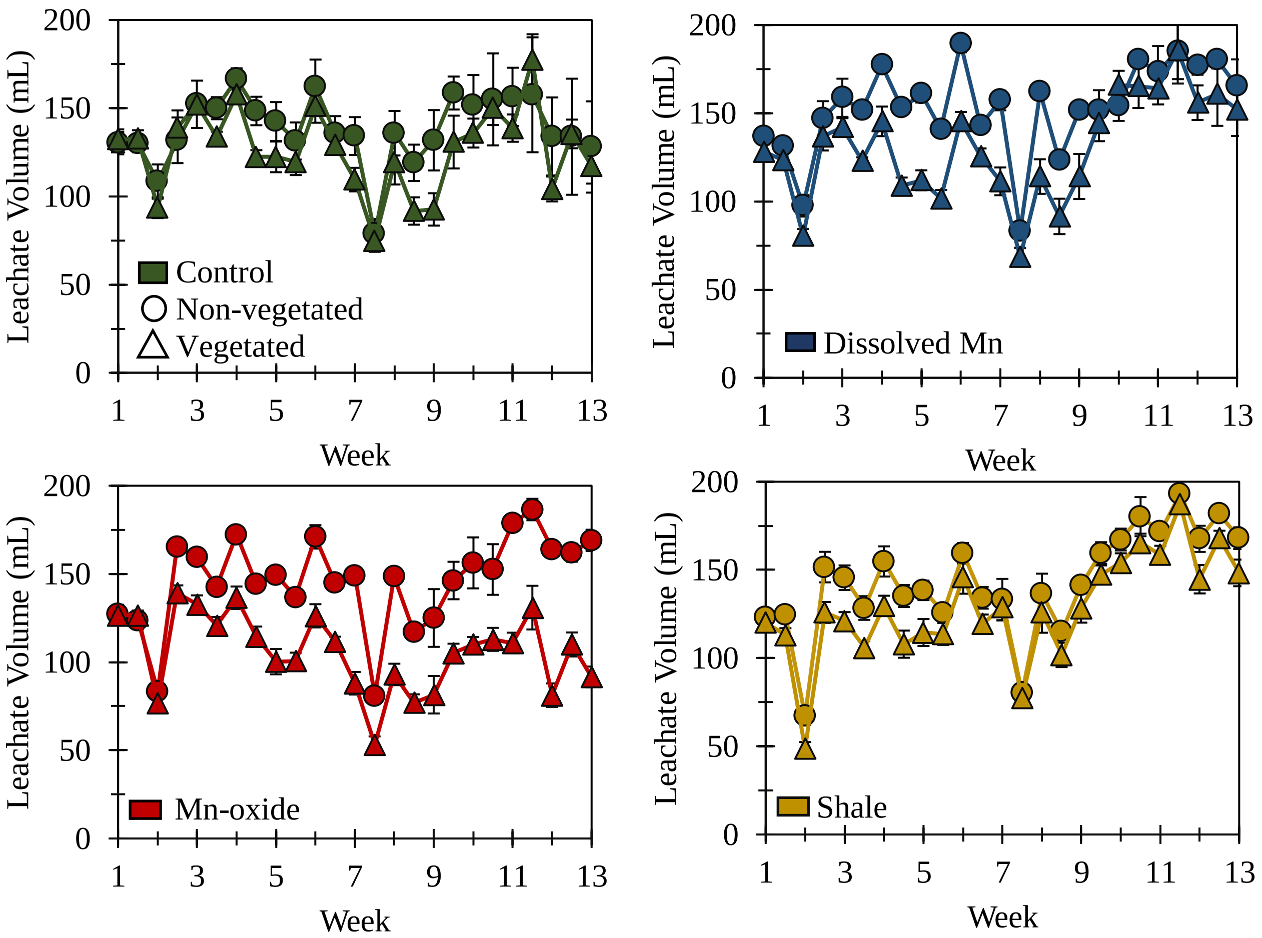

Figure 16. Leachate volume (mL) for each treatment over time. Error bars represent the standard error of the replicate average.

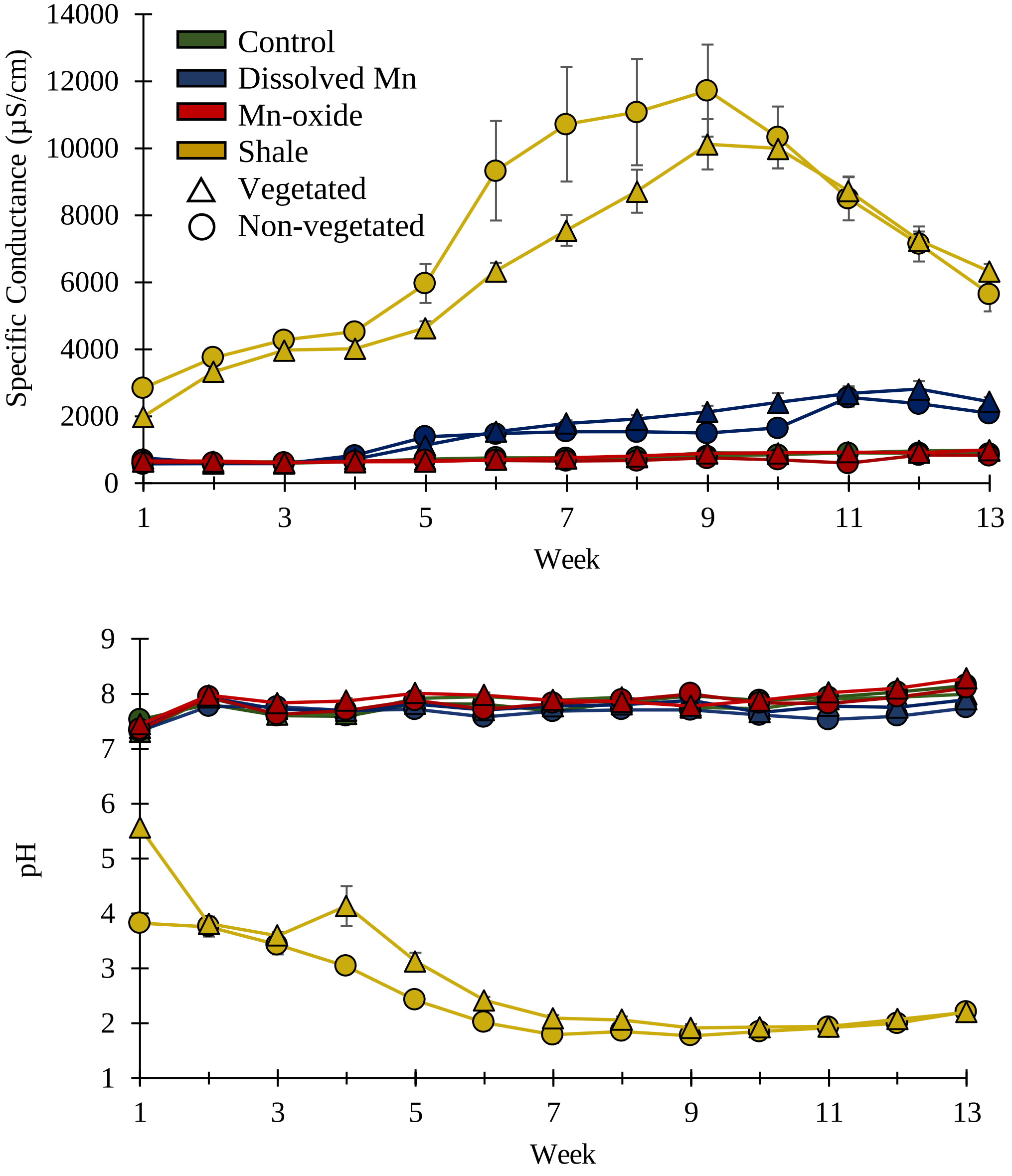

Figure 17. Averaged leachate specific conductance (top) and pH (bottom) for each treatment, vegetated and non-vegetated. Error bars represent the standard error of the replicate averages.

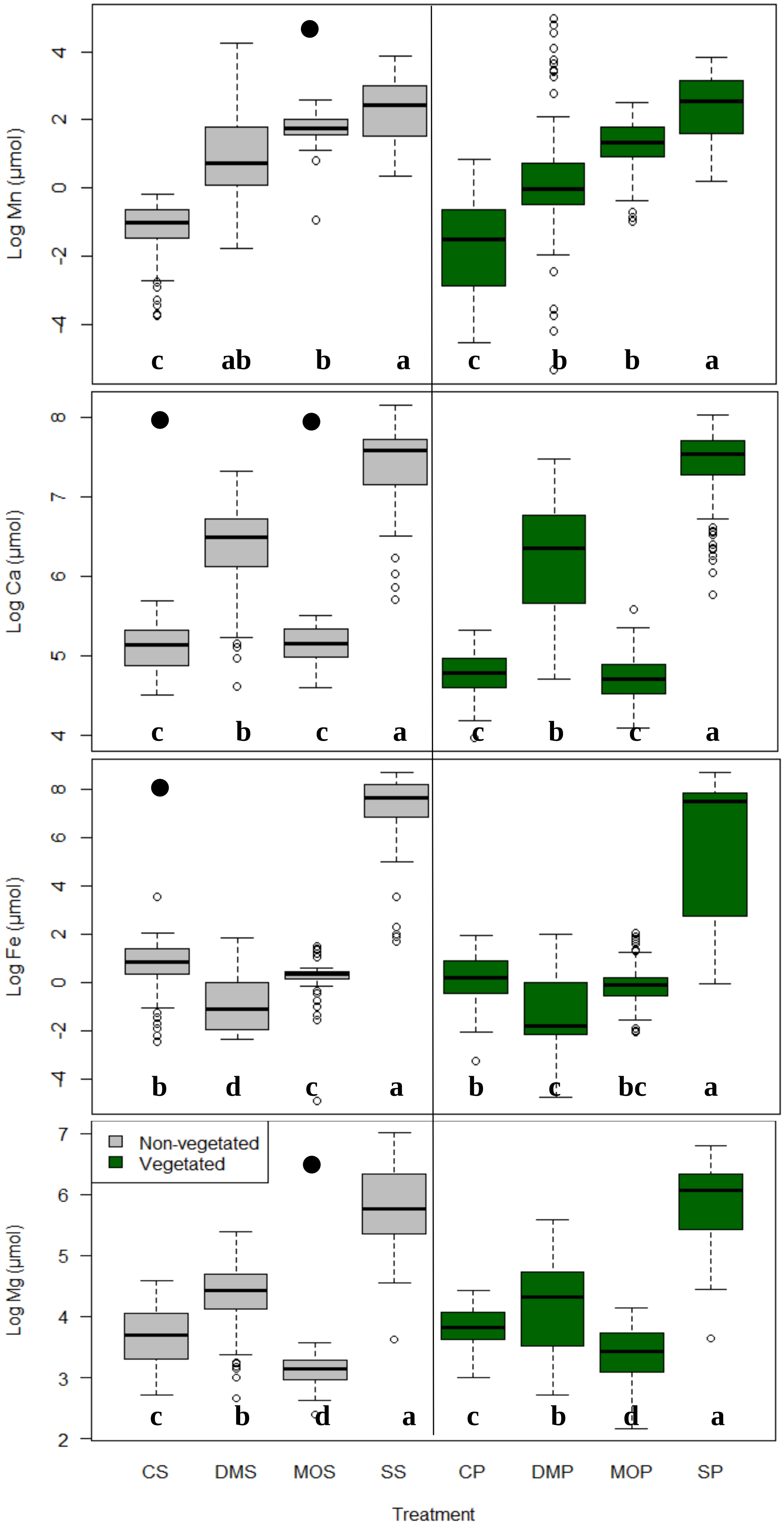

Figure 18. Boxplots of cumulative leached Mn, Ca, Fe, and Mg in each treatment, non-vegetated (grey boxes; control = CS, dissolved Mn = DMS, Mn-oxide = MOS, and shale = SS) and vegetated (green boxes; control = CP, dissolved Mn = DMP, Mn-oxide = MOP, and shale = SP). Dashed lines lead out from the boxes to horizontal lines that represent the maximum and minimum values, while outliers are depicted by no-fill circles. The top and bottom of each box represents the upper and lower quartiles, respectively. The line in the middle of each box represents the median. Treatments with the same letters indicate statistical similarities, whereas the lack of similar letters indicate statistical differences between treatments only, separated by the vertical line (p-values in Table 7). Filled circles on the top of each graph over non-vegetated treatments indicate a difference between non-vegetated and vegetated values within a treatment. Ether the effect of vegetation or the effect of treatment was tested, not the interaction (i.e. CS is not compared to DMP, MOP, or SP).

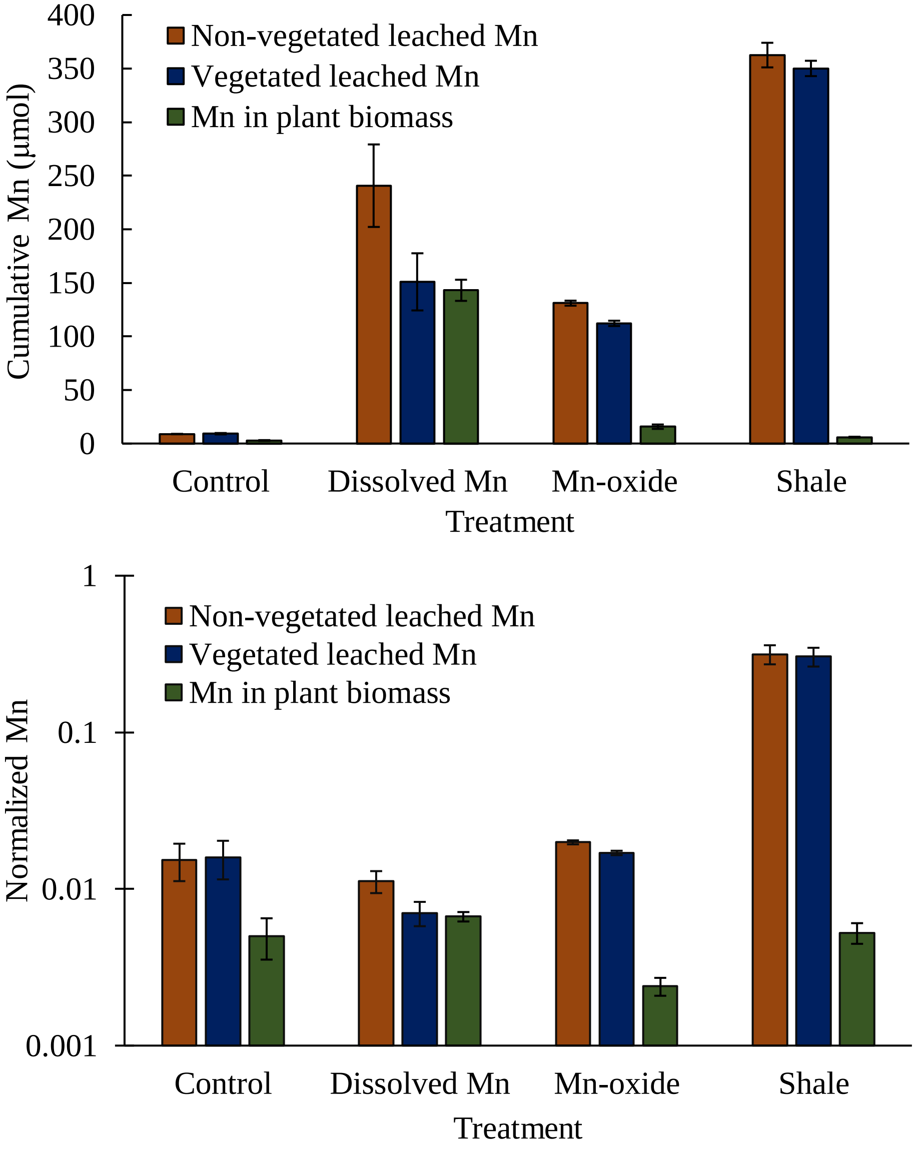

Figure 19. Cumulative leached Mn and total Mn in plant biomass for each treatment (top), leached Mn and total Mn in plant biomass normalized to the sum of total added Mn and total soil Mn (bottom).

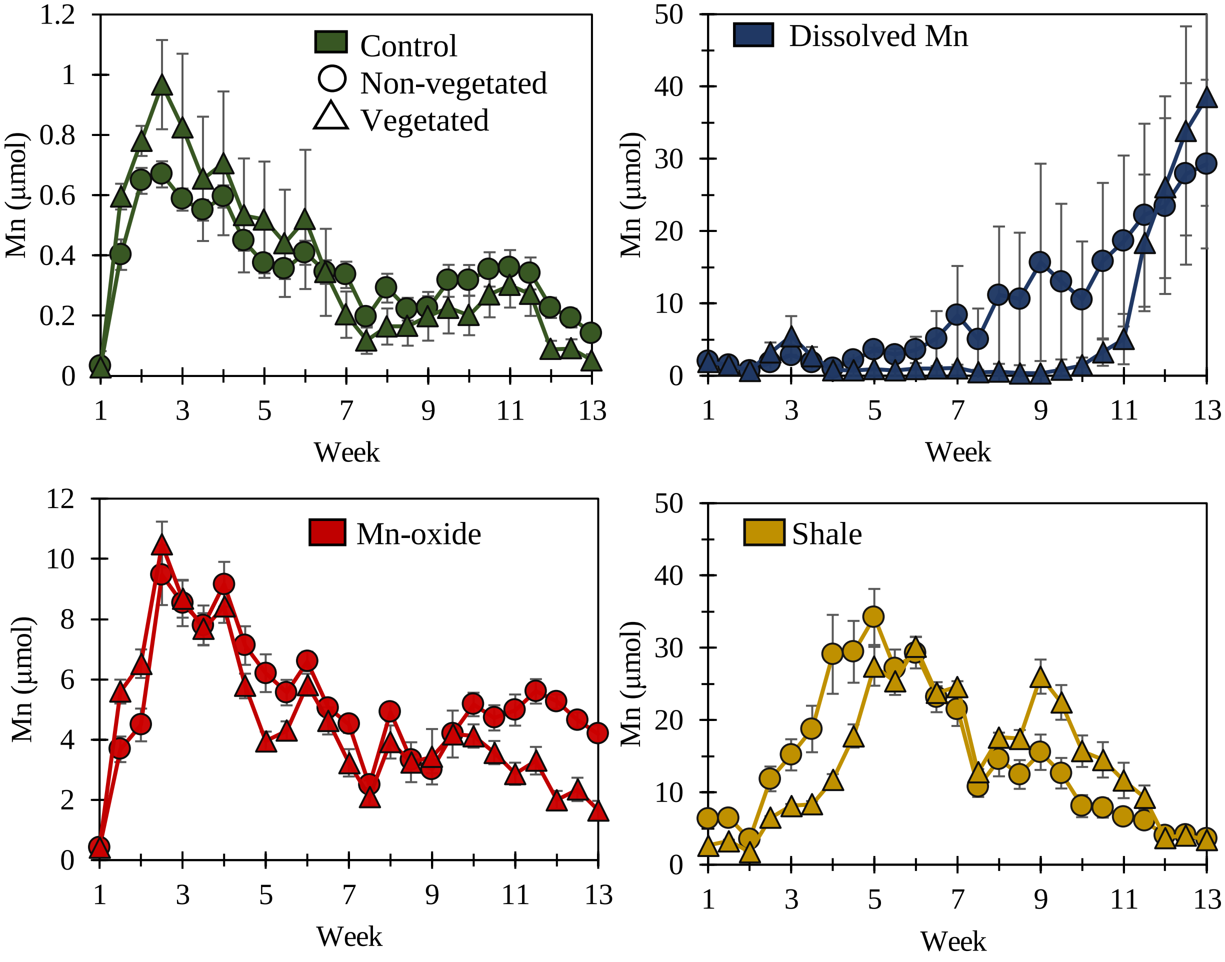

Figure 20. Averaged leached Mn measured using ICP-OES over time for each treatment, vegetated (triangles) and non-vegetated (circles). Error bars indicate the highest of the analytical error and the standard error of averaged replicates. All symbols have an associated error bar, although some are smaller than the symbol. Y-axis scales are different between some treatments.

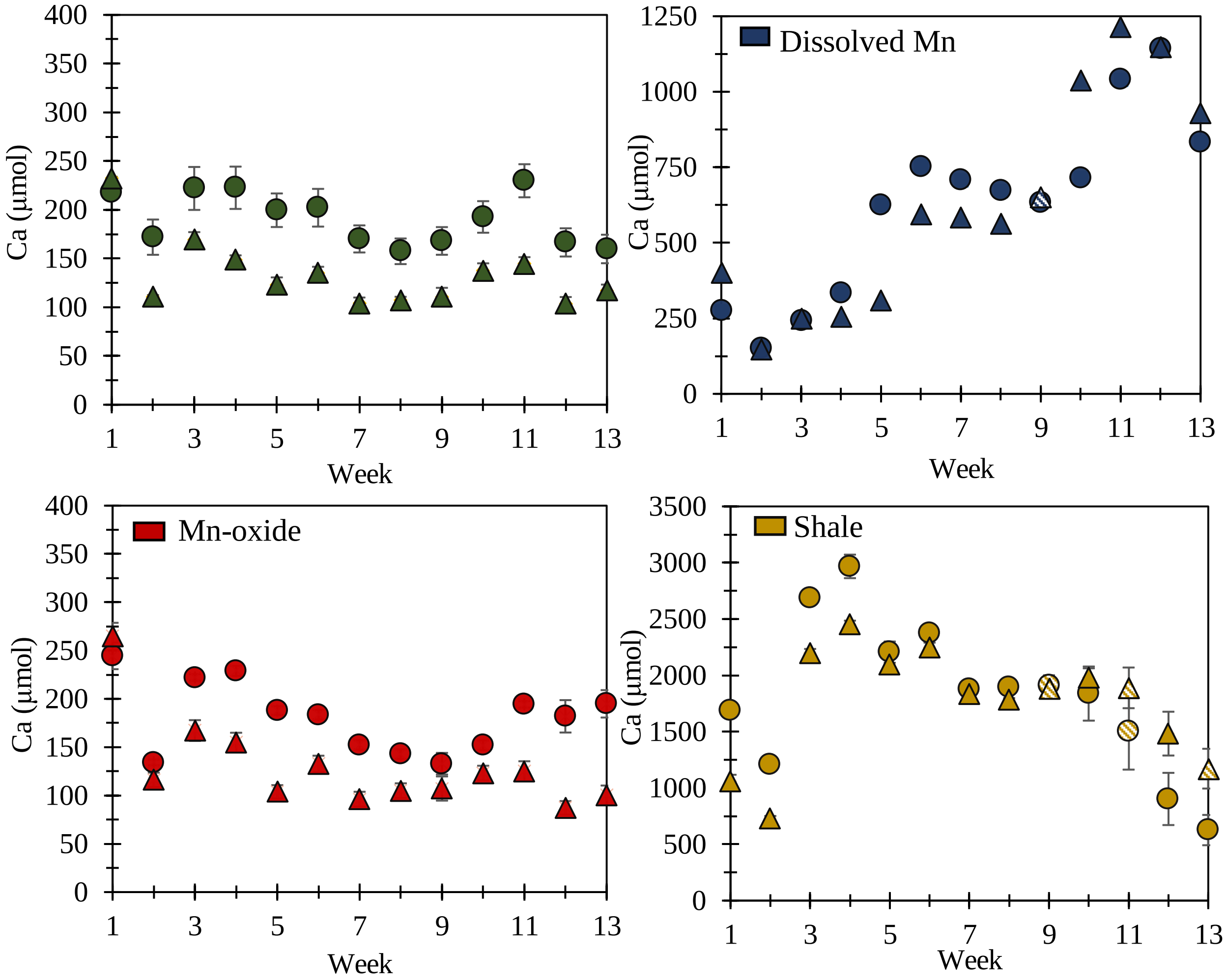

Figure 21. Averaged leached Ca measured using ICP-OES over time for each treatment, vegetated (triangles) and non-vegetated (circles). Error bars indicate the highest of the analytical error and the standard error of averaged replicates. All symbols have an associated error bar, although some are smaller than the symbol. Y-axis scales are different between some treatments. Averages that include values above the detection limit of the instrument (>DL) are indicated by diagonal stripes.

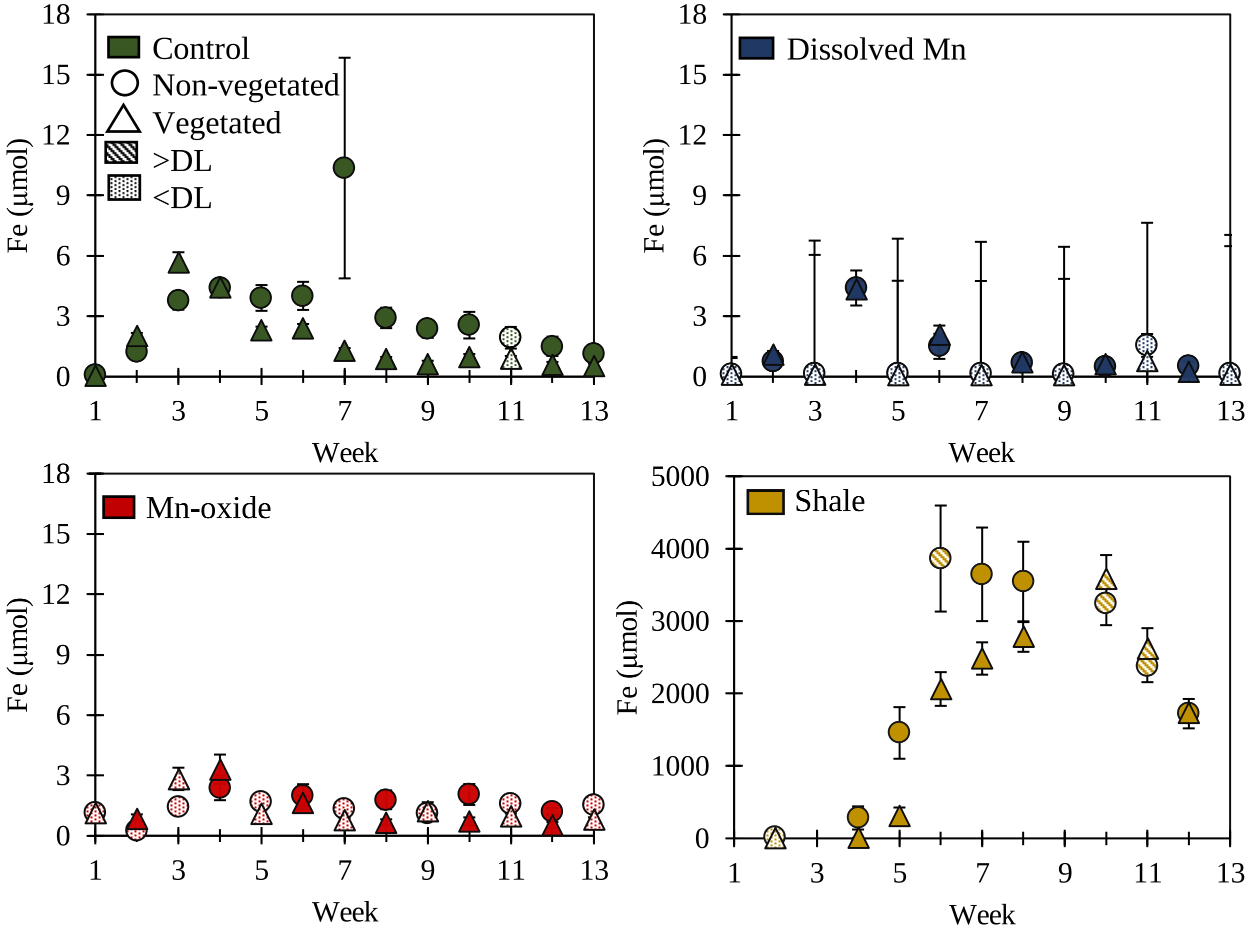

Figure 22. Averaged leached Fe measured using ICP-OES over time for each treatment, vegetated (triangles) and non-vegetated (circles). Error bars indicate the highest of the analytical error and the standard error of averaged replicates. All symbols have an associated error bar, although some are smaller than the symbol. Y-axis scales are different between some treatments. Averages that include values above (>DL) or below (<DL) the detection limit of the instrument are indicated by diagonal stripes and dots, respectively.

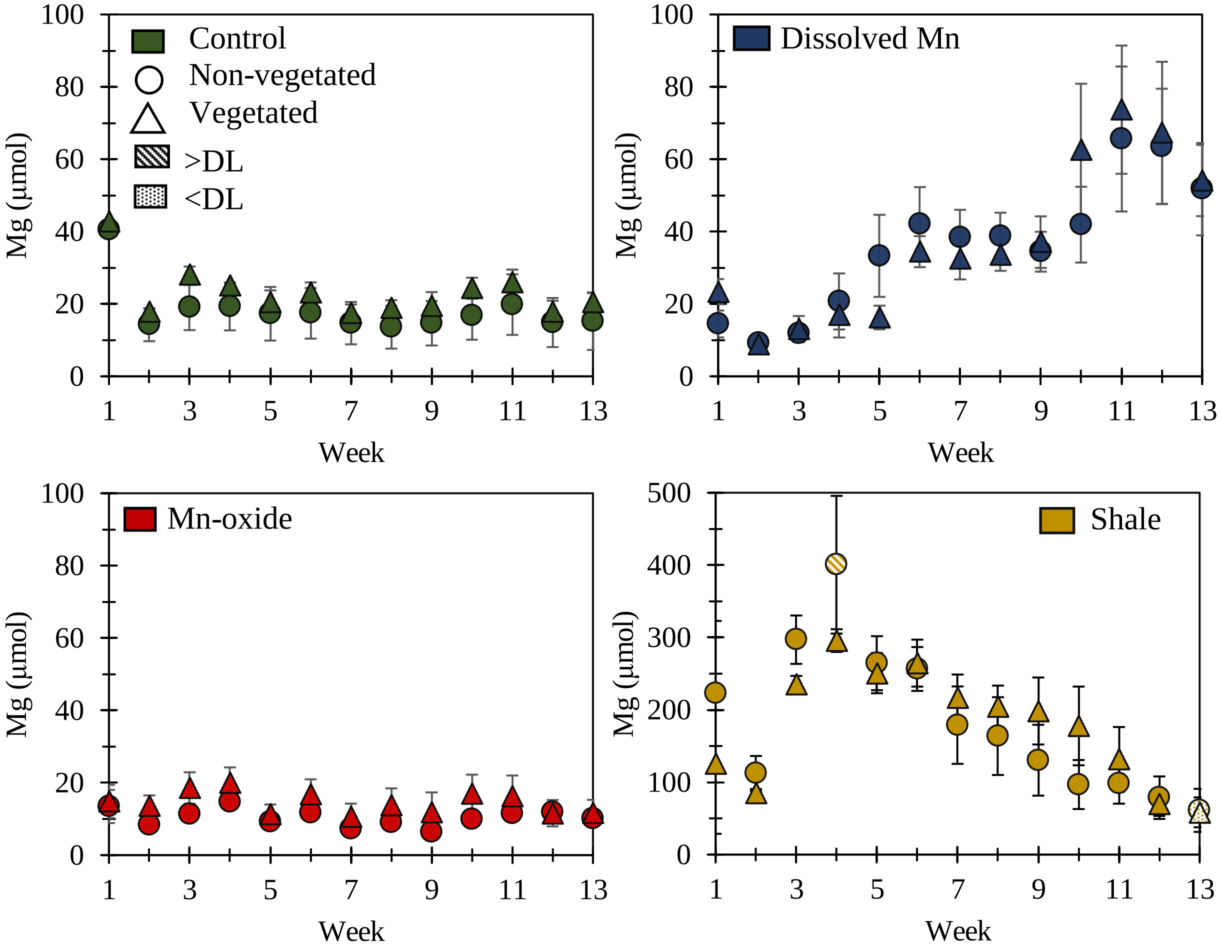

Figure 23. Averaged leached Mg measured using ICP-OES over time for each treatment, vegetated (triangles) and non-vegetated (circles). Error bars indicate the highest of the analytical error and the standard error of averaged replicates. All symbols have an associated error bar, although some are smaller than the symbol. Y-axis scales are different between some treatments. Averages that include values above (>DL) or below (<DL) the detection limit of the instrument are indicated by diagonal stripes and dots, respectively.

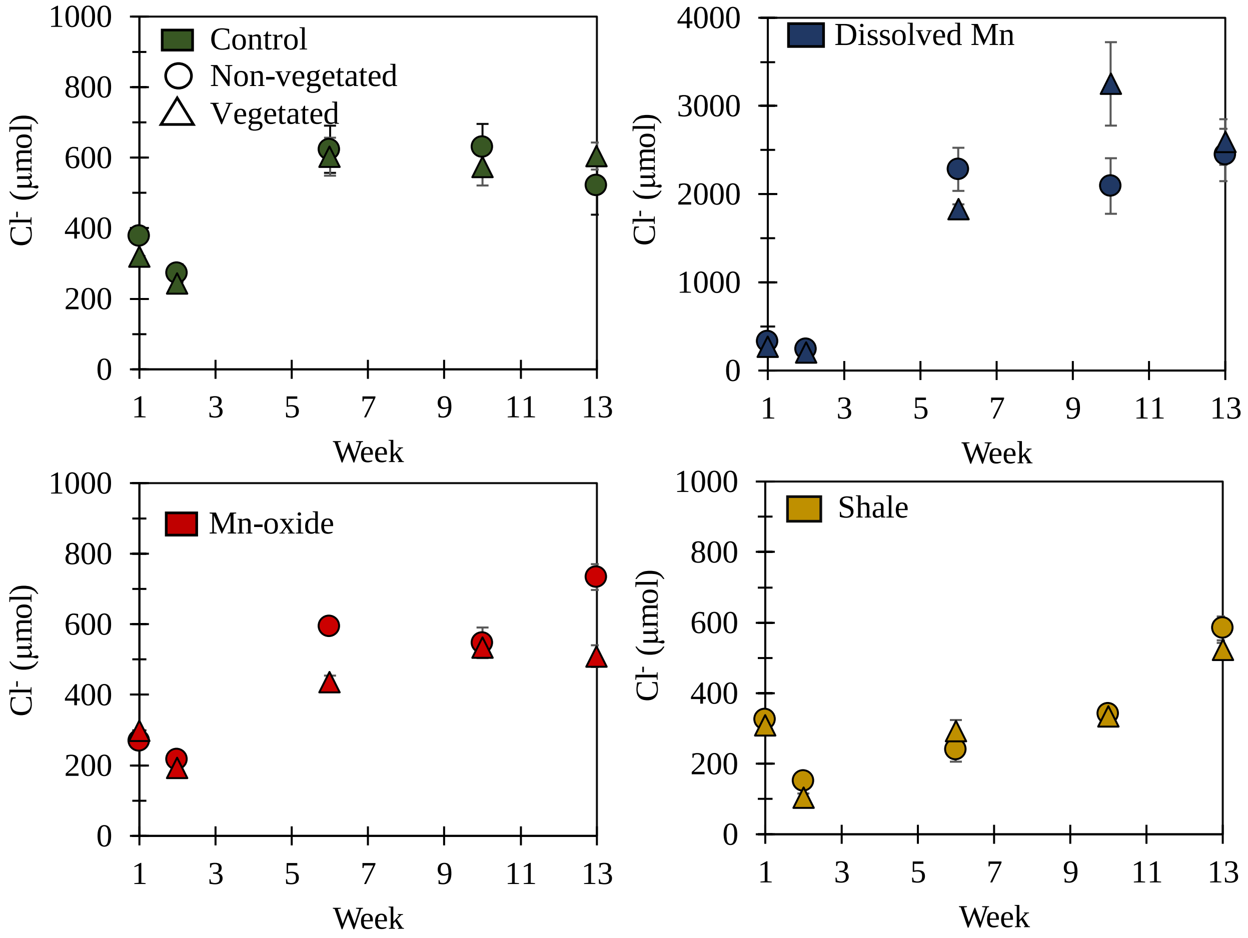

Figure 24. Averaged leached Cl$^-$ measured using ICS over time for each treatment, vegetated (triangles) and non-vegetated (circles). Error bars indicate the highest of the analytical error and the standard error of averaged replicates. All symbols have an associated error bar, although some are smaller than the symbol. Y-axis scales are different between some treatments.

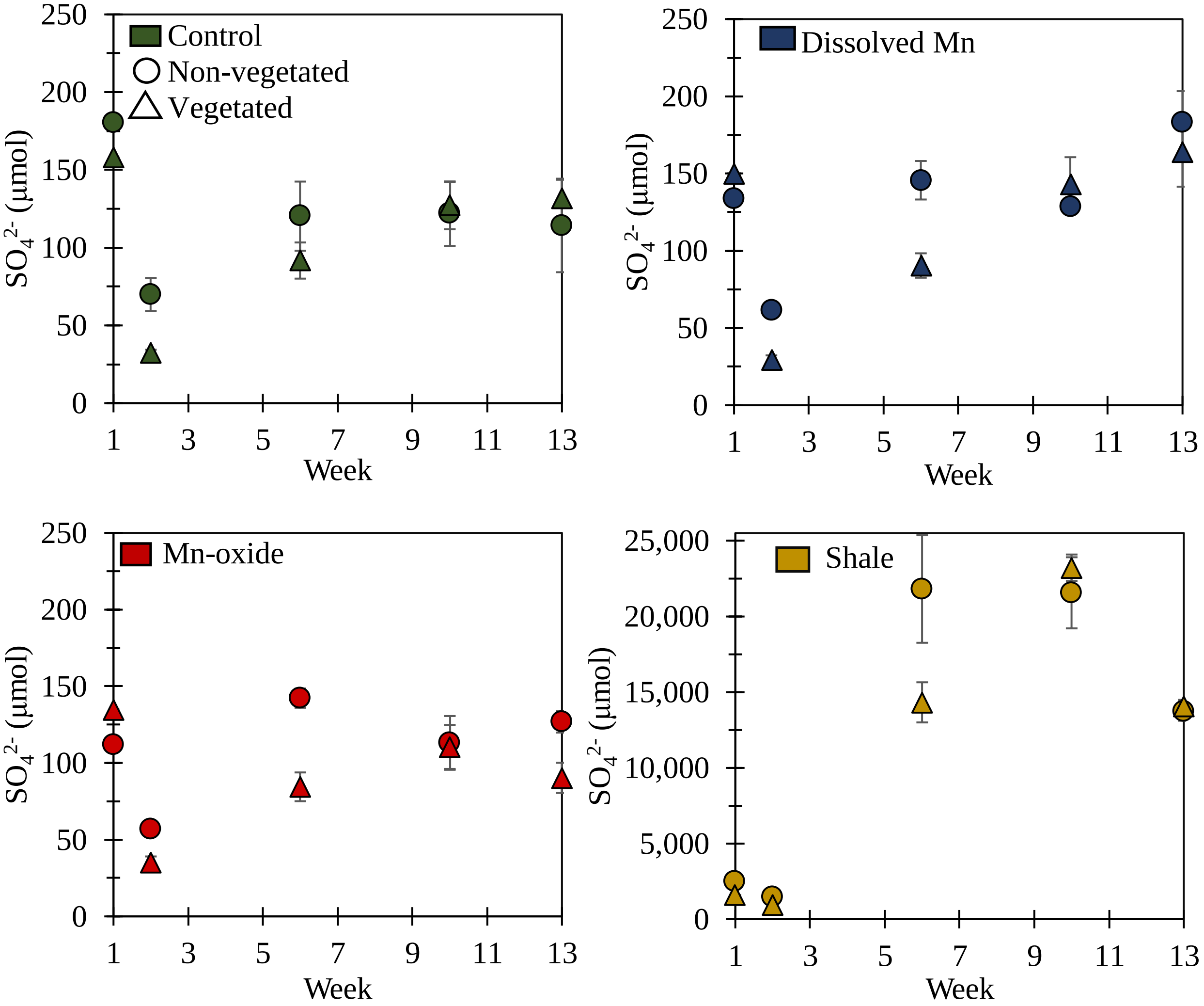

Figure 25. Averaged leached SO_4^{2-} measured using ICS over time for each treatment, vegetated (triangles) and non-vegetated (circles). Error bars indicate the highest of the analytical error and the standard error of averaged replicates. All symbols have an associated error bar, although some are smaller than the symbol. Y-axis scales are different between some treatments.

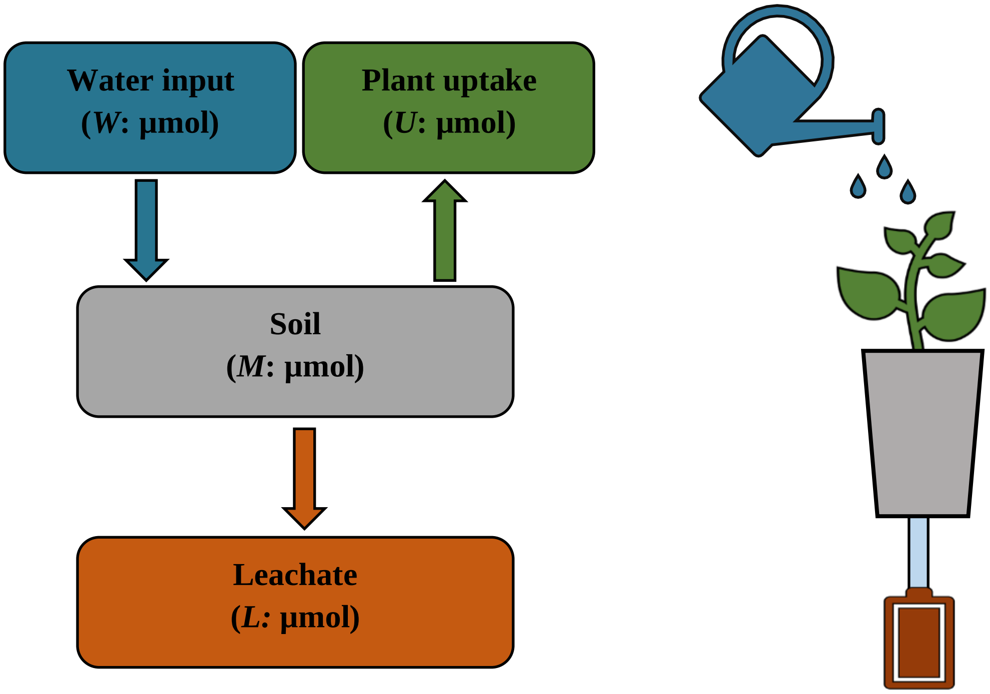

Figure 26. Manganese mass balance model (left) and a cartoon depicting the mass balance model in the greenhouse (right). Added water (greenhouse tap water + dissolved Mn where added) was considered an input flux, while the output fluxes are element release into soil leachate and plant uptake in the vegetated treatments. Pot soil and plant biomass were reservoirs.

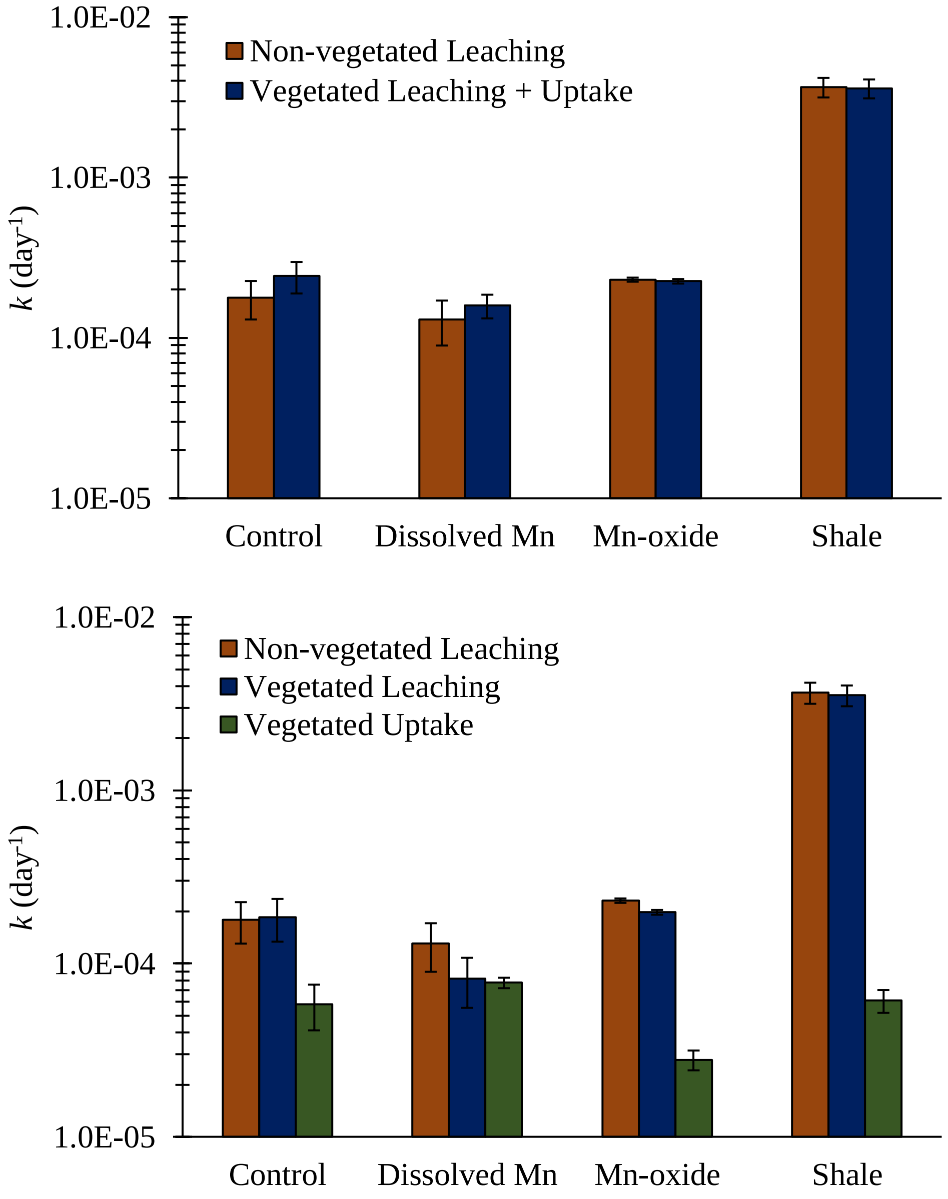

Figure 27. Pseudo-first order rate constants for Mn weathering. Top: vegetated and non-vegetated total Mn weathering rates (leachate + uptake) for each treatment (k_T). Bottom: The same non-vegetated leaching rate as the top, but the vegetated Mn weathering rates are split into leaching rate and uptake rate. Error bars represent the higher of the analytical error and the standard error of the average.

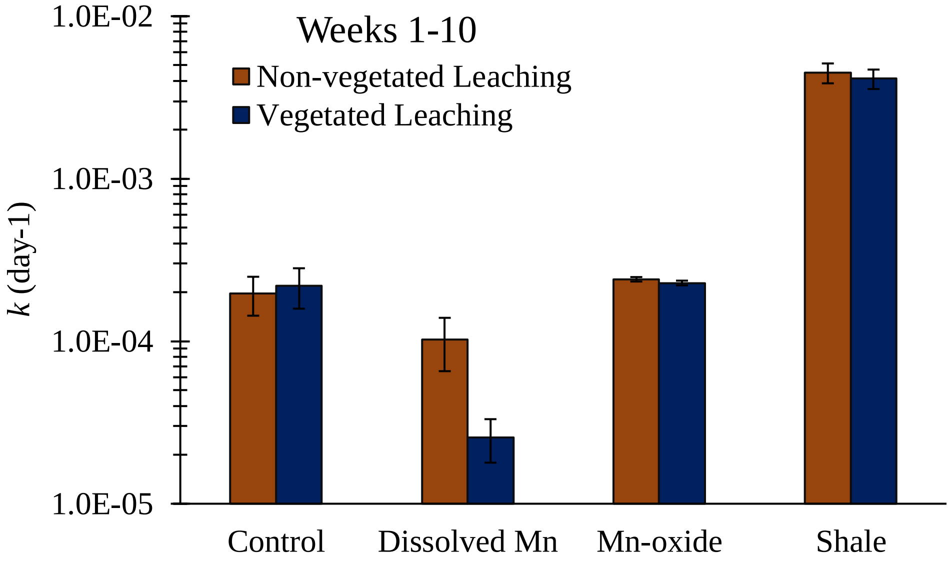

Figure 28. Pseudo-first order rate constants for Mn weathering, weeks 1-10. Error bars represent the higher of the analytical error and the standard error of the average.

Tables

Table 1. Quartz sand diffraction patterns by XRD and the associated mineral phase, as shown in Figure 4 where the x-axis is 2-theta (degrees) and the y-axis is counts per second (cps).

Peak	2-theta	Height (cps)	Phase
1	20.817	776	Quartz
2	21.104	7481	Quartz
3	26.504	424	Unknown
4	26.848	6834	Quartz
5	36.748	3867	Quartz
6	39.647	343	Quartz
7	40.545	437	Quartz
8	42.650	846	Quartz
9	45.963	214	Quartz
10	50.410	507	Quartz
11	55.02	117	Quartz
12	55.53	51	Quartz
13	57.463	41	Quartz
14	60.182	425	Quartz
15	64.219	171	Quartz
16	65.73	15	Unknown
17	66.02	43	Quartz
18	67.965	209	Quartz
19	68.373	431	Quartz
20	70.50	8	Unknown
21	73.615	276	Quartz
22	75.836	227	Quartz
23	77.901	410	Quartz
24	80.160	329	Quartz
25	81.343	941	Unknown
26	81.712	1481	Quartz
27	84.007	220	Quartz
28	85.086	36	Unknown
29	87.27	10	Quartz

Table 2. Huff Run shale diffraction patterns by XRD and the associated mineral phase, as shown in Figure 5 where the x-axis is 2-theta (degrees) and the y-axis is counts per second (cps). Peaks one, four, and ten were omitted due to unlikely rare-mineral phase readings (charoite).

Peak No.	2-theta(deg)	Height(cps)	Phase name
2	8.752	258	Illite
3	12.30	547	Kaolinite
5	19.89	216	Kaolinite, Illite
6	20.771	446	Quartz
7	24.811	280	Kaolinite
8	26.607	1989	Quartz, Kaolinite, Illite
9	28.48	246	Pyrite
11	29.91	52	Illite
12	32.984	383	Pyrite,
13	34.92	120	Kaolinite, Illite
14	36.444	118	Quartz, Illite
15	37.01	208	Pyrite
16	39.352	102	Quartz, Kaolinite
17	40.722	200	Pyrite
18	42.354	101	Quartz
19	45.63	87	Quartz, Kaolinite, Illite
20	47.426	174	Pyrite
21	50.07	110	Quartz
22	51.97	34	Unknown
23	56.27	235	Pyrite
24	59.88	90	Quartz
25	61.623	49	Pyrite, Illite
26	64.21	47	Quartz, Pyrite
27	68.12	46	Quartz
28	78.90	17	Pyrite

Table 3. Lab-synthesized Mn-oxide diffraction patterns by XRD and the associated mineral phase, as shown in Figure 6 where the x-axis is 2-theta (degrees) and the y-axis is counts per second (cps).

Peak No.	2-theta (deg)	Height(cps)	Phase name
1	2.601	1617	Unknown
2	31.75	11.6	Unknown
3	36.615	53	Unknown
4	65.59	17	Unknown

Table 4. Initial and final Mn concentrations in soil media for each vegetated and non-vegetated treatment as measured by x-ray fluorescence. Error represents the highest of the analytical error and standard error of the replicate average.

	Treatment	Initial Soil Mn (μmol kg^{-1})	Final Soil Mn (μmol kg^{-1})	Difference (μmol kg^{-1})
Non-vegetated	Control	232 (± 62)	142 (± 19)	Not significant
	Dissolved Mn	232 (± 62)	11,920 (± 1,193)	+ 11,688 (± 1,194)
	Mn-oxide	2,641 (± 62)	2,726 (± 127)	Not significant
	Shale	459 (± 62)	305 (± 56)	- 154 (± 84)
Vegetated	Control	232 (± 62)	174 (± 16)	Not significant
	Dissolved Mn	232 (± 62)	9,799 (± 363)	+ 9,567 (± 368)
	Mn-oxide	2,641 (± 62)	2,542 (± 74)	Not significant
	Shale	459 (± 62)	184 (± 13)	- 275 (± 64)

Table 5. Pairwise one-way ANOVA comparisons between total biomass in each treatment (foliar + non-foliar), foliar only, and non-foliar only (model not significant) ($\alpha = 0.05$). See Figure 11.

	p-value ($\alpha = 0.05$)		
	Foliar + Non-foliar	Foliar	Non-foliar
Overall Model	0.038	0.005	Not significant
CP:DMP	0.203	0.374	
CP:MOP	0.902	0.491	
CP:SP	0.903	0.279	
DMP:MOP	0.027	0.013	
DMP:SP	0.469	0.997	
MOP:SP	0.445	0.008	

Table 6. Foliar and non-foliar concentrations of major elements through acid digestion and ICP analysis of treatment-homogenized material. Error represent the highest of the analytical error and the standard error of averaged replicates (n = 2). Measured NIST 1570a standard values are different between foliar and non-foliar sets due to different instrument runs. $^{+}$NIST 1570a certified value, $^{++}$NIST1570a measured value.

	P %	**K %**	**Ca %**	**Mg %**	**S %**	**Mn mg/kg**	**Fe mg/kg**	**Cu mg/kg**	**B mg/kg**	**Al* mg/kg**	**Zn mg/kg**	**Na* mg/kg**
Foliar												
NIST 1570a^{+}	**0.52**	**2.90**	**1.53**			**76**		**12**	**38**	**310**	**82**	**20,000**
NIST 1570a^{++}	0.55 ± 0.01	2.96 ± 0.02	1.54 ± 0.01	0.88 ± 0.01	0.50 ± 0.01	78 ± 1	238 ± 1	13 ± 1	44 ± 1	117 ± 3	82 ± 2	16,286 ± 81
Control	0.54 ± 0.01	1.05 ± 0.02	1.52 ± 0.01	0.53 ± 0.01	0.17 ± 0.01	46 ± 1	76 ± 1	5.90 ± 0.08	62 ± 2	33 ± 48	25 ± 1	114 ± 930
Dissolved Mn	0.25 ± 0.01	1.53 ± 0.02	2.57 ± 0.01	0.4 ± 0.01	0.13 ± 0.01	4593 ± 30	85 ± 1	3.13 ± 0.08	78 ± 2	33 ± 48	22 ± 1	246 ± 930
Mn-oxide	0.45 ± 0.01	1.06 ± 0.02	1.90 ± 0.01	0.53 ± 0.01	0.17 ± 0.01	371 ± 1	73 ± 1	6.4 ± 0.08	67 ± 2	30 ± 48	25 ± 1	18 ± 930
Shale	0.14 ± 0.01	0.76 ± 0.02	0.86 ± 0.03	0.33 ± 0.01	0.26 ± 0.01	251 ± 1	190 ± 4	4.43 ± 0.08	56 ± 2	48 ± 48	22 ± 1	484 ± 930
Non-Foliar												
NIST 1570a*	**0.52**	**2.90**	**1.53**			**76**		**12**	**38**	**310**	**82**	**20,000**
NIST 1570a**	0.49 ± 0.01	2.75 ± 0.01	1.41 ± 0.01	0.81 ± 0.01	0.46 ± 0.01	72 ± 1	215 ± 1	12 ± 1	42 ± 1	96 ± 2	74 ± 1	13,176 ± 16
Control	0.15 ± 0.01	0.53 ± 0.05	0.94 ± 0.04	0.15 ± 0.01	0.15 ± 0.01	43 ± 1	653 ± 3	6.13 ± 0.17	14 ± 1	701 ± 71	23 ± 3	1028 ± 2275
Dissolved Mn	0.14 ± 0.01	0.52 ± 0.05	0.85 ± 0.04	0.10 ± 0.01	0.12 ± 0.01	2463 ± 18	734 ± 11	4.92 ± 0.17	15 ± 1	930 ± 71	22 ± 3	722 ± 2275
Mn-oxide	0.24 ± 0.01	0.83 ± 0.15	1.14 ± 0.23	0.24 ± 0.05	0.19 ± 0.04	161 ± 32	649 ± 116	8.82 ± 2.03	20 ± 4	808 ± 158	30 ± 6	1391 ± 2275
Shale	0.08 ± 0.01	0.29 ± 0.05	0.68 ± 0.04	0.09 ± 0.01	0.35 ± 0.01	71 ± 3	3449 ± 149	6.49 ± 0.22	15 ± 1	813 ± 77	19 ± 3	673 ± 2275

*High error due to low recovery during combustion and acid digestion

Table 7. Pairwise analysis of deviance comparisons (two-way ANOVA and chi square) for leachate volume, Ca, Fe, Mg, and Mn ($\alpha = 0.17$). Either vegetation or treatment was tested, but not the interaction between the two factors. See associated boxplots of tested data (Figure 14 for leachate volume and Figure 16 for cations).

Pair	**P-value ($\alpha = 0.017$)**					**Factor Tested**
	Leachate Volume	**Mn**	**Ca**	**Fe**	**Mg**	
Overall Model	$< 2.2 \times 10^{-16}$	0.637	6.7×10^{-11}	0.005	0.006	Vegetation
Overall Model	2.6×10^{-10}	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	Treatment
CS:CP	2.2×10^{-6}	0.805	1.5×10^{-14}	8.3×10^{-4}	0.027	Vegetation (Control)
DMS:DMP	8.2×10^{-7}	0.246	0.579	0.987	0.751	Vegetation (Dissolved Mn)
MOS:MOP	$< 2.2 \times 10^{-16}$	1.8×10^{-5}	$< 2.2 \times 10^{-16}$	0.245	5.9×10^{-8}	Vegetation (Mn-oxide)
SS:SP	0.002	0.918	0.760	0.056	0.869	Vegetation (Shale)
CS:DMS	0.001	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	7.3×10^{-7}	$< 2.2 \times 10^{-16}$	Treatment (Non-vegetated)
CS:MOS	0.091	$< 2.2 \times 10^{-16}$	0.465	1.5×10^{-4}	$< 2.2 \times 10^{-16}$	Treatment (Non-vegetated)
CS:SS	0.582	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	Treatment (Non-vegetated)
DMS:MOS	0.102	0.019	$< 2.2 \times 10^{-16}$	0.009	$< 2.2 \times 10^{-16}$	Treatment (Non-vegetated)
DMS:SS	0.007	0.179	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	Treatment (Non-vegetated)
MOS:SS	0.272	1.4×10^{-14}	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	Treatment (Non-vegetated)
CP:DMP	0.003	2.6×10^{-11}	$< 2.2 \times 10^{-16}$	3.6×10^{-4}	2.8×10^{-12}	Treatment (Vegetated)
CP:MOP	1.4×10^{-4}	$< 2.2 \times 10^{-16}$	0.274	0.047	7.2×10^{-14}	Treatment (Vegetated)
CP:SP	0.034	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	Treatment (Vegetated)
DMP:MOP	4.46×10^{-13}	0.161	$< 2.2 \times 10^{-16}$	0.023	$< 2.2 \times 10^{-16}$	Treatment (Vegetated)
DMP:SP	0.350	0.006	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	Treatment (Vegetated)
MOP:SP	1.7×10^{-10}	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	$< 2.2 \times 10^{-16}$	Treatment (Vegetated)

Table 8. Calculated Mn mass balance input and output values. Values are cumulative totals. Error represents the highest of the analytical error and standard error of the replicate average. ΔSoil is calculated from input-outputs (equation 6).

		Input	Output		
	Treatment	Water (*W*: µmol)	Uptake (*U*: µmol)	Leachate (*L*: µmol)	ΔSoil (µmol)
Non-vegetated	Control	1.4 (± < 0.1)		8.9 (± 0.2)	-8 (± 0.2)
	Dissolved Mn	20901 (± < 0.1)		241 (± 39)	+20,660 (± 39)
	Mn-oxide	1.4 (± < 0.1)		131 (± 2)	-130 (± 2)
	Shale	1.4 (± < 0.1)		363 (± 11)	-361 (± 11)
Vegetated	Control	1.4 (± < 0.1)	2.9 (± 0.4)	9.3 (± 0.6)	-11 (± 1)
	Dissolved Mn	20901 (± < 0.1)	143 (± 10)	151 (± 27)	+20,607 (± 28)
	Mn-oxide	1.4 (± < 0.1)	16 (± 2)	112 (± 2)	-127 (± 3)
	Shale	1.4 (± < 0.1)	6.0 (± 0.4)	350 (± 7)	-355 (± 7)

Appendix A

Table A1. Replicate foliar and non-foliar (stem + roots) biomass and leaf counts. n.d. = no data.

Replicate	Foliar Weight (g)	Non-foliar Weight (g)	Final Leaf Count
CP1	0.61	n.d.	21
CP2	0.85	2.13	13
CP3	0.12	1.19	3
CP4	1.06	4.10	17
CP5	n/a	0.78	n/a
CP6	0.23	2.09	4
CP7	n/a	1.56	n/a
CP8	0.91	3.26	10
CP9	1.70	4.07	24
CP10	1.15	3.10	22
DMP1	0.21	1.67	10
DMP2	0.36	1.74	8
DMP3	0.65	2.37	24
DMP4	0.33	2.17	4
DMP5	0.62	1.86	20
DMP6	0.79	1.81	13
DMP7	1.03	1.84	14
DMP8	0.65	1.99	19
DMP9	0.45	1.94	9
DMP10	0.92	3.32	17
MOP1	0.95	2.71	14
MOP2	0.67	2.89	8
MOP3	1.10	2.98	22
MOP4	1.01	3.02	16
MOP5	1.19	3.45	17
MOP6	1.12	3.40	20
MOP7	1.30	3.16	26
MOP8	1.13	2.18	18
MOP9	0.97	5.30	12
MOP10	0.84	1.24	16
SP1	0.46	2.10	4
SP2	0.50	2.66	7
SP3	0.37	2.11	5
SP4	0.62	2.41	14
SP5	0.84	3.28	13
SP6	0.64	2.09	7
SP7	0.46	2.86	6
SP8	0.51	2.31	5
SP9	0.69	4.47	8
SP10	0.65	3.52	8

Table A2. Replicate leachate volume (mL) each week. Weeks ending in ".5" indicate the second measurement taken mid-week.

Week	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	10.5	11	11.5	12	12.5	13
CS1	131	124	126	123	174	160	159	160	158	149	196	152	148	84	169	151	148	177	182	187	171	209	162	165	158
CS2	135	132	116	108	158	163	186	166	147	147	185	147	141	80	145	118	124	145	95	55	116	56	81	17	61
CS3	110	127	76	148	127	129	152	120	112	91	109	98	100	59	92	87	85	131	137	153	122	104	80	107	71
CS4	149	148	127	174	186	155	174	153	172	136	150	142	161	107	142	126	187	180	189	198	204	212	182	193	188
CS5	126	119	97	106	116	143	162	143	123	134	171	140	121	63	131	113	115	160	156	182	169	207	165	187	162
CP1	112	119	52	79	141	122	160	124	101	131	167	122	79	70	92	79	86	146	149	158	143	182	86	151	116
CP2	122	138	87	163	155	137	167	132	116	132	144	130	97	62	93	85	74	112	118	134	127	139	95	128	94
CP3	98	105	96	88	125	145	157	104	92	126	177	136	94	68	66	65	41	95	141	163	141	193	106	163	157
CP4	137	140	115	150	152	127	147	115	121	115	136	123	108	71	116	102	101	110	114	129	154	143	129	128	136
CP5	143	130	115	154	156	139	144	123	119	144	171	145	139	97	144	133	153	194	177	211	145	182	148	141	147
CP6	154	142	93	164	158	135	157	123	123	105	134	103	102	75	145	68	94	61	139	127	154	219	113	146	130
CP7	131	134	108	147	152	141	168	121	128	126	107	112	118	114	203	109	104	200	171	175	188	234	115	165	145
CP8	157	162	89	135	173	134	162	141	182	138	202	169	136	85	119	116	104	180	140	166	120	244	79	145	96
CP9	136	133	101	153	166	141	168	136	151	117	162	129	133	62	136	102	99	120	115	134	105	119	88	104	66
CP10	133	124	80	158	143	116	147	104	91	61	112	124	89	44	80	58	70	90	95	104	110	118	83	83	83
DMS1	135	139	105	168	180	155	188	157	173	142	204	154	174	88	168	125	159	132	140	166	202	206	183	179	188
DMS2	133	124	107	110	118	155	183	158	146	142	189	143	139	67	159	123	142	178	182	192	188	215	178	190	184
DMS3	137	131	98	147	159	152	177	153	161	141	190	143	157	83	162	123	152	152	154	180	174	185	177	180	165
DMS4	150	128	104	156	173	149	175	150	170	140	173	142	160	95	158	119	151	120	162	180	186	204	189	189	183
DMS5	129	134	74	154	164	148	163	147	155	139	192	133	156	82	163	126	154	176	133	183	118	115	158	163	106
DMP1	108	104	71	80	108	122	84	80	101	107	126	108	108	58	138	117	132	169	166	186	163	199	135	165	150
DMP2	128	128	82	155	152	131	132	101	113	66	133	132	86	54	82	15	27	195	217	222	179	232	174	193	172
DMP3	114	113	60	146	135	117	141	97	111	96	154	132	143	98	165	130	157	177	178	210	220	269	220	220	225
DMP4	127	120	89	164	164	126	171	122	146	118	179	137	146	77	142	99	156	114	134	111	117	129	153	134	133
DMP5	121	118	98	113	133	122	154	94	76	90	134	100	73	61	100	74	84	133	149	127	145	99	172	16	46
DMP6	147	139	77	146	149	124	164	115	117	111	154	123	103	56	94	89	107	113	137	133	149	134	143	184	166
DMP7	128	127	82	160	162	122	169	118	103	115	151	136	119	68	114	93	116	115	159	129	154	182	153	142	180
DMP8	125	121	64	125	131	109	129	128	117	101	132	120	107	67	96	96	93	113	155	162	147	194	107	163	131
DMP9	150	137	86	143	143	128	143	118	125	106	158	147	138	94	141	117	156	175	179	201	184	210	173	198	185
DMP10	133	127	95	137	143	129	167	115	111	107	134	121	91	52	69	85	113	138	187	172	182	208	130	195	133

Table A2. (cont.) Replicate leachate volume (mL) each week. Weeks ending in ".5" indicate the second measurement taken mid-week.

Week	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	10.5	11	11.5	12	12.5	13
MOS1	109	113	71	150	150	138	155	140	139	129	146	133	147	73	133	111	115	107	101	97	184	207	154	177	147
MOS2	136	137	89	173	171	155	173	155	156	146	183	153	155	80	156	127	71	163	172	168	164	169	157	145	176
MOS3	127	124	84	166	160	143	172	144	150	137	171	145	149	81	149	117	125	146	156	153	179	187	164	162	169
MOS4	125	133	84	166	158	132	181	140	147	130	174	137	146	78	151	118	145	167	169	172	186	183	173	162	183
MOS5	139	112	90	173	159	145	180	142	156	142	181	157	148	92	154	112	169	148	183	173	181	187	172	164	170
MOP1	127	127	77	139	133	121	137	114	100	101	126	112	88	53	93	77	82	105	110	113	111	131	81	110	92
MOP2	127	122	76	139	137	134	144	132	115	113	123	117	90	58	91	84	153	110	114	121	119	110	106	102	102
MOP3	122	124	79	166	152	138	169	149	130	122	164	118	121	54	113	88	76	137	133	160	144	192	88	138	99
MOP4	142	149	102	151	156	139	158	101	110	89	126	110	102	70	113	78	103	99	115	115	122	170	91	119	105
MOP5	127	127	77	139	133	121	137	114	100	101	126	112	88	53	93	77	82	105	110	113	111	131	81	110	92
MOP6	127	123	86	148	140	125	139	123	106	99	114	104	92	55	97	87	90	115	117	107	101	91	78	81	76
MOP7	121	116	51	127	101	99	107	86	51	78	92	106	72	36	98	83	54	80	92	86	73	65	51	70	60
MOP8	134	129	85	118	121	98	102	104	107	112	156	124	59	57	65	49	50	97	88	85	98	171	40	121	67
MOP9	105	125	58	131	119	106	135	98	72	79	110	94	59	23	56	54	31	86	104	117	116	139	92	136	118
MOP10	135	124	76	134	136	127	138	122	111	113	125	120	109	73	111	94	95	118	118	112	114	109	104	113	106
SS1	122	118	57	124	128	114	133	143	130	113	147	112	92	68	95	108	126	172	148	200	165	212	156	187	163
SS2	122	120	61	139	131	110	135	114	122	121	146	130	131	82	131	115	138	137	158	143	169	159	145	171	147
SS3	133	134	84	168	157	140	170	144	152	131	159	143	151	86	155	124	152	160	173	169	174	195	180	184	175
SS4	121	126	60	167	149	138	171	147	141	137	171	146	132	78	142	113	142	160	175	203	173	196	173	178	172
SS5	118	125	74	160	163	140	165	128	147	127	174	140	160	87	159	115	148	169	182	186	177	204	184	189	183
SP1	128	127	63	151	153	125	163	143	153	128	183	144	156	91	161	127	161	177	180	188	189	208	185	192	185
SP2	102	101	42	122	106	108	112	100	119	100	105	98	116	76	103	100	116	130	153	174	155	191	139	162	144
SP3	104	110	47	88	115	111	129	99	56	94	130	107	79	62	86	94	96	146	123	136	139	182	109	156	119
SP4	161	115	53	114	104	91	119	55	113	153	193	134	145	97	112	52	178	155	158	174	169	188	121	168	142
SP5	106	94	32	126	102	96	106	105	108	116	153	132	133	72	205	106	127	144	149	159	144	178	136	149	131
SP6	119	124	53	152	122	112	154	133	124	135	177	97	151	79	150	121	146	166	176	174	177	178	183	185	180
SP7	124	106	39	119	124	113	130	115	111	103	116	115	130	82	107	123	121	156	161	182	160	202	152	176	171
SP8	128	111	43	118	116	105	129	118	119	115	133	134	131	80	132	108	122	134	147	161	158	185	157	171	154
SP9	109	109	44	136	133	112	139	119	127	99	127	110	104	54	103	87	97	125	135	145	151	177	144	162	139
SP10	121	134	71	133	135	86	115	92	115	94	142	124	143	80	100	100	120	141	158	161	145	185	121	159	118
Pot Blank	273	273	273	211	219	178	207	188	219	181	236	175	204	112	227	180	212	220	222	226	173	234	223	217	211
Amount Watered	200	200	200	225	250	200	225	200	250	200	250	200	250	200	250	200	250	250	250	250	250	250	250	250	250

Table A3. Replicate leachate pH each week.

Week	1	2	3	4	5	6	7	8	9	10	11	12	13
CS1	7.45	7.61	7.37	7.49	7.82	7.62	7.39	7.69	7.89	7.66	7.8	7.81	8.12
CS2	7.57	7.73	7.47	7.44	7.76	7.71	7.82	7.76	7.96	8.07	8.21	8.35	8.51
CS3	7.65	7.96	7.87	7.71	7.89	8.09	7.83	8.03	8.12	8	8.19	8.38	8.36
CS4	7.45	7.84	7.6	7.68	7.77	7.87	7.68	7.77	7.98	7.81	7.75	7.83	7.83
CS5	7.51	7.88	7.69	7.65	7.87	7.78	7.66	7.98	7.87	7.83	7.73	7.77	7.92
CP1	7.68	7.83	7.84	7.77	8.12	7.9	7.93	8.22	8.08	7.87	8.11	8	8.05
CP2	7.21	8.01	7.8	7.9	8.06	7.94	7.92	8.12	7.71	7.66	7.98	8.05	8.07
CP3	7.37	8	7.83	7.78	7.98	7.9	7.91	8.19	8.13	8.1	8.16	8.07	8
CP4	7.39	7.92	7.62	7.61	7.93	7.94	7.85	8.04	7.49	7.8	7.85	8.04	8.05
CP5	6.97	7.73	7.28	7.35	7.74	7.85	7.61	7.69	7.5	7.54	7.58	7.42	7.51
CP6	7.16	7.82	7.5	7.65	7.87	7.97	7.94	7.88	7.98	7.86	7.84	7.81	7.96
CP7	7.36	8.08	7.43	7.52	8.01	8.09	8.01	8.02	7.9	7.55	7.74	7.95	8.14
CP8		7.96	7.61	7.51	7.86	8.08	7.99	8.1	8.01	7.59	8.11	8.17	8.26
CP9		7.95	7.51	7.46	7.61	7.71	7.78	7.62	7.28	7.62	7.92	7.94	7.75
CP10		7.91	7.76	7.69	7.96	8.07	7.84	7.46	7.38	7.69	7.71	7.94	8.11
DMS1	7.32	7.92	7.66	7.54	7.56	7.61	7.52	7.52	7.41	7.54	7.29	7.54	7.65
DMS2		7.84	7.75	7.46	7.76	7.42	7.72	7.6	7.61	7.61	7.56	7.56	7.67
DMS3			8.11	7.95	7.82	7.7	7.86	7.87	7.9	7.69	7.8	7.63	7.91
DMS4		7.8	7.66	7.78	7.75	7.58	7.78	7.7	7.92	7.69	7.46	7.64	7.81
DMS5		7.52	7.62	7.73	7.67	7.55	7.5	7.86	7.67	7.52	7.54	7.59	7.66
DMP1	7.37	8.1	7.8	7.86	7.75	7.63	7.87	7.82	7.87	7.61	7.95	7.96	7.84
DMP2		7.98	7.82	7.8	7.97	7.62	7.91	7.16	7.63	7.49	7.59	7.82	7.68
DMP3		8.01	7.69	7.57	7.84	7.55	7.65	7.88	7.91	7.5	7.64	7.3	7.78
DMP4		7.86	7.57	7.62	7.81	7.52	7.68	7.91	7.98	7.88	7.8	7.82	7.91
DMP5		7.86	8.01	7.77	7.98	7.84	7.96	7.97	7.99	7.64	7.81	7.99	8.35
DMP6		7.85	7.69	7.49	7.8	7.72	7.73	7.56	7.97	7.79	7.76	7.52	7.82
DMP7		7.88	7.54	7.76	7.66	7.77	7.67	7.93	7.8	7.74	7.66	7.56	7.79
DMP8		7.88	7.75	7.71	7.67	7.69	7.72	7.99	7.94	7.78	7.8	7.95	8.01
DMP9		7.83	7.76	7.81	7.81	7.79	7.71	7.91	7.86	7.58	7.72	7.63	7.67
DMP10		8.06	7.56	7.54	7.84	7.88	7.84	7.89	7.81	7.63	8.02	7.95	8.06

Table A3. Replicate leachate pH each week.

Week	1	2	3	4	5	6	7	8	9	10	11	12	13
MOS1	7.35	8.06	7.4	7.56	7.83	7.71	7.8	7.92	8.13	8.02	7.81	7.78	8.08
MOS2		7.91	7.47	7.44	7.87	7.64	7.77	7.8	8.15	7.87	7.83	7.91	8.1
MOS3			7.86	7.91	8.06	7.89	7.95	8.05	8.11	7.95	8.03	8.12	8.31
MOS4		7.85	7.64	7.77	7.85	7.8	7.72	7.81	7.89	7.82	7.68	7.81	8.15
MOS5		7.94	7.73	7.8	7.78	7.52	7.89	7.82	7.72	7.48	7.75	8.08	7.88
MOP1				8.16	8.21	8.22	7.91	7.99	7.4	7.38	8.02	7.84	8.29
MOP2	7.44	8.17	8.03	7.94	7.92	7.84	8.05	7.1	7.66	7.95	7.96	8.06	8.27
MOP3		8	7.81	7.79	7.96	7.87	7.66	7.96	7.45	7.67	7.88	7.68	7.92
MOP4		7.94	7.82	7.69	7.79	7.96	7.84	7.72	8.04	7.9	7.94	7.99	8.12
MOP5		7.9	7.96	7.88	7.8	8.09	8	8.05		7.88	7.9	8.19	8.29
MOP6		7.84	7.56	7.66	7.97	7.82	7.76	7.98	7.89	7.83	7.94	8.2	8.37
MOP7		8.06	7.85	7.97	8.25	8.16	8.06	8.29	8.33	8.21	7.92	8.32	8.51
MOP8		7.99	7.89	7.99	8.13	7.98	8.09	8.34	8.37	8.17	8.26	8.44	8.53
MOP9		7.95	7.71	7.88	8.02	7.84	7.49	7.57	7.47	7.84	8.32	8.17	8.22
MOP10		7.88	7.84	7.74	8.06	7.99	7.95	7.52	7.37	7.92	8.05	8.09	8.25
SS1	3.82	3.12	2.79	2.65	2.45	2.39	2.26	2.15	2.18	2.13	2.16	2.23	2.41
SS2		3.65	3.33	3.03	2.44	1.98	1.75	1.82	1.66	1.72	1.82	1.88	2.06
SS3		3.92	3.61	3.39	2.84	2.3	1.98	2.03	1.82	1.81	1.85	1.92	2.23
SS4		3.89	3.62	3.05	2.1	1.61	1.42	1.59	1.56	1.73	1.82	1.91	2.13
SS5		4.21	3.78	3.04	2.27	1.79	1.52	1.64	1.61	1.81	1.93	2.04	2.2
SP1	5.56	3.79	3.71	5.57	3.06	2.22	1.86	1.78	1.56	1.82	1.92	2.08	2.24
SP2		3.9	4.01	6.82	2.86	2.43	2.08	2.07	2.03	1.99	1.93	2.02	2.17
SP3		3.79	3.63	3.5	3.18	2.82	2.46	2.4	2.26	2.24	2.27	2.32	2.39
SP4		4.01	3.69	3.75	2.53	2.45	2.19	2.19	2.1	2.03	2.06	2.16	2.31
SP5			3.75	3.98	2.95	2.23	1.86	1.83	1.66	1.73	1.79	1.96	2.05
SP6		3.98	3.56	3.9	4.23	2.31	1.85	1.8	1.63	1.81	1.89	1.99	2.13
SP7		3.73	3.38	3.52	3.19	2.51	2.15	2.24	2.07	2.11	2.04	2.12	2.24
SP8		3.75	3.47	3.65	3.72	2.64	2.12	2.14	2.01	1.97	1.91	2.05	2.21
SP9		3.66	3.33	3.21	2.84	2.18	2.18	2.09	1.96	1.77	1.79	2	2.16
SP10		3.66	3.37	3.42	2.63	2.33	2.12	2.02	1.83	1.8	1.77	1.98	2.05
Pot Blank	7.88	7.11	7.6	8.22	7.9	8.28	7.61	7.66	7.72	7.69	7.45	7.84	7.84
Filter Blank	5.22	6.78	5.93	6.21	5.64	5.44	7.68	6.12	5.39	5.77	5.38	5.94	5.6
Greenhouse tap				8.52	8.79	9.04	8.67	9.06	9.07	9.12	9.11	9.07	9.1

Table A4. Replicate leachate specific conductance (μS/cm) each week.

Week	1	2	3	4	5	6	7	8	9	10	11	12	13
CS1	781	615	585	623	750	742	730	757	789	827	882	834	819
CS2	797	618	595	636	720	792	785	795	827	842	899	966	985
CS3	656	611	614	691	786	795	792	796	830	864	937	928	955
CS4	556	570	586	643	667	666	664	681	727	788	873	818	771
CS5	663	591	595	620	664	785	801	803	862	891	943	932	899
CP1	826	642	579	633	756	797	842	876	926	974	1013	1001	975
CP2	631	617	678	665	649	709	683	780	1022	967	907	834	912
CP3	752	616	586	590	842	815	839	850	938	895	963	931	905
CP4	611	604	617	643	674	720	720	783	1014	974	864	865	913
CP5	633	592	600	608	584	612		644	657	640	805	966	846
CP6	625	602	588	630	625	645	657	679	722	711	767	1164	1061
CP7	639	603	595	644	651	687	655	698	742	804	975	967	906
CP8		645	623	665	711	757	753	764	813	875	1003	1131	1137
CP9		619	862	740	882	843	771	851	988	904	841	887	1129
CP10		620	645	640	678	772	796	890	1218	1134	1014	951	980
DMS1	578	589	576	953	1504	1459	1615	1520	1572	1517	2743	2377	2093
DMS2		603	600	1065	1483	1771	1815	1837	1708	1973	3304	2248	1976
DMS3			596	636	1669	1594	1545	1581	1597	1454	1680	2043	1710
DMS4		581	565	775	1276	1315	1529	1431	1363	1833	2811	2847	2405
DMS5		557	589	689	1014	1215	1223	1295	1252	1471	2263	2322	2217
DMP1	753	619	556	1020	1322	1648	1614	1570	2433	2508	2137	2052	2097
DMP2		606	570	615	1124	1605	2202	2470	2554	2687	2525	2358	2323
DMP3		624	796	930	1194	1476	1560	1517	1486	1391	2154	2196	2035
DMP4		593	611	662	955	1304	1387	1620	1602	1583	4470	3911	2850
DMP5		614	577	827	1343	1740	1785	2412	2744	2984	2692	2476	2729
DMP6		586	589	653	1131	1447	1512	1684	1688	1453	2352	4172	3259
DMP7		601	631	692	1211	1768	1651	1824	1775	1379	3107	3359	2199
DMP8		587	564	595	996	1606	2098	2369	2445	3273	2247	2956	2739
DMP9		580	554	618	1035	1414	1948	1686	1625	3603	2363	2306	2029
DMP10		582	555	627	984	1393	2090	2013	3008	3249	2656	2325	2142

Table A4. (cont.) Replicate leachate specific conductance (µS/cm) each week.

Week	1	2	3	4	5	6	7	8	9	10	11	12	13
MOS1	615	604	580	650	693	708	725	700	744	738	742	983	1029
MOS2		615	628	665	696	686	658	660	896	701	40	774	845
MOS3			618	628	658	667	654	683	740	698	727	722	733
MOS4		617	607	638	660	681	647	661	691	718	767	826	737
MOS5		632	606	678	712	670	634	647	673	671	716	886	811
MOP1				612	608	649	743	791	941	845	870	761	906
MOP2	654	652	583	642	681	742	763	822	682	943	901	880	973
MOP3		609	587	588	597	623	604	655	792	669	683	768	772
MOP4		650	624	641	651	684	728	764	863	882	936	957	1090
MOP5		663	619	616	650	721	730	826	862	1049	1113	1054	1031
MOP6		665	617	672	652	703	716	773	862	856	804	891	985
MOP7		640	648	652	653	714	753	762	848	852	844	846	1174
MOP8		662	627	630	630	674	785	895	928	1007	890	1302	1240
MOP9		630	632	703	745	856	1038	1115	1453	1145	1270	855	883
MOP10		687	620	641	638	652	667	668	744	785	964	818	901
SS1	2841	3861	4824	4745	4982	5691	5850	6019	6897	7485	6946	5815	4910
SS2		3640	4161	4670	5968	8959	10957	11859	13461	12410	10154	8569	4252
SS3		3428	4099	4152	4536	6863	8180	9140	10926	11067	9345	7559	6044
SS4		3969	4064	4561	7834	13944	15491	14930	14946	11743	8994	7699	7273
SS5		3860	4235	4496	6483	11174	13103	13437	12362	8902	7009	6058	5740
SP1	1992	3507	3992	3794	4410	7117	9362	12159	13117	9776	7241	5873	5309
SP2		3193	3954	3841	4608	6656	7691	8127	8962	9370	9205	7885	6935
SP3		2971	3743	4187	4472	5182	5323	6208	7033	7464	6930	6221	5889
SP4		2980	3938	4003	6163	6055	6395	7040	8005	8767	7758	6571	5583
SP5			3996	4032	4784	7725	9951	10510	13627	13007	10355	7913	7148
SP6		3412	4048	3973	4078	6595	8999	11633	12799	9818	7861	6836	5871
SP7		3317	4005	3932	4206	5588	6785	7130	7911	7859	7774	7130	6020
SP8		3638	3964	4108	4056	5368	7010	7665	8872	9505	9156	7579	6369
SP9		3570	4007	4262	4660	6514	6980	8102	9989	12210	10315	7966	6625
SP10		3408	4082	4067	4961	6508	6981	8575	10842	12084	10587	8455	7468
Pot Blank	570	681	576	638	661	632	709	673	693	726	728	767	730
Filter Blank	13.2	17	11.3	26	10.6	9.5	70	10.2	14	30	10.5	35	6.7
Greenhouse tap				563	537	553	593	570	611	586	583	685	629

Table A5. Control cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
1	CS1	0.12	0.14	67.09	0.60	0.04	0.03			17.40	0.11	0.01	0.02	44.00	2.77
1	CP1	0.15	0.14	70.27	0.60	0.02	0.03			18.03	0.11	0.01	<0.00	40.26	2.77
2	CS1	0.03	0.01	42.22	0.31	0.90	0.02	34.67	0.09	10.12	0.10	0.24	0.02	43.30	0.18
2	CS2	0.11	0.01	56.51	0.31	0.64	0.02	26.86	0.09	9.33	0.10	0.30	0.02	39.00	0.18
2	CS3	0.18	0.01	80.79	0.75	0.41	0.02	10.83	0.09	6.46	0.10	0.35	0.02	32.74	0.18
2	CS4	0.14	0.01	65.31	0.75	0.61	0.02	7.68	0.09	4.94	0.10	0.33	0.02	41.02	0.18
2	CS5	0.15	0.01	73.04	0.75	0.65	0.02	10.31	0.09	5.81	0.10	0.30	0.02	30.36	0.18
2	CP1	0.11	0.01	52.41	0.31	0.74	0.02	38.37	0.09	12.14	0.10	0.45	0.02	43.24	0.18
2	CP2	0.07	0.01	45.64	0.31	1.48	0.07	34.04	0.09	10.29	0.10	0.42	0.02	50.23	0.18
2	CP3	0.09	0.01	50.14	0.31	1.21	0.07	38.23	0.09	11.38	0.10	0.49	0.02	39.97	0.18
2	CP4	0.07	0.01	45.37	0.31	1.18	0.07	28.95	0.09	10.30	0.10	0.66	0.02	48.42	0.18
2	CP5	0.05	0.01	42.91	0.31	1.09	0.02	28.54	0.09	9.75	0.10	0.34	0.02	47.35	0.18
2	CP6	0.07	0.01	45.01	0.31	1.05	0.02	27.95	0.09	9.54	0.10	0.42	0.02	48.72	0.18
2	CP7	0.07	0.01	46.63	0.31	1.55	0.07	31.99	0.09	10.65	0.10	0.42	0.02	48.31	0.18
2	CP8	0.09	0.01	49.46	0.31	0.79	0.02	38.05	0.09	11.03	0.10	0.40	0.02	48.53	0.18
2	CP9	0.08	0.01	47.65	0.31	1.49	0.07	31.76	0.09	10.99	0.10	0.45	0.02	47.08	0.18
2	CP10	0.08	0.01	47.61	0.31	1.47	0.07	32.50	0.09	10.69	0.10	0.54	0.02	45.90	0.18
3	CS1	0.02	0.14	39.77	0.13	1.59	0.18			9.82	0.11	0.18	0.02	50.63	2.77
3	CS2	0.09	0.14	53.00	0.60	1.87	0.18			8.87	0.11	0.26	0.02	45.68	2.77
3	CS3	0.13	0.14	70.86	0.60	1.02	0.18			5.85	0.11	0.20	0.02	42.96	2.77
3	CS4	0.11	0.14	58.27	0.60	1.00	0.18			4.65	0.11	0.17	0.02	51.97	2.77
3	CS5	0.14	0.14	70.30	0.60	1.46	0.18			5.72	0.11	0.26	0.02	38.87	2.77
3	CP1	0.05	0.14	42.95	0.13	1.34	0.18			10.56	0.11	0.16	0.02	41.58	2.77
3	CP2	0.06	0.14	45.40	0.13	2.23	0.18			10.89	0.11	0.02	<0.00	62.16	2.77
3	CP3	0.04	0.14	41.78	0.13	2.08	0.18			10.28	0.11	0.24	0.02	44.76	2.77
3	CP4	0.03	0.14	38.33	0.13	2.19	0.18			10.06	0.11	0.27	0.02	58.89	2.77

Table A5. (cont.) Control cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
3	CP5	0.03	0.14	42.40	0.13	2.84	0.18			9.92	0.11	0.20	0.02	52.93	2.77
3	CP6	0.03	0.14	40.64	0.13	2.03	0.18			9.70	0.11	0.19	0.02	57.63	2.77
3	CP7	0.01	0.14	40.70	0.13	2.21	0.18			9.73	0.11	0.20	0.02	52.60	2.77
3	CP8	0.06	0.14	46.69	0.13	1.04	0.18			8.42	0.11	0.73	0.02	50.09	2.77
3	CP9	0.11	0.14	60.67	0.60	2.20	0.18			12.75	0.11	31.62	1.07	61.56	2.77
3	CP10	0.03	0.14	46.36	0.13	2.72	0.18			10.64	0.11	0.49	0.02	58.16	2.77
4	CS1	0.05	0.01	37.66	0.31	1.54	0.07	20.98	0.09	9.32	0.10	0.18	0.02	64.78	0.19
4	CS2	0.09	0.01	47.67	0.31	1.57	0.07	15.09	0.09	7.94	0.10	0.18	0.02	61.49	0.19
4	CS3	0.14	0.01	67.76	0.75	1.19	0.07	7.65	0.09	5.68	0.10	0.21	0.02	61.99	0.19
4	CS4	0.11	0.01	53.58	0.31	1.14	0.07	5.38	0.09	4.21	0.10	0.17	0.02	69.19	0.19
4	CS5	0.12	0.01	61.11	0.75	1.95	0.07	8.48	0.09	5.06	0.10	0.25	0.02	56.88	0.19
4	CP1	0.07	0.01	43.80	0.31	1.01	0.07	25.55	0.09	9.15	0.10	0.10	0.02	58.44	0.19
4	CP2	0.03	0.01	37.30	0.31	1.32	0.07	18.06	0.09	8.74	0.10	0.01	0.02	75.57	0.19
4	CP3	0.05	0.01	34.60	0.31	1.82	0.07	21.97	0.09	9.10	0.10	0.18	0.02	58.25	0.19
4	CP4	0.05	0.01	35.15	0.31	1.35	0.07	16.69	0.09	8.56	0.10	0.21	0.02	73.11	0.19
4	CP6	0.04	0.01	33.33	0.31	1.71	0.07	16.28	0.09	8.49	0.10	0.16	0.02	71.67	0.18
4	CP7	0.03	0.01	37.67	0.31	1.68	0.07	19.21	0.09	8.76	0.10	0.21	0.02	68.69	0.19
4	CP8	0.06	0.01	38.44	0.31	1.44	0.07	23.89	0.09	8.79	0.10	0.39	0.02	70.79	0.19
4	CP9	0.07	0.01	42.37	0.31	1.78	0.07	20.24	0.09	9.72	0.10	19.97	0.40	76.00	0.19
4	CP10	0.04	0.01	36.95	0.31	2.05	0.07	18.65	0.09	8.71	0.10	0.67	0.02	81.48	0.19
5	CS1	0.05	0.14	44.08	0.13	1.64	0.18			10.79	0.11	0.17	0.02	82.98	2.77
5	CS2	0.07	0.14	51.48	0.60	1.57	0.18			8.50	0.11	0.14	0.02	77.78	2.77
5	CS3	0.13	0.14	72.51	0.60	1.02	0.18			5.97	0.11	0.18	0.02	77.52	2.77
5	CS4	0.08	0.14	52.23	0.60	1.05	0.18			3.98	0.11	0.13	0.02	78.41	2.77
5	CS5	0.07	0.14	60.56	0.60	2.39	0.18			4.68	0.11	0.19	0.02	67.75	2.77
5	CP1	0.08	0.14	49.81	0.60	0.66	0.03			11.07	0.11	0.07	0.02	78.26	2.77

Table A5. (cont.) Control cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
5	CP2	0.03	0.14	35.54	0.13	1.39	0.18			8.08	0.11	0.02	0.02	79.38	2.77
5	CP3	0.09	0.14	54.53	0.60	1.01	0.18			13.66	0.11	0.17	0.02	88.29	2.77
5	CP4	0.03	0.14	37.22	0.13	1.11	0.18			8.75	0.11	0.19	0.02	83.15	2.77
5	CP5	0.01	0.14	30.59	0.13	1.19	0.18			7.28	0.11	0.09	0.02	69.36	2.77
5	CP6	0.02	0.14	32.05	0.13	1.20	0.18			7.74	0.11	0.09	0.02	79.42	2.77
5	CP7	0.04	0.14	37.85	0.13	1.26	0.18			8.69	0.11	0.15	0.02	76.26	2.77
5	CP8	0.06	0.14	42.70	0.13	0.61	0.03			8.50	0.11	0.44	0.02	77.91	2.77
5	CP9	0.06	0.14	45.50	0.13	1.07	0.18			10.94	0.11	35.71	1.07	80.54	2.77
5	CP10	0.02	0.14	36.13	0.13	1.05	0.18			8.66	0.11	0.65	0.02	83.48	2.77
6	CS1	0.05	0.01	36.00	0.31	1.37	0.07	12.88	0.09	8.74	0.10	0.15	0.02	92.58	0.19
6	CS2	0.09	0.01	48.32	0.31	1.28	0.07	10.14	0.09	8.17	0.10	0.13	0.02	93.60	0.19
6	CS3	0.13	0.01	62.63	0.75	0.95	0.02	7.56	0.09	5.09	0.10	0.16	0.02	91.07	0.19
6	CS4	0.08	0.01	44.48	0.31	1.03	0.07	4.52	0.09	3.39	0.10	0.14	0.02	81.87	0.19
6	CS5	0.12	0.01	58.30	0.31	2.30	0.07	7.14	0.09	4.58	0.10	0.22	0.02	85.18	0.19
6	CP1	0.08	0.01	42.22	0.31	0.66	0.02	16.49	0.09	10.29	0.10	0.04	0.02	96.10	0.19
6	CP2	0.05	0.01	33.69	0.31	0.99	0.02	9.08	0.09	7.48	0.10	0.02	0.02	96.67	0.19
6	CP3	0.08	0.01	42.68	0.31	0.77	0.02	17.14	0.09	10.97	0.10	0.15	0.02	96.32	0.19
6	CP4	0.06	0.01	35.29	0.31	0.99	0.02	8.69	0.09	8.12	0.10	0.10	0.02	94.02	0.19
6	CP5	0.02	0.01	27.12	0.31	1.03	0.07	10.50	0.09	6.73	0.10	0.10	0.02	78.50	0.19
6	CP6	0.04	0.01	27.58	0.31	1.39	0.07	10.15	0.09	7.16	0.10	0.12	0.02	87.70	0.19
6	CP7	0.05	0.01	35.34	0.31	0.81	0.02	12.29	0.09	8.28	0.10	0.11	0.02	84.15	0.19
6	CP8	0.09	0.01	40.50	0.31	0.62	0.02	14.57	0.09	8.10	0.10	0.21	0.02	91.12	0.19
6	CP9	0.08	0.01	35.92	0.31	0.87	0.02	10.56	0.09	9.41	0.10	20.02	0.40	95.14	0.19
6	CP10	0.06	0.01	36.96	0.31	0.77	0.02	10.04	0.09	8.94	0.10	0.66	0.02	105.24	0.19
7	CS1	0.62	0.14	40.17	0.13	13.40	0.18			9.08	0.11	0.20	0.02	90.79	2.77
7	CS2	0.04	0.14	47.39	0.13	1.48	0.18			8.10	0.11	0.11	0.02	97.84	2.77

Table A5. (cont.) Control cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
7	CS3	0.01	0.14	61.31	0.60	1.86	0.18			5.17	0.11	0.15	0.02	91.32	2.77
7	CS4	0.01*	0.14	45.42	0.13	2.06	0.18			3.46	0.11	0.14	0.02	81.80	2.77
7	CS5	0.09	0.14	59.74	0.60	2.77	0.18			4.78	0.11	0.20	0.02	94.37	2.77
7	CP1	0.08	0.14	51.70	0.60	0.34	0.03			11.72	0.11	0.08	0.02	104.50	2.77
7	CP2	0.03	0.14	33.70	0.13	0.70	0.03			7.59	0.11	0.02	<0.00	94.26	2.77
7	CP3	0.05	0.14	46.37	0.13	0.69	0.03			11.36	0.11	0.12	0.02	99.88	2.77
7	CP4	0.03	0.14	35.86	0.13	0.80	0.03			8.33	0.11	0.10	0.02	93.23	2.77
7	CP5	0.01	0.14	27.73	0.13	0.89	0.03			7.04	0.11	0.08	0.02	78.38	2.77
7	CP6	0.01*	0.14	33.87	0.13	0.85	0.03			8.13	0.11	0.08	0.02	85.77	2.77
7	CP7	0.04	0.14	35.27	0.13	0.67	0.03			8.42	0.11	0.09	0.02	83.16	2.77
7	CP8	0.04	0.14	38.77	0.13	0.54	0.03			8.03	0.11	0.33	0.02	94.75	2.77
7	CP9	0.04	0.14	36.12	0.13	0.72	0.03			9.06	0.11	4.61	1.07	100.80	2.77
7	CP10	0.04	0.14	40.49	0.13	0.40	0.03			9.68	0.11	0.02	0.02	109.40	2.77
8	CS1	0.04	0.01	35.46	0.31	1.32	0.07	12.79	0.09	8.45	0.10	0.14	0.02	105.60	1.87
8	CS2	0.07	0.01	46.35	0.31	1.07	0.02	11.20	0.09	7.77	0.10	0.12	0.02	108.50	1.87
8	CS3	0.10	0.01	56.16	0.31	0.72	0.02	8.32	0.09	4.38	0.10	0.12	0.02	99.44	1.87
8	CS4	0.06	0.01	40.65	0.31	0.94	0.02	7.70	0.09	3.12	0.10	0.11	0.02	86.71	1.87
8	CS5	0.11	0.01	53.71	0.31	1.95	0.07	9.40	0.09	4.20	0.10	0.17	0.02	100.50	1.87
8	CP1	0.08	0.01	42.56	0.31	0.32	0.02	13.11	0.09	10.96	0.10	0.07	0.02	113.30	1.87
8	CP2	0.07	0.01	35.94	0.31	0.45	0.02	7.06	0.09	8.35	0.10	0.01	0.02	105.50	1.87
8	CP3	0.08	0.01	39.68	0.31	0.33	0.02	16.06	0.09	10.52	0.10	0.11	0.02	109.20	1.87
8	CP4	0.05	0.01	34.48	0.31	0.53	0.02	8.15	0.09	8.27	0.10	0.05	0.02	104.50	1.87
8	CP5	0.04	0.01	29.22	0.31	0.57	0.02	9.07	0.09	7.01	0.10	0.09	0.02	82.92	1.87
8	CP6	0.06	0.01	31.69	0.31	0.40	0.02	8.05	0.09	7.73	0.10	0.02	0.02	90.84	1.87
8	CP7	0.07	0.01	35.69	0.31	0.48	0.02	11.79	0.09	8.44	0.10	0.02	0.02	90.56	1.87
8	CP8	0.06	0.01	34.52	0.31	0.40	0.02	13.87	0.09	7.63	0.10	0.26	0.02	101.90	1.87

Table A5. (cont.) Control cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
8	CP9	0.06	0.01	36.26	0.31	0.47	0.02	7.16	0.09	9.53	0.10	4.08	0.40	110.50	1.87
8	CP10	0.08	0.01	38.88	0.31	0.25	0.02	7.34	0.09	9.88	0.10	0.08	0.02	125.40	1.87
9	CS1	0.05	0.14	37.97	0.13	1.13	0.18			9.34	0.11	0.11	0.02	101.70	2.77
9	CS2	0.09	0.14	50.79	0.60	1.02	0.18			8.48	0.11	0.12	0.02	102.30	2.77
9	CS3	0.12	0.14	58.44	0.60	0.51	0.03			4.80	0.11	0.09	0.02	100.70	2.77
9	CS4	0.08	0.14	46.21	0.13	0.76	0.03			3.56	0.11	0.08	0.02	90.82	2.77
9	CS5	0.12	0.14	62.14	0.60	1.60	0.18			4.91	0.11	0.16	0.02	104.50	2.77
9	CP1	0.08	0.14	44.30	0.13	0.29	0.03			11.84	0.11	0.05	0.02	120.40	2.77
9	CP2	0.11	0.14	55.53	0.60	0.11	0.03			13.76	0.11	0.20	0.02	127.40	2.77
9	CP3	0.01*	0.14	51.74	0.60	0.64	0.03			11.96	0.11	0.04	0.02	116.20	2.77
9	CP4	0.10	0.14	56.78	0.60	0.17	0.03			13.73	0.11	0.42	0.02	119.90	2.77
9	CP5	0.02	0.14	30.28	0.13	0.52	0.03			7.82	0.11	0.09	0.02	84.73	2.77
9	CP6	0.06	0.14	36.09	0.13	0.30	0.03			8.91	0.11	0.04	<0.00	94.11	2.77
9	CP7	0.07	0.14	39.19	0.13	0.26	0.03			9.39	0.11	0.01	<0.00	91.26	2.77
9	CP8	0.06	0.14	38.47	0.13	0.25	0.03			8.49	0.11	0.08	0.02	107.90	2.77
9	CP9	0.05	0.14	55.79	0.60	1.13	0.18			13.58	0.11	3.15	1.07	120.60	2.77
9	CP10	0.14	0.14	70.30	0.60	0.10	0.03			17.51	0.11	0.08	0.02	148.90	2.77
10	CS1	0.01*	0.01	37.93	0.31	1.20	0.07	14.31	0.09	9.17	0.10	0.15	0.02	107.80	1.87
10	CS2	0.10	0.01	48.41	0.31	0.44	0.02	13.30	0.09	8.13	0.10	0.11	0.02	109.60	1.87
10	CS3	0.10	0.01	57.74	0.31	0.63	0.02	10.79	0.09	4.65	0.10	0.13	0.02	107.80	1.87
10	CS4	0.09	0.01	47.81	0.31	0.68	0.02	11.16	0.09	3.80	0.10	0.11	0.02	99.05	1.87
10	CS5	0.12	0.01	62.51	10.09	1.78	0.07	12.68	0.09	4.97	0.10	0.16	0.02	113.80	1.87
10	CP1	0.09	0.01	44.54	0.31	0.32	0.02	12.58	0.09	11.51	0.10	0.10	0.02	136.30	1.87
10	CP2	0.08	0.01	43.01	0.31	0.30	0.02	4.29	0.09	10.16	0.10	0.20	0.02	133.40	1.87
10	CP3	0.06	0.01	41.35	0.31	0.32	0.02	15.54	0.09	11.22	0.10	0.10	0.02	117.40	1.87
10	CP4	0.07	0.01	44.49	0.31	0.66	0.02	7.16	0.09	10.34	0.10	0.21	0.02	135.00	1.87

Table A5. (cont.) Control cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
10	CP5	0.03	0.01	26.89	0.31	0.77	0.02	9.10	0.09	6.96	0.10	0.10	0.02	84.97	1.87
10	CP6	0.05	0.01	32.02	0.31	0.40	0.02	7.24	0.09	8.17	0.10	0.02	0.02	98.20	1.87
10	CP7	0.08	0.01	40.37	0.31	0.46	0.02	12.76	0.09	9.61	0.10	0.02	0.02	102.10	1.87
10	CP8	0.08	0.01	39.75	0.31	0.37	0.02	13.30	0.09	10.39	0.10	0.01	0.02	122.60	1.87
10	CP9	0.06	0.01	38.74	0.31	0.25	0.02	3.04	0.09	9.10	0.10	0.03	0.02	131.60	1.87
10	CP10	0.10	0.01	53.77	0.31	0.15	0.02	4.24	0.09	12.59	0.10	0.03	0.02	159.70	1.87
11	CS1	0.50*	0.12	43.46	0.06	0.50*	0.18	16.59	0.10	11.01	0.36	0.17	<0.00	115.40	1.14
11	CS2	0.50*	0.12	58.54	0.64	0.50*	0.18	15.64	0.10	9.32	0.36	0.13	<0.00	115.10	1.14
11	CS3	0.50*	0.12	67.07	0.64	0.50*	0.18	12.97	0.10	5.43	0.36	0.15	<0.00	120.40	1.14
11	CS4	0.50*	0.12	58.00	0.64	0.50*	0.18	14.05	0.10	4.41	0.36	0.14	<0.00	115.00	1.14
11	CS5	0.50*	0.12	67.42	0.64	1.45	0.18	15.06	0.10	5.22	0.36	0.15	<0.00	119.90	1.14
11	CP1	0.50*	0.12	48.27	0.06	0.50*	0.18	12.70	0.10	12.10	0.36	0.12	<0.00	139.30	1.14
11	CP2	0.50*	0.12	37.37	0.06	0.50*	0.18	3.41	0.10	8.62	0.36	0.17	<0.00	135.90	1.14
11	CP3	0.50*	0.12	47.05	0.06	0.50*	0.18	16.72	0.10	12.44	0.36	0.12	<0.00	127.50	1.14
11	CP4	0.50*	0.12	36.42	0.06	0.50*	0.18	6.34	0.10	8.51	0.36	0.27	<0.00	131.70	1.14
11	CP5	0.50*	0.12	37.42	0.06	0.50*	0.18	12.05	0.10	9.78	0.36	0.12	<0.00	104.20	1.14
11	CP6	0.06	0.14	37.14	0.13	0.29	0.03			9.32	0.11	0.08	<0.00	98.11	2.77
11	CP7	0.10	0.14	50.29	0.60	0.27	0.03			12.78	0.11	0.01	<0.00	119.80	2.77
11	CP8	0.09	0.14	48.13	0.13	0.16	0.03			13.03	0.11	0.02	<0.00	128.90	2.77
11	CP9	0.04	0.14	31.43	0.13	0.20	0.03			7.78	0.11	0.02	<0.00	119.80	2.77
11	CP10	0.06	0.14	43.47	0.13	0.25	0.03			10.14	0.11	0.20	<0.00	141.30	2.77
12	CS1	0.06	0.01	34.87	0.31	0.58	0.02	15.53	0.09	8.63	0.10	0.10	0.02	115.30	1.87
12	CS2	0.12	0.01	57.77	0.31	0.10	0.02	16.29	0.09	9.66	0.10	0.09	0.02	123.90	1.87
12	CS3	0.12	0.01	57.25	0.31	0.43	0.02	13.49	0.09	4.75	0.10	0.09	0.02	120.10	1.87
12	CS4	0.10	0.01	45.54	0.31	0.69	0.02	13.69	0.09	3.53	0.10	0.11	0.02	111.20	1.87
12	CS5	0.11	0.01	53.64	0.31	1.34	0.07	16.13	0.09	4.42	0.10	0.12	0.02	125.70	1.87
12	CP1	0.07	0.01	39.80	0.31	0.20	0.02	12.96	0.09	10.35	0.10	0.07	0.02	144.90	1.87

Table A5. (cont.) Control cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
12	CP2	0.03	0.01	28.31	0.31	0.76	0.02	4.83	0.09	6.53	0.10	0.01	0.02	135.90	1.87
12	CP3	0.09	0.01	40.03	0.31	0.26	0.02	17.20	0.09	10.20	0.10	0.09	0.02	131.50	1.87
12	CP4	0.03	0.01	29.06	0.31	0.45	0.02	6.30	0.09	6.93	0.10	0.02	0.02	135.40	1.87
12	CP5	0.04	0.01	42.99	0.31	0.54	0.02	13.96	0.09	10.44	0.10	0.13	0.02	126.90	1.87
12	CP6	0.12	0.01	56.45	0.31	0.14	0.02	12.42	0.09	13.23	0.10	0.04	0.02	156.30	1.87
12	CP7	0.08	0.01	41.08	0.31	0.11	0.02	15.96	0.09	10.20	0.10	0.02	0.02	133.70	1.87
12	CP8	0.11	0.01	50.51	0.31	0.10	0.02	17.18	0.09	12.15	0.10	0.01	0.02	158.90	1.87
12	CP9	0.06	0.01	33.14	0.31	0.20	0.02	3.24	0.09	7.78	0.10	0.02	0.02	130.30	1.87
12	CP10	0.05	0.01	35.63	0.31	0.51	0.02	3.55	0.09	8.10	0.10	0.13	0.02	148.80	1.87
13	CS1	0.05	0.14	36.50	0.13	0.43	0.03			9.36	0.11	0.07	0.02	108.00	2.77
13	CS2	0.12	0.14	60.55	0.60	0.10	0.03			10.92	0.11	0.06	0.02	120.50	2.77
13	CS3	0.12	0.14	58.87	0.60	0.27	0.03			5.22	0.11	0.08	0.02	119.00	2.77
13	CS4	0.07	0.14	43.18	0.13	0.50	0.03			3.44	0.11	0.05	0.02	100.30	2.77
13	CS5	0.09	0.14	51.10	0.60	1.17	0.18			4.10	0.11	0.10	0.02	116.40	2.77
13	CP1	0.07	0.14	39.20	0.13	0.21	0.03			10.03	0.11	0.02	<0.00	133.20	2.77
13	CP2	0.04	0.14	33.71	0.13	0.59	0.03			8.17	0.11	0.01	<0.00	132.10	2.77
13	CP3	0.06	0.14	40.57	0.13	0.36	0.03			10.46	0.11	0.10	<0.00	116.40	2.77
13	CP4	0.05	0.14	32.57	0.13	0.28	0.03			7.86	0.11	0.02	<0.00	134.50	2.77
13	CP5	0.04	0.14	32.75	0.13	0.11	0.03			8.31	0.11	0.05	<0.00	114.80	2.77
13	CP6	0.08	0.14	45.21	0.13	0.27	0.03			10.95	0.11	0.02	<0.00	147.10	2.77
13	CP7	0.07	0.14	39.30	0.13	0.07	0.03			9.76	0.11	0.01	<0.00	125.40	2.77
13	CP8	0.10	0.14	48.30	0.13	0.08	0.03			11.93	0.11	0.01	<0.00	160.40	2.77
13	CP9	0.10	0.14	53.06	0.60	0.07	0.03			12.74	0.11	0.02	<0.00	152.50	2.77
13	CP10	0.05	0.14	35.73	0.13	0.50	0.03			8.01	0.11	0.01	<0.00	149.30	2.77

***Not all upper and lower detection limits are the same due to differences in standards and dilutions between instrument runs.

Table A6. Dissolved Mn treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
1	DMS1	0.28	0.15	80.49	3.50	0.05*	2.33			5.91	0.66	0.82	0.21	24.63	9.71
1	DMP1	0.51	0.15	125.30	3.50	0.05*	2.33			10.20	0.66	0.82	0.21	12.23	9.71
2	DMS1	0.13	0.07	62.32	2.97	0.46	0.04	8.09	0.98	5.33	0.90	0.41	0.19	39.40	0.95
2	DMS2	0.15	0.07	69.18	2.97	0.58	0.04	8.67	0.98	5.75	0.90	0.47	0.19	35.98	0.95
2	DMS3	0.13	0.07	58.20	2.97	0.54	0.04	6.31	0.98	4.95	0.90	0.38	0.19	45.24	0.95
2	DMS4	0.13	0.07	66.59	2.97	0.38	0.04	8.34	0.98	5.58	0.90	0.39	0.19	36.47	0.95
2	DMS5	0.11	0.07	54.57	2.97	0.27	0.04	7.57	0.98	4.70	0.90	0.26	0.19	40.32	0.95
2	DMP1	0.18	0.07	84.24	2.97	0.42	0.04	11.32	0.98	7.04	0.90	0.59	0.19	23.73	0.95
2	DMP2	0.15	0.07	71.92	2.97	0.68	0.04	12.00	0.98	6.16	0.90	0.48	0.19	32.05	0.95
2	DMP3	0.16	0.07	75.60	2.97	0.53	0.04	10.89	0.98	6.40	0.90	0.47	0.19	34.32	0.95
2	DMP4	0.14	0.07	68.42	2.97	1.10	0.77	9.24	0.98	5.61	0.90	0.39	0.19	39.21	0.95
2	DMP5	0.17	0.07	82.67	2.97	0.26	0.04	10.53	0.98	6.86	0.90	0.52	0.19	26.35	0.95
2	DMP6	0.14	0.07	68.30	2.97	1.03	0.77	8.94	0.98	5.54	0.90	0.54	0.19	35.03	0.95
2	DMP7	0.14	0.07	69.18	2.97	1.13	0.77	8.99	0.98	5.76	0.90	0.40	0.19	38.61	0.95
2	DMP8	0.14	0.07	69.27	2.97	1.33	0.77	9.74	0.98	5.73	0.90	0.47	0.19	33.18	0.95
2	DMP9	0.14	0.07	68.23	2.97	0.63	0.04	9.54	0.98	5.60	0.90	0.48	0.19	31.98	0.95
2	DMP10	0.14	0.07	71.37	2.97	0.68	0.04	10.88	0.98	6.05	0.90	0.46	0.19	29.43	0.95
3	DMS1	0.05*	0.15	59.35	3.50	0.05*	2.33			4.13	0.66	1.02	0.21	51.04	9.71
3	DMS2	0.21	0.15	68.53	3.50	0.05*	2.33			4.74	0.66	1.02	0.21	45.83	9.71
3	DMS3	0.19	0.15	59.84	3.50	0.05*	2.33			4.09	0.66	0.94	0.21	46.44	9.71
3	DMS4	0.16	0.15	56.46	3.50	0.05*	2.33			3.80	0.66	0.92	0.21	48.60	9.71
3	DMS5	0.23	0.15	71.56	3.50	0.05*	2.33			4.98	0.66	1.00	0.21	37.16	9.71
3	DMP1	0.21	0.15	65.09	3.50	0.05*	2.33			4.67	0.66	1.05	0.21	43.26	9.71
3	DMP2	0.37	0.15	110.50	3.50	0.05*	2.33			10.65	0.66	1.29	0.21	47.73	9.71
3	DMP3	0.20	0.15	62.00	3.50	0.05*	2.33			4.26	0.66	0.99	0.21	49.66	9.71
3	DMP4	0.28	0.15	80.49	3.50	0.05*	2.33			5.91	0.66	0.82	0.21	24.63	9.71

Table A6. (cont.) Dissolve Mn treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
3	DMP5	0.24	0.15	69.26	3.50	0.05*	2.33			4.73	0.66	1.02	0.21	35.83	9.71
3	DMP6	0.19	0.15	62.28	3.50	0.05*	2.33			4.23	0.66	0.98	0.21	45.38	9.71
3	DMP7	0.22	0.15	67.75	3.50	0.05*	2.33			4.66	0.66	1.04	0.21	52.90	9.71
3	DMP8	0.20	0.15	67.41	3.50	0.05*	2.33			4.59	0.66	1.01	0.21	37.81	9.71
3	DMP9	0.20	0.15	63.47	3.50	0.05*	2.33			4.35	0.66	11.79	0.21	41.97	9.71
3	DMP10	0.05*	0.15	58.89	3.50	0.05*	2.33			4.22	0.66	0.98	0.21	42.64	9.71
4	DMS1	0.18	0.07	89.40	2.97	1.75	0.77	6.61	0.98	7.80	0.90	0.42	0.19	75.81	10.39
4	DMS2	0.21	0.07	119.20	9.53	1.97	0.77	7.77	0.98	10.03	0.90	0.46	0.19	68.56	10.39
4	DMS3	0.08	0.07	50.81	2.97	1.58	0.77	5.11	0.98	4.54	0.90	0.34	0.19	64.53	10.39
4	DMS4	0.13	0.07	66.37	2.97	1.26	0.77	6.84	0.98	5.72	0.90	0.23	0.19	71.69	10.39
4	DMS5	0.10	0.07	51.32	2.97	0.39	0.04	5.97	0.98	4.51	0.90	0.19	0.19	68.18	10.39
4	DMP1	0.22	0.07	118.00	9.53	1.65	0.77	8.45	0.98	10.17	0.90	0.36	0.19	57.63	10.39
4	DMP2	0.11	0.07	55.69	2.97	1.50	0.77	8.15	0.98	4.94	0.90	0.27	0.19	52.39	10.39
4	DMP3	0.19	0.07	111.80	9.53	2.96	0.77	10.52	0.98	14.47	0.90	0.74	0.19	59.53	10.39
4	DMP4	0.10	0.07	55.80	2.97	1.48	0.77	7.24	0.98	4.65	0.90	0.25	0.19	61.30	10.39
4	DMP5	0.16	0.07	84.22	2.97	1.65	0.77	7.95	0.98	7.22	0.90	0.27	0.19	57.09	10.39
4	DMP6	0.10	0.07	53.27	2.97	1.41	0.77	6.10	0.98	4.67	0.90	0.20	0.19	63.61	10.39
4	DMP7	0.10	0.07	54.38	2.97	1.40	0.77	5.83	0.98	4.84	0.90	0.24	0.19	73.41	10.39
4	DMP8	0.10	0.07	55.66	2.97	1.48	0.77	7.52	0.98	4.91	0.90	0.26	0.19	49.59	10.39
4	DMP9	0.10	0.07	55.52	2.97	1.43	0.77	7.45	0.98	4.69	0.90	0.22	0.19	57.93	10.39
4	DMP10	0.10	0.07	55.46	2.97	1.81	0.77	6.47	0.98	4.71	0.90	0.23	0.19	57.40	10.39
5	DMS1	0.33	0.15	175.50	3.50	0.05*	2.33			13.43	4.55	1.33	0.21	108.00	17.25
5	DMS2	0.30	0.15	182.10	3.50	0.05*	2.33			13.61	4.55	1.26	0.21	90.27	17.25
5	DMS3	0.42	0.15	206.10	3.50	0.05*	2.33			15.32	4.55	1.51	0.21	105.90	17.25
5	DMS4	0.22	0.15	131.30	3.50	0.05*	2.33			9.56	4.55	1.05	0.21	102.30	17.25
5	DMS5	0.05*	0.15	83.33	3.50	0.05*	2.33			5.83	4.55	0.97	0.21	110.20	17.25

Table A6. (cont.) Dissolve Mn treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
5	DMP1	0.28	0.15	161.00	3.50	0.05*	2.33			12.18	4.55	0.52	0.21	80.46	17.25
5	DMP2	0.16	0.15	112.50	3.50	0.05*	2.33			8.27	4.55	0.55	0.21	93.00	17.25
5	DMP3	0.15	0.15	120.70	3.50	0.05*	2.33			9.33	4.55	0.53	0.21	97.26	17.25
5	DMP4	0.05*	0.15	80.02	3.50	0.05*	2.33			5.55	4.55	0.39	0.21	99.78	17.25
5	DMP5	0.26	0.15	152.60	3.50	0.05*	2.33			11.46	4.55	0.62	0.21	98.35	17.25
5	DMP6	0.11	0.15	98.73	3.50	0.05*	2.33			7.26	4.55	0.36	0.21	113.10	17.25
5	DMP7	0.13	0.15	99.05	3.50	0.05*	2.33			7.38	4.55	0.26	0.21	132.20	17.25
5	DMP8	0.13	0.15	98.52	3.50	0.05*	2.33			7.02	4.55	0.42	0.21		
5	DMP9	0.11	0.15	93.76	3.50	0.05*	2.33			6.79	4.55	0.44	0.21		
5	DMP10	0.05*	0.15	85.42	3.50	0.05*	2.33			5.83	4.55	0.37	0.21		
6	DMS1	0.25	0.07	161.30	9.53	0.25	0.04	10.55	0.98	13.28	0.90	0.47	0.19	99.62	10.39
6	DMS2	0.33	0.07	213.20	9.53	0.10	0.04	11.55	0.98	16.49	0.90	0.50	0.19	101.80	10.39
6	DMS3	0.30	0.07	178.30	9.53	0.09	0.04	10.46	0.98	13.52	0.90	3.03	0.19	101.90	10.39
6	DMS4	0.21	0.07	133.80	9.53	1.07	0.77	10.01	0.98	10.83	0.90	0.34	0.19	97.31	10.39
6	DMS5	0.20	0.07	110.70	9.53	0.52	0.04	10.14	0.98	8.73	0.90	0.26	0.19	106.60	10.39
6	DMP1	0.32	0.07	196.50	9.53	0.25	0.04	9.55	0.98	15.59	0.90	0.39	0.19	94.89	10.39
6	DMP2	0.31	0.07	183.90	9.53	0.39	0.04	10.90	0.98	14.90	0.90	0.50	0.19	98.11	10.39
6	DMP3	0.27	0.07	155.30	9.53	0.37	0.04	10.20	0.98	12.60	0.90	0.50	0.19	109.90	10.39
6	DMP4	0.22	0.07	123.40	9.53	1.61	0.77	4.28	0.98	9.95	0.90	0.35	0.19	110.20	10.39
6	DMP5	0.33	0.07	201.90	9.53	0.09	0.04	8.85	0.98	16.51	0.90	0.07	0.19	105.20	10.39
6	DMP6	0.24	0.07	138.50	9.53	0.72	0.04	5.10	0.98	11.46	0.90	0.29	0.19	124.00	10.39
6	DMP7	0.29	0.07	172.70	9.53	0.67	0.04	4.06	0.98	13.90	0.90	0.25	0.19	157.70	10.39
6	DMP8	0.31	0.07	190.70	9.53	1.45	0.77	8.52	0.98	15.06	0.90	0.49	0.19	93.85	10.39
6	DMP9	0.24	0.07	134.73	2.97	1.40	0.77	4.25	0.98	11.46	0.90	0.42	0.19	108.40	
6	DMP10	0.26	0.07	136.50	9.53	1.08	0.77	5.24	0.98	10.81	0.90	0.38	0.19	121.00	10.39
7	DMS1	0.31	0.15	192.30	3.50	0.05*	2.33			15.16	4.55	0.63	0.21		

Table A6. (cont.) Dissolve Mn treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
7	DMS2	0.43	0.15	227.00	3.50	0.05*	2.33			16.81	4.55	0.59	0.21	107.00	17.25
7	DMS3	0.31	0.15	173.90	3.50	0.05*	2.33			12.47	4.55	12.46	0.21	109.40	17.25
7	DMS4	0.31	0.15	178.20	3.50	0.05*	2.33			13.76	4.55	0.53	0.21	93.68	17.25
7	DMS5	0.16	0.15	130.60	3.50	0.05*	2.33			9.79	4.55	0.38	0.21	97.28	17.25
7	DMP1	0.32	0.15	188.40	3.50	0.05*	2.33			14.19	4.55	0.50	0.21	115.20	17.25
7	DMP2	0.54	0.15	275.60	3.50	0.05*	2.33			22.03	4.55	0.69	0.21	146.30	17.25
7	DMP3	0.24	0.15	163.50	3.50	0.05*	2.33			13.39	4.55	0.59	0.21		
7	DMP4	0.23	0.15	149.00	3.50	0.05*	2.33			11.21	4.55	0.45	0.21		
7	DMP5	0.39	0.15	216.60	3.50	0.05*	2.33			16.67	4.55	0.39	0.21	118.70	17.25
7	DMP6	0.24	0.15	154.40	3.50	0.05*	2.33			11.91	4.55	0.37	0.21	136.00	17.25
7	DMP7	0.30	0.15	176.80	3.50	0.05*	2.33			13.83	4.55	0.54	0.21	136.50	17.25
7	DMP8	0.54	0.15	278.20	3.50	0.05*	2.33			21.70	4.55	0.65	0.21		
7	DMP9	0.46	0.15	240.30	3.50	0.05*	2.33			18.58	4.55	0.72	0.21		
7	DMP10	0.42	0.15	254.50	3.50	0.05*	2.33			19.91	4.55	0.37	0.21	158.20	17.25
8	DMS1	0.30	0.07	167.00	9.53	0.15	0.04	13.28	0.98	14.04	0.90	0.44	0.19	91.54	10.39
8	DMS2	0.36	0.07	220.00	9.53	0.14	0.04	14.07	0.98	16.61	0.90	0.43	0.19	96.72	10.39
8	DMS3	0.31	0.07	165.30	9.53	0.21	0.04	12.68	0.98	12.65	0.90	16.65	0.19	92.60	10.39
8	DMS4	0.28	0.07	152.80	9.53	0.30	0.04	14.58	0.98	12.79	0.90	1.07	0.66	83.76	10.39
8	DMS5	0.24	0.07	126.40	9.53	0.40	0.04	18.40	0.98	10.75	0.90	0.30	0.19	87.28	10.39
8	DMP1	0.30	0.07	165.50	9.53	0.39	0.04	13.81	0.98	13.31	0.90	0.33	0.19	109.10	10.39
8	DMP2	0.40	0.07	244.10	9.53	0.09	0.04	19.52	0.98	21.22	0.90	0.17	0.19	128.40	10.39
8	DMP3	0.29	0.07	151.90	9.53	0.12	0.04	12.99	0.98	13.26	0.90	0.39	0.19	103.00	10.39
8	DMP4	0.30	0.07	163.90	9.53	1.28	0.77	8.02	0.98	13.56	0.90	0.28	0.19	108.70	10.39
8	DMP5	0.41	0.07	257.30	9.53	0.28	0.04	7.98	0.98	20.24	0.90	0.19	0.19	110.80	10.39
8	DMP6	0.30	0.07	176.40	9.53	0.21	0.04	5.54	0.98	14.16	0.90	0.25	0.19	119.60	10.39
8	DMP7	0.34	0.07	201.70	9.53	0.18	0.04	6.42	0.98	16.41	0.90	0.24	0.19	114.60	10.39

Table A6. (cont.) Dissolve Mn treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
8	DMP8	0.38	0.07	192.20	9.53	0.37	0.04	9.42	0.98	18.12	0.90	0.40	0.19	101.70	10.39
8	DMP9	0.33	0.07	191.10	9.53	0.62	0.04	4.41	0.98	15.34	0.90	0.41	0.19	100.60	10.39
8	DMP10	0.38	0.07	233.60	9.53	0.03	0.04	5.24	0.98	18.84	0.90	0.11	0.19	134.50	10.39
9	DMS1	0.36	0.15	191.80	3.50	0.05*	2.33			15.01	4.55	0.55	0.21	105.90	17.25
9	DMS2	0.33	0.15	194.80	3.50	0.05*	2.33			14.01	4.55	1.44	0.21	117.30	17.25
9	DMS3	0.31	0.15	174.30	3.50	0.05*	2.33			12.53	4.55	25.46	2.93	107.10	17.25
9	DMS4	0.23	0.15	150.70	3.50	0.05*	2.33			12.09	4.55	0.88	0.21	90.35	17.25
9	DMS5	0.17	0.15	126.90	3.50	0.05*	2.33			9.84	4.55	0.10	0.21	99.54	17.25
9	DMP1	0.45	0.15	260.50	3.50	0.05*	2.33			18.80	4.55	0.34	0.21	126.40	17.25
9	DMP2	0.49	0.15	261.20	3.50	0.05*	2.33			22.83	4.55	0.01		137.40	17.25
9	DMP3	0.25	0.15	150.50	3.50	0.05*	2.33			12.37	4.55	0.20	0.21	119.50	17.25
9	DMP4	0.20	0.15	168.90	3.50	0.05*	2.33			13.41	4.55	0.01		114.70	17.25
9	DMP5	0.59	0.15	305.10	3.50	0.05*	2.33			22.91	4.55	0.01		135.60	17.25
9	DMP6	0.34	0.15	185.20	3.50	0.05*	2.33			14.80	4.55	0.11	0.21	131.90	17.25
9	DMP7	0.31	0.15	196.90	3.50	0.05*	2.33			15.60	4.55	0.15	0.21	130.70	17.25
9	DMP8	0.48	0.15	254.20	3.50	0.05*	2.33			19.83	4.55	0.29	0.21	127.60	17.25
9	DMP9	0.32	0.15	185.40	3.50	0.05*	2.33			14.34	4.55	0.20	0.21	113.70	17.25
9	DMP10	0.65	0.15	322.70	3.50	0.05*	2.33			26.61	4.55	0.29	0.21	163.10	17.25
10	DMS1	0.31	0.07	175.20	9.53	0.10	0.04	12.47	0.98	14.88	0.90	0.43	0.19	90.14	10.39
10	DMS2	0.38	0.07	237.10	9.53	0.19	0.04	15.30	0.98	17.75	0.90	2.37	0.66	118.70	10.39
10	DMS3	0.27	0.07	139.70	9.53	0.25	0.04	11.84	0.98	11.07	0.90	15.09	0.66	104.10	10.39
10	DMS4	0.38	0.07	224.90	9.53	0.19	0.04	11.02	0.98	19.91	0.90	0.67	0.19	90.80	10.39
10	DMS5	0.27	0.07	151.50	9.53	0.21	0.04	12.84	0.98	12.27	0.90	0.21	0.19	101.20	10.39
10	DMP1	0.41	0.07	260.90	9.53	0.22	0.04	13.12	0.98	19.80	0.90	1.04	0.66	112.70	10.39
10	DMP2	0.41	0.07	266.90	9.53	0.03	0.04	15.88	0.98	23.16	0.90	0.53	0.19	132.90	10.39
10	DMP3	0.26	0.07	135.20	9.53	0.58	0.04	9.31	0.98	11.77	0.90	0.32	0.19	104.20	10.39

Table A6. (cont.) Dissolve Mn treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
10	DMP4	0.31	0.07	168.10	9.53	0.15	0.04	11.12	0.98	14.28	0.90	0.07	0.19	110.20	10.39
10	DMP5	0.48	0.07	332.60	9.53	0.22	0.04	6.60	0.98	25.25	0.90	0.53	0.19	124.00	10.39
10	DMP6	0.26	0.07	136.10	9.53	0.22	0.04	3.61	0.98	12.29	0.90	0.21	0.19	112.40	10.39
10	DMP7	0.26	0.07	137.90	9.53	0.15	0.04	3.50	0.98	11.78	0.90	0.20	0.19	104.80	10.39
10	DMP8	0.45	0.07	334.70	9.53	0.21	0.04	11.53	0.98	26.95	0.90	0.48	0.19	174.90	10.39
10	DMP9	0.50	0.07	375.80	9.53	0.18	0.04	17.53	0.98	36.00	0.90	0.70	0.19	179.50	10.39
10	DMP10	0.49	0.07	352.70	9.53	0.12	0.04	7.82	0.98	29.20	0.90	0.66	0.19	145.10	10.39
11	DMS1	0.50*	0.12	298.80	0.64	0.50*	0.18	16.06	0.10	26.21	0.36	0.58	0.00	114.70	1.14
11	DMS2	0.50*	0.12	221.20	0.64	0.50*	0.18	16.34	0.10	17.00	0.36	8.34	0.12	138.80	1.14
11	DMS3	0.50*	0.12	170.00	0.64	0.50*	0.18	13.76	0.10	13.74	0.36	19.59	0.12	127.40	1.14
11	DMS4	0.50*	0.12	290.80	0.64	0.50*	0.18	16.24	0.10	28.77	0.36	0.80	0.00	143.70	1.14
11	DMS5	0.50*	0.12	221.00	0.64	0.50*	0.18	15.82	0.10	19.84	0.36	0.19	0.00	122.80	1.14
11	DMP1	0.50*	0.12	213.70	0.64	0.50*	0.18	13.08	0.10	17.04	0.36	1.72	0.12	122.50	1.14
11	DMP2	0.50*	0.12	256.00	0.64	0.50*	0.18	17.46	0.10	22.55	0.36	0.75	0.00	145.00	1.14
11	DMP3	0.50*	0.12	204.20	0.64	0.50*	0.18	11.32	0.10	18.71	0.36	0.33	0.00	131.20	1.14
11	DMP4	0.50*	0.12	568.60	0.64	0.50*	0.18	21.28	0.10	45.32	0.36	12.11	0.12	151.30	1.14
11	DMP5	0.50*	0.12	306.10	0.64	0.50*	0.18	6.87	0.10	23.57	0.36	0.64	0.00	139.80	1.14
11	DMP6	0.44	0.15	233.80	3.50	0.05*	2.33			22.19	4.55	0.12	0.21	135.70	17.25
11	DMP7	0.70	0.15	347.80	3.50	0.05*	2.33			32.08	4.55	0.45	0.21	144.40	17.25
11	DMP8	0.64	0.15	322.60	3.50	0.05*	2.33			27.29	4.55	0.32	0.21	186.30	17.25
11	DMP9	0.45	0.15	241.10	3.50	0.05*	2.33			19.80	4.55	0.49	0.21	131.80	17.25
11	DMP10	0.33	0.15	269.30	3.50	0.05*	2.33			22.42	4.55	0.03	0.00	158.50	17.25
12	DMS1	0.40	0.07	260.30	9.53	0.03	0.04	15.16	0.98	20.58	0.90	2.41	0.66	109.00	10.39
12	DMS2	0.36	0.07	212.80	9.53	0.08	0.04	15.85	0.98	15.93	0.90	14.83	0.66	123.30	10.39
12	DMS3	0.33	0.07	185.80	9.53	0.45	0.04	12.73	0.98	15.30	0.90	17.98	0.66	107.20	10.39
12	DMS4	0.42	0.07	298.10	9.53	0.16	0.04	17.68	0.98	27.49	0.90	1.00	0.66	134.30	10.39
12	DMS5	0.37	0.07	335.50	9.53	0.12	0.04	15.34	0.98	20.93	0.90	0.20	0.19	153.60	10.39

Table A6. (cont.) Dissolve Mn treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Week	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
12	DMP1	0.32	0.07	188.70	9.53	0.07	0.04	12.79	0.98	14.72	0.90	6.59	0.66	118.80	10.39
12	DMP2	0.37	0.07	230.40	9.53	0.03	0.04	17.39	0.98	18.68	0.90	1.04	0.66	128.50	10.39
12	DMP3	0.34	0.07	200.70	9.53	0.04	0.04	12.94	0.98	17.71	0.90	0.46	0.19	125.70	10.39
12	DMP4	0.58	0.07	443.80	9.53	0.05	0.04	22.75	0.98	29.67	0.90	42.67	0.66	134.00	10.39
12	DMP5	0.38	0.07	253.20	9.53	0.02	0.04	7.70	0.98	18.69	0.90	0.80	0.19	142.00	10.39
12	DMP6	0.58	0.07	491.70	9.53	0.12	0.04	13.25	0.98	45.08	0.90	16.33	0.66	165.20	10.39
12	DMP7	0.51	0.07	366.00	9.53	0.19	0.04	14.90	0.98	35.00	0.90	21.75	0.66	138.90	10.39
12	DMP8	0.45	0.07	308.90	9.53	0.14	0.04	14.35	0.98	24.51	0.90	0.76	0.19	147.70	10.39
12	DMP9	0.38	0.07	229.00	9.53	0.19	0.04	14.92	0.98	18.15	0.90	1.35	0.66	120.60	10.39
12	DMP10	0.36	0.07	233.40	9.53	0.00	0.04	12.77	0.98	18.75	0.90	0.10	0.19	140.70	10.39
13	DMS1	0.36	0.15	210.20	3.50	0.05*	2.33			17.74	4.55	5.96	0.21	105.60	17.25
13	DMS2	0.33	0.15	177.50	3.50	0.05*	2.33			13.78	4.55	19.62	2.93	117.90	17.25
13	DMS3	0.25	0.15	150.20	3.50	0.05*	2.33			12.92	4.55	18.19	2.93	111.40	17.25
13	DMS4	0.49	0.15	250.00	3.50	0.05*	2.33			22.88	4.55	4.80	0.21	119.80	17.25
13	DMS5	0.40	0.15	222.30	3.50	0.05*	2.33			20.09	4.55	0.09	0.21	117.50	17.25
13	DMP1	0.32	0.15	197.60	3.50	0.05*	2.33			15.51	4.55	14.08	2.93	121.80	17.25
13	DMP2	0.48	0.15	240.00	3.50	0.05*	2.33			19.39	4.55	1.42	0.21	120.90	17.25
13	DMP3	0.27	0.15	180.30	3.50	0.05*	2.33			15.55	4.55	1.00	0.21	133.90	17.25
13	DMP4	0.61	0.15	293.70	3.50	0.05*	2.33			21.30	4.55	39.73	2.93	130.20	17.25
13	DMP5	0.53	0.15	271.50	3.50	0.05*	2.33			20.43	4.55	1.12	0.21	172.80	17.25
13	DMP6	0.70	0.15	336.70	3.50	0.05*	2.33			32.39	4.55	48.07	2.93	152.50	17.25
13	DMP7	0.40	0.15	207.30	3.50	0.05*	2.33			18.94	4.55	18.29	2.93	121.10	17.25
13	DMP8	0.62	0.15	298.00	3.50	0.05*	2.33			21.73	4.55	13.15	2.93	130.80	17.25
13	DMP9	0.38	0.15	198.80	3.50	0.05*	2.33			15.63	4.55	2.42	0.21	116.20	17.25
13	DMP10	0.43	0.15	221.60	3.50	0.05*	2.33			17.87	4.55	0.01	0.21	127.80	17.25

***Not all upper and lower detection limits are the same due to differences in standards and dilutions between instrument runs.

Table A7. Mn-oxide treatment cation concentrations in soil leachate each week (Wk). Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. **Value above detection (100 mg/L).

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
1	MOS1	0.05*	0.24	77.45	4.38	0.50*	0.06			5.93	0.88	0.20	0.00	25.33	17.25
1	MOP2	0.05*	0.24	83.84	4.38	0.50*	0.06			6.54	0.88	0.18	0.00	27.89	17.25
2	MOS1	0.05	0.07	69.34	2.97	0.36	0.04	12.48	1.03	5.83	0.75	2.91	0.73	35.47	1.06
2	MOS2	0.13	0.07	60.45	2.97	0.23	0.04	11.27	1.03	5.21	0.75	3.66	0.73	41.70	1.06
2	MOS3	0.13	0.07	63.59	2.97	0.01*	0.04	13.52	1.03	5.61	0.75	2.19	0.73	39.33	1.06
2	MOS4	0.15	0.07	64.90	2.97	0.14	0.04	12.44	1.03	5.60	0.75	3.64	0.73	37.95	1.06
2	MOS5	0.14	0.07	65.10	2.97	0.16	0.04	13.00	1.03	5.55	0.75	4.67	0.73	40.98	1.06
2	MOP1	0.12	0.07	64.99	2.97	0.09	0.04	24.94	1.03	12.42	0.75	3.24	0.73	51.48	1.06
2	MOP2	0.15	0.07	74.79	2.97	0.20	0.04	14.39	1.03	6.23	0.75	4.96	0.73	36.99	1.06
2	MOP3	0.13	0.07	64.34	2.97	0.10	0.04	12.48	1.03	5.35	0.75	3.65	0.73	39.81	1.06
2	MOP4	0.09	0.07	49.14	2.97	1.30	0.83	26.32	1.03	11.67	0.75	5.46	0.73	47.60	1.06
2	MOP5	0.09	0.07	48.76	2.97	0.47	0.04	32.89	1.03	12.04	0.75	3.72	0.73	44.49	1.06
2	MOP6	0.10	0.07	52.81	2.97	1.28	0.83	30.66	1.03	12.38	0.75	6.46	0.73	44.24	1.06
2	MOP7	0.17	0.07	78.37	2.97	0.47	0.04	13.95	1.03	6.38	0.75	4.33	0.73	39.07	1.06
2	MOP8	0.10	0.07	50.95	2.97	0.71	0.04	30.46	1.03	12.20	0.75	4.66	0.73	44.62	1.06
2	MOP9	0.08	0.07	47.70	0.90	1.20	0.83	28.20	1.03	11.16	0.75	4.16	0.73	49.36	1.06
2	MOP10	0.16	0.07	75.91	2.97	0.42	0.04	20.82	1.03	9.70	0.75	6.12	0.73	37.31	1.06
3	MOS1	0.05*	0.24	57.36	4.38	0.50*	0.06			4.07	0.88	2.70	0.36	48.71	17.25
3	MOS2	0.05*	0.24	57.16	4.38	0.50*	0.06			4.00	0.88	3.98	0.36	56.94	17.25
3	MOS3	0.05*	0.24	56.97	4.38	0.50*	0.06			4.16	0.88	2.66	0.36		
3	MOS4	0.05*	0.24	53.00	4.38	0.50*	0.06			3.76	0.88	3.19	0.36	54.76	17.25
3	MOS5	0.05*	0.24	54.70	4.38	0.50*	0.06			3.94	0.88	3.98	0.36		
3	MOP1	0.05*	0.24	44.75	4.38	0.50*	0.06			9.94	0.88	2.90	0.36	61.53	17.25
3	MOP2	0.05*	0.24	61.55	4.38	0.50*	0.06			4.42	0.88	3.07	0.36	49.28	17.25
3	MOP3	0.05*	0.24	52.11	4.38	0.50*	0.06			3.61	0.88	2.52	0.36	56.66	17.25
3	MOP4	0.05*	0.24	43.24	4.38	1.92	0.06			9.48	0.88	4.16	0.36	62.69	17.25

Table A7. (cont.) Mn-oxide treatment cation concentrations in soil leachate each week (Wk). Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. **Value above detection (100 mg/L).

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
3	MOP5	0.05*	0.24	38.51	4.38	0.50*	0.06			8.72	0.88	2.66	0.36	57.08	17.25
3	MOP6	0.05*	0.24	44.88	4.38	2.61	0.06			9.63	0.88	4.84	0.36	58.31	17.25
3	MOP7	0.05*	0.24	69.83	4.38	1.06	0.06			5.18	0.88	3.65	0.36	50.25	17.25
3	MOP8	0.05*	0.24	47.09	4.38	1.50	0.06			10.28	0.88	4.17	0.36	54.99	17.25
3	MOP9	0.05*	0.24	42.11	4.38	1.74	0.06			9.65	0.88	3.33	0.36	63.23	17.25
3	MOP10	0.05*	0.24	60.88	4.38	1.07	0.06			7.04	0.88	4.60	0.36		
4	MOS1	0.12	0.07	54.80	2.97	1.05	0.83	9.67	1.03	4.88	0.75	2.73	0.73	62.93	2.98
4	MOS2	0.12	0.07	56.52	2.97	1.42	0.83	8.18	1.03	4.90	0.75	4.21	0.73	68.71	2.98
4	MOS3	0.10	0.07	51.49	2.97	0.31	0.04	8.44	1.03	4.57	0.75	2.83	0.73	63.82	2.98
4	MOS4	0.09	0.07	49.70	0.90	0.54	0.04	8.60	1.03	4.51	0.75	3.33	0.73	64.53	2.98
4	MOS5	0.10	0.07	53.82	2.97	0.55	0.04	9.07	1.03	4.84	0.75	3.67	0.73	69.57	2.98
4	MOP1	0.07	0.07	39.56	0.90	0.25	0.04	18.27	1.03	9.42	0.75	3.14	0.73	63.29	2.98
4	MOP2	0.11	0.07	57.62	2.97	0.70	0.04	10.17	1.03	5.23	0.75	2.96	0.73	59.04	2.98
4	MOP3	0.09	0.07	44.18	0.90	0.27	0.04	8.05	1.03	4.07	0.75	2.30	0.73	61.98	2.98
4	MOP4	0.06	0.07	38.89	0.90	2.18	0.83	17.36	1.03	9.61	0.75	3.65	0.73	70.54	2.98
4	MOP5	0.05	0.07	33.91	0.90	0.41	0.04	16.94	1.03	8.82	0.75	2.60	0.73	62.99	2.98
4	MOP6	0.06	0.07	42.06	0.90	3.08	0.83	19.25	1.03	10.30	0.75	4.74	0.73	70.28	2.98
4	MOP7	0.09	0.07	62.01	2.97	1.36	0.83	10.29	1.03	5.73	0.75	3.41	0.73	56.99	2.98
4	MOP8	0.06	0.07	42.55	0.90	1.70	0.83	21.94	1.03	10.40	0.75	3.74	0.73	58.55	2.98
4	MOP9	0.06	0.07	40.22	0.90	2.02	0.83	17.38	1.03	10.77	0.75	3.42	0.73	78.94	2.98
4	MOP10	0.10	0.07	54.24	2.97	1.59	0.83	12.98	1.03	7.28	0.75	3.93	0.73	58.76	2.98
5	MOS1	0.05*	0.24	52.74	4.38	0.50*	0.06			3.77	0.88	1.99	0.36	81.48	17.25
5	MOS2	0.05*	0.24	53.17	4.38	1.18	0.06			3.55	0.88	3.28	0.36	84.29	17.25
5	MOS3	0.05*	0.24	48.77	4.38	0.50*	0.06			3.23	0.88	2.18	0.36	79.30	17.25
5	MOS4	0.05*	0.24	46.94	4.38	0.50*	0.06			3.17	0.88	2.51	0.36	80.51	17.25
5	MOS5	0.05*	0.24	51.06	4.38	0.50*	0.06			3.59	0.88	3.24	0.36	85.44	17.25

Table A7. (cont.) Mn-oxide treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. **Value above detection (100 mg/L).

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
5	MOP1	0.05*	0.24	32.06	4.38	0.50*	0.06			6.76	0.88	1.91	0.36	81.64	17.25
5	MOP2	0.05*	0.24	55.88	4.38	0.50*	0.06			3.97	0.88	2.11	0.36	75.30	17.25
5	MOP3	0.05*	0.24	40.00	4.38	0.50*	0.06			2.60	0.88	1.19	0.36	73.30	17.25
5	MOP4	0.05*	0.24	35.06	4.38	0.50*	0.06			7.91	0.88	1.75	0.36	83.44	17.25
5	MOP5	0.05*	0.24	34.84	4.38	0.50*	0.06			7.95	0.88	1.83	0.36	81.83	17.25
5	MOP6	0.05*	0.24	34.71	4.38	1.61	0.06			7.79	0.88	3.20	0.36	84.39	17.25
5	MOP7	0.05*	0.24	56.24	4.38	0.50*	0.06			4.17	0.88	2.30	0.36	71.77	17.25
5	MOP8	0.05*	0.24	39.11	4.38	0.50*	0.06			8.07	0.88	2.66	0.36	72.76	17.25
5	MOP9	0.05*	0.24	41.53	4.38	0.50*	0.06			8.28	0.88	2.30	0.36	95.52	17.25
5	MOP10	0.05*	0.24	45.71	4.38	0.50*	0.06			5.17	0.88	2.39	0.36	71.82	17.25
6	MOS1	0.07	0.07	47.16	0.90	0.52	0.04	7.69	1.03	4.23	0.75	2.08	0.73	84.40	2.98
6	MOS2	0.08	0.07	44.16	0.90	1.38	0.83	6.81	1.03	3.84	0.75	2.81	0.73	85.49	2.98
6	MOS3	0.08	0.07	41.22	0.90	0.43	0.04	6.77	1.03	3.58	0.75	2.35	0.73	81.51	2.98
6	MOS4	0.08	0.07	41.76	0.90	0.46	0.04	7.10	1.03	3.74	0.75	2.33	0.73	83.60	2.98
6	MOS5	0.07	0.07	41.47	0.90	0.49	0.04	6.70	1.03	3.79	0.75	2.45	0.73	84.54	2.98
6	MOP1	0.06	0.07	35.26	0.90	0.32	0.04	9.65	1.03	8.00	0.75	2.01	0.73	83.04	2.98
6	MOP2	0.11	0.07	54.86	2.97	0.43	0.04	6.51	1.03	4.88	0.75	2.30	0.73	84.63	2.98
6	MOP3	0.08	0.07	38.14	0.90	0.26	0.04	5.33	1.03	3.30	0.75	1.58	0.73	78.87	2.98
6	MOP4	0.06	0.07	34.62	0.90	0.56	0.04	11.84	1.03	8.92	0.75	2.32	0.73	87.11	2.98
6	MOP5	0.07	0.07	37.86	0.90	0.38	0.04	11.48	1.03	9.60	0.75	2.68	0.73	88.77	2.98
6	MOP6	0.05	0.07	35.26	0.90	1.68	0.83	11.39	1.03	9.04	0.75	3.15	0.73	93.05	2.98
6	MOP7	0.11	0.07	58.24	2.97	0.58	0.04	7.73	1.03	5.02	0.75	2.68	0.73	77.16	2.98
6	MOP8	0.06	0.07	38.65	0.90	1.24	0.83	16.08	1.03	9.47	0.75	3.04	0.73	77.52	2.98
6	MOP9	0.07	0.07	46.77	0.90	1.16	0.83	9.87	1.03	10.56	0.75	3.10	0.73	114.65 **	2.98
6	MOP10	0.08	0.07	41.84	0.90	0.69	0.04	8.42	1.03	5.78	0.75	2.47	0.73	77.10	2.98
7	MOS1	0.05*	0.24	45.59	4.38	0.50*	0.06			3.14	0.88	1.51	0.36		

Table A7. (cont.) Mn-oxide treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. **Value above detection (100 mg/L).

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
7	MOS2	0.05*	0.24	41.39	4.38	0.50*	0.06			2.66	0.88	2.28	0.36		
7	MOS3	0.05*	0.24	40.58	4.38	0.50*	0.06			2.60	0.88	1.92	0.36		
7	MOS4	0.05*	0.24	39.02	4.38	0.50*	0.06			2.54	0.88	1.85	0.36		
7	MOS5	0.05*	0.24	38.42	4.38	0.50*	0.06			2.53	0.88	1.99	0.36		
7	MOP1	0.05*	0.24	35.14	4.38	0.50*	0.06			7.60	0.88	1.50	0.36		
7	MOP2	0.05*	0.24	53.46	4.38	0.50*	0.06			3.67	0.88	1.81	0.36		
7	MOP3	0.05*	0.24	33.28	4.38	0.50*	0.06			2.03	0.88	0.89	0.36		
7	MOP4	0.05*	0.24	38.66	4.38	0.50*	0.06			8.63	0.88	1.70	0.36		
7	MOP5	0.05*	0.24	36.34	4.38	0.50*	0.06			8.24	0.88	1.81	0.36		
7	MOP6	0.05*	0.24	35.43	4.38	0.50*	0.06			7.63	0.88	2.10	0.36		
7	MOP7	0.05*	0.24	58.73	4.38	0.50*	0.06			3.87	0.88	1.74	0.36		
7	MOP8	0.05*	0.24	42.58	4.38	0.50*	0.06			9.30	0.88	2.64	0.36		
7	MOP9	0.05*	0.24	64.35	4.38	0.50*	0.06			12.11	5.32	4.24	0.36		
7	MOP10	0.05*	0.24	40.19	4.38	0.50*	0.06			4.65	0.88	1.74	0.36		
8	MOS1	0.08	0.07	42.88	0.90	0.37	0.04	8.51	1.03	3.77	0.75	1.74	0.73	90.99	2.98
8	MOS2	0.07	0.07	39.15	0.90	1.35	0.83	8.48	1.03	3.31	0.75	2.53	0.73	87.40	2.98
8	MOS3	0.06	0.07	39.28	0.90	0.58	0.04	8.80	1.03	3.38	0.75	2.22	0.73	90.49	2.98
8	MOS4	0.06	0.07	35.80	0.90	0.47	0.04	8.30	1.03	3.16	0.75	2.00	0.73	88.65	2.98
8	MOS5	0.06	0.07	35.79	0.90	0.61	0.04	7.83	1.03	3.22	0.75	2.05	0.73	87.83	2.98
8	MOP1	0.06	0.07	39.84	0.90	0.22	0.04	6.37	1.03	9.41	0.75	2.12	0.73	105**	2.98
8	MOP2	0.08	0.07	55.38	2.97	0.52	0.04	3.77	1.03	4.61	0.75	2.08	0.73	107**	2.98
8	MOP3	0.05	0.07	33.73	0.90	0.21	0.04	5.01	1.03	2.94	0.75	1.20	0.73	87.49	2.98
8	MOP4	0.07	0.07	40.56	0.90	0.33	0.04	9.11	1.03	9.58	0.75	1.57	0.73	99.95	2.98
8	MOP5	0.05	0.07	40.86	0.90	0.14	0.04	7.02	1.03	9.99	0.75	2.03	0.73	106**	2.98
8	MOP6	0.04	0.07	36.00	0.90	1.14	0.83	7.56	1.03	8.79	0.75	2.23	0.73	107**	2.98
8	MOP7	0.11	0.07	53.97	0.90	0.33	0.04	6.20	1.03	4.52	0.75	1.95	0.73	95.38	2.98

Table A7. (cont.) Mn-oxide treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. **Value above detection (100 mg/L).

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
8	MOP8	0.10	0.07	46.91	0.90	0.45	0.04	13.62	1.03	11.69	0.75	3.11	0.73	114**	2.98
8	MOP9	0.11	0.07	66.32	2.97	0.27	0.04	7.31	1.03	15.62	0.75	4.88	0.73	147**	2.98
8	MOP10	0.07	0.07	39.12	0.90	0.43	0.04	6.45	1.03	5.44	0.75	2.00	0.73	88.90	2.98
9	MOS1	0.05*	0.24	45.95	4.38	0.50*	0.06			3.15	0.88	1.43	0.36		
9	MOS2	0.05*	0.24	55.84	4.38	0.50*	0.06			3.76	0.88	1.71	0.36		
9	MOS3	0.05*	0.24	39.76	4.38	0.50*	0.06			2.68	0.88	1.66	0.36		
9	MOS4	0.05*	0.24	37.05	4.38	0.50*	0.06			2.35	0.88	1.37	0.36		
9	MOS5	0.05*	0.24	36.52	4.38	0.50*	0.06			2.38	0.88	1.54	0.36		
9	MOP1	0.05*	0.24	50.71	4.38	0.50*	0.06			10.41	5.32	2.86	0.36		
9	MOP2	0.05*	0.24	37.98	4.38	1.03	0.06			2.36	0.88	2.12	0.36		
9	MOP3	0.05*	0.24	55.15	4.38	0.50*	0.06			3.57	0.88	0.95	0.36		
9	MOP4	0.05*	0.24	42.07	4.38	0.50*	0.06			9.38	0.88	1.28	0.36		
9	MOP5														
9	MOP6	0.05*	0.24	39.33	4.38	0.50*	0.06			8.93	0.88	1.47	0.36		
9	MOP7	0.05*	0.24	63.27	4.38	0.50*	0.06			4.53	0.88	1.38	0.36		
9	MOP8	0.05*	0.24	47.47	4.38	0.50*	0.06			10.76	0.88	2.37	0.36		
9	MOP9	0.05*	0.24	96.89	4.38	0.50*	0.06			18.25	5.32	7.00	0.36		
9	MOP10	0.05*	0.24	41.64	4.38	3.14	0.06			4.70	0.88	1.39	0.36		
10	MOS1	0.08	0.07	43.61	0.90	0.48	0.04	9.59	1.03	3.96	0.75	1.75	0.73	99.53	2.98
10	MOS2	0.07	0.07	40.21	0.90	1.32	0.83	9.92	1.03	3.51	0.75	2.64	0.73	92.72	2.98
10	MOS3	0.07	0.07	37.01	0.90	0.57	0.04	9.19	1.03	3.41	0.75	2.08	0.73	92.48	2.98
10	MOS4	0.07	0.07	38.19	0.90	0.31	0.04	9.58	1.03	3.43	0.75	1.85	0.73	96.84	2.98
10	MOS5	0.05	0.07	36.76	0.90	1.02	0.83	9.47	1.03	3.40	0.75	1.97	0.73	89.44	2.98
10	MOP1	0.06	0.07	37.29	0.90	0.18	0.04	3.77	1.03	8.04	0.75	1.22	0.73	124**	2.98
10	MOP2	0.11	0.07	57.42	2.97	0.21	0.04	2.18	1.03	4.97	0.75	2.34	0.73	133**	2.98
10	MOP3	0.04	0.07	31.72	0.90	0.42	0.04	3.59	1.03	2.88	0.75	1.15	0.73	92.85	2.98

Table A7. (cont.) Mn-oxide treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. **Value above detection (100 mg/L).

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
10	MOP4	0.06	0.07	41.25	0.90	0.34	0.04	7.64	1.03	11.46	0.75	1.85	0.73	121**	2.98
10	MOP5	0.06	0.07	46.87	0.90	0.12	0.04	4.97	1.03	12.07	0.75	2.41	0.73	153**	2.98
10	MOP6	0.05	0.07	36.45	0.90	0.38	0.04	4.91	1.03	10.36	0.75	2.04	0.73	125**	2.98
10	MOP7	0.11	0.07	57.87	2.97	0.19	0.04	4.14	1.03	5.32	0.75	1.76	0.73	114**	2.98
10	MOP8	0.10	0.07	50.97	2.97	0.27	0.04	10.96	1.03	13.29	0.75	2.87	0.73	138**	2.98
10	MOP9	0.05	0.07	46.29	0.90	1.21	0.83	3.99	1.03	11.90	0.75	2.97	0.73	181**	2.98
10	MOP10	0.08	0.07	42.20	0.90	0.35	0.04	4.68	1.03	5.96	0.75	1.96	0.73	106**	2.98
11	MOS1	0.50*	0.12	44.85	0.06	0.50*	0.18	10.50	0.10	3.75	0.36	1.30	0.12	97.52	1.14
11	MOS2	0.50*	0.12	44.24	0.06	0.50*	0.18	11.00	0.10	3.53	0.36	2.43	0.12	94.31	1.14
11	MOS3	0.50*	0.12	40.84	0.06	0.50*	0.18	10.23	0.10	3.61	0.36	1.74	0.12	92.39	1.14
11	MOS4	0.50*	0.12	44.74	0.06	0.50*	0.18	10.56	0.10	3.59	0.36	1.64	0.12	100.80	1.14
11	MOS5	0.50*	0.12	42.91	0.06	0.50*	0.18	10.83	0.10	3.48	0.36	1.75	0.12	93.41	1.14
11	MOP1	0.50*	0.12	35.13	0.06	0.50*	0.18	3.01	0.10	8.09	0.36	0.70	0.00	130.10	1.14
11	MOP2	0.50*	0.12	54.28	0.64	0.50*	0.18	1.46	0.10	4.53	0.36	1.91	0.12	125.60	1.14
11	MOP3	0.50*	0.12	32.08	0.06	0.50*	0.18	3.10	0.10	2.61	0.36	1.02	0.00	96.54	1.14
11	MOP4	0.50*	0.12	47.31	0.06	0.50*	0.18	6.28	0.10	12.19	0.36	0.92	0.00	125.80	1.14
11	MOP5	0.50*	0.12	49.93	0.06	0.50*	0.18	2.41	0.10	12.58	0.36	1.27	0.12	165.20	1.14
11	MOP6	0.05*	0.24	36.01	4.38	0.50*	0.06			9.39	0.88	1.37	0.36		
11	MOP7	0.05*	0.24	59.00	4.38	0.50*	0.06			4.92	0.88	1.24	0.36		
11	MOP8	0.05*	0.24	65.11	4.38	0.50*	0.06			14.73	5.32	2.73	0.36		
11	MOP9	0.05*	0.24	32.08	4.38	0.50*	0.06			7.58	0.88	1.59	0.36		
11	MOP10	0.05*	0.24	41.64	4.38	0.50*	0.06			5.09	0.88	1.47	0.36		
12	MOS1	0.12	0.07	60.16	2.97	0.42	0.04	14.40	1.03	5.33	0.75	2.09	0.73	126**	2.98
12	MOS2	0.08	0.07	41.28	0.90	0.51	0.04	12.96	1.03	3.78	0.75	2.35	0.73	102**	2.98
12	MOS3	0.07	0.07	36.78	0.90	0.55	0.04	9.46	1.03	3.35	0.75	1.85	0.73	95.56	2.98
12	MOS4	0.09	0.07	44.04	0.90	0.23	0.04	11.79	1.03	3.91	0.75	1.85	0.73	110**	2.98
12	MOS5	0.08	0.07	40.00	0.90	0.37	0.04	11.82	1.03	3.69	0.75	2.05	0.73	98.09	2.98

Table A7. (cont.) Mn-oxide treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. **Value above detection (100 mg/L).

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
12	MOP1	0.06	0.07	34.76	0.90	0.10	0.04	5.44	1.03	8.17	0.75	0.48	0.22	139**	2.98
12	MOP2	0.09	0.07	46.73	0.90	0.21	0.04	2.20	1.03	4.21	0.75	1.98	0.73	131**	2.98
12	MOP3	0.07	0.07	38.96	0.90	0.15	0.04	4.22	1.03	3.50	0.75	0.74	0.22	106**	2.98
12	MOP4	0.07	0.07	40.57	0.90	0.23	0.04	5.65	1.03	10.43	0.75	0.23	0.22	142**	2.98
12	MOP5	0.07	0.07	38.45	0.90	0.29	0.04	1.71	1.03	9.57	0.75	1.40	0.73	174**	2.98
12	MOP6	0.06	0.07	37.38	0.90	0.28	0.04	4.72	1.03	10.02	0.75	1.60	0.73	132**	2.98
12	MOP7	0.12	0.07	62.33	2.97	0.36	0.04	3.43	1.03	5.86	0.75	1.64	0.73	130**	2.98
12	MOP8	0.11	0.07	60.52	2.97	0.30	0.04	10.21	1.03	15.05	0.75	2.10	0.73	202**	2.98
12	MOP9	0.02	0.07	27.80	0.90	0.69	0.04	4.37	1.03	7.04	0.75	1.64	0.73	146**	2.98
12	MOP10	0.06	0.07	42.75	0.90	1.13	0.83	3.99	1.03	5.79	0.75	1.71	0.73	118**	2.98
13	MOS1	0.05*	0.24	58.42	4.38	0.50*	0.06			4.31	0.88	1.50	0.36		
13	MOS2	0.05*	0.24	44.66	4.38	0.50*	0.06			3.23	0.88	1.99	0.36		
13	MOS3	0.05*	0.24	37.97	4.38	0.50*	0.06			2.68	0.88	1.46	0.36		
13	MOS4	0.05*	0.24	45.03	4.38	0.50*	0.06			3.10	0.88	1.43	0.36		
13	MOS5	0.05*	0.24	44.12	4.38	0.50*	0.06			3.20	0.88	1.51	0.36		
13	MOP1	0.05*	0.24	32.81	4.38	0.50*	0.06			7.17	0.88	0.41	0.00		
13	MOP2	0.05*	0.24	50.63	4.38	0.50*	0.06			3.61	0.88	1.65	0.36		
13	MOP3	0.05*	0.24	34.31	4.38	0.50*	0.06			2.33	0.88	0.41	0.00		
13	MOP4	0.05*	0.24	45.58	4.38	0.50*	0.06			10.75	0.88	0.26	0.00		
13	MOP5	0.05*	0.24	34.20	4.38	0.50*	0.06			7.72	0.88	0.58	0.36		
13	MOP6	0.05*	0.24	40.66	4.38	0.50*	0.06			10.14	0.88	1.05	0.36		
13	MOP7	0.05*	0.24	74.73	4.38	0.50*	0.06			6.09	0.88	1.28	0.36		
13	MOP8	0.05*	0.24	54.69	4.38	0.50*	0.06			11.52	5.32	2.03	0.36		
13	MOP9	0.05*	0.24	27.13	4.38	0.50*	0.06			6.56	0.88	1.00	0.36		
13	MOP10	0.05*	0.24	44.20	4.38	0.50*	0.06			5.27	0.88	1.27	0.36		

***Not all upper and lower detection limits are the same due to differences in standards and dilutions between instrument runs.

Table A8. Shale treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. Value above detection: 100**, 500^{o}, or $1000^{\#}$ mg/L.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
1	SS1	5.00*	1.25	549.92	9.53			24.66	0.36	101.20	19.66	2.84	0.12	49.47	10.39
1	SP1	5.00*	1.25	353.30	19.35			21.96	0.36	58.53	19.66	1.20	0.12	30.74	19.66
2	SS1	5.44	0.31	667.62	14.43	34.30	9.55	12.79	0.13	82.37	3.69	4.47	0.09	56.77	4.59
2	SS2	0.06	0.09	711.69	14.43	5.00*	9.55	13.57	0.13	74.60	3.69	2.55	0.09	53.42	4.59
2	SS3	0.51	0.09	636.22	14.43	5.00*	9.55	18.42	0.13	82.67	3.69	1.91	0.09	71.85	4.59
2	SS4	0.57	0.09	796.80	14.43	5.00*	9.55	14.96	0.13	103.85	3.69	2.73	0.09	75.07	4.59
2	SS5	0.65	0.09	792.17	14.43	5.00*	9.55	18.08	0.13	122**	3.69	2.68	0.09	60.92	4.59
2	SP1	0.56	0.09	651.90	14.43	5.00*	9.55	22.55	0.13	97.69	3.69	2.20	0.09	76.36	4.59
2	SP2	0.51	0.09	571.79	14.43	5.00*	9.55	24.44	0.13	91.56	3.69	1.76	0.09	75.65	4.59
2	SP3	0.46	0.09	510.94	14.43	5.00*	9.55	21.42	0.13	79.80	3.69	1.95	0.09	59.21	4.59
2	SP4	0.45	0.09	529.91	14.43	5.00*	9.55	20.25	0.13	87.91	3.69	1.88	0.09	54.50	4.59
2	SP5	0.54	0.09	615.52	14.43	5.00*	9.55	18.92	0.13	101.23	3.69	2.10	0.09	72.36	4.59
2	SP6	0.53	0.09	625.53	14.43	5.00*	9.55	19.30	0.13	105.63	3.69	1.90	0.09	60.76	4.59
2	SP7	0.48	0.09	584.60	14.43	5.00*	9.55	19.87	0.13	102.84	3.69	1.99	0.09	71.24	4.59
2	SP8	0.48	0.09	629.59	14.43	5.00*	9.55	22.87	0.13	105.91	3.69	1.98	0.09	95.78	4.59
2	SP9	0.45	0.09	675.45	14.43	5.00*	9.55	20.51	0.13	102.87	3.69	2.14	0.09	65.11	4.59
2	SP10			617.13	14.43	5.00*	9.55								
3	SS1	30.70		725.49	9.53			12.67	0.36	102.70	19.66	8.44	0.12	75.42	10.39
3	SS2	5.00*	1.25	750.77	9.53			23.12	0.36	112.30	19.66	4.73	0.12	70.62	10.39
3	SS3	5.00*	1.25	728.81	9.53			20.35	0.36	101.50	19.66	3.88	0.12	74.11	10.39
3	SS4	5.00*	1.25	716.26	9.53			20.64	0.36	129.90	19.66	6.66	0.12	85.52	10.39
3	SS5	5.00*	1.25	774.86	9.53			20.27	0.36	123.10	19.66	4.96	0.12	80.53	10.39
3	SP1	5.00*	1.25	748.00	9.53			24.54	0.36	113.00	19.66	3.94	0.12	76.21	10.39
3	SP2	5.00*	1.25	734.04	9.53			25.19	0.36	112.70	19.66	3.44	0.12	77.77	10.39
3	SP3	5.00*	1.25	668.71	9.53			23.35	0.36	95.15	19.66	3.71	0.12	72.69	10.39
3	SP4	5.00*	1.25	712.31	9.53			22.87	0.36	109.60	19.66	3.34	0.12	77.04	10.39

Table A8. (cont.) Shale treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. Value above detection: 100**, 500^{o}, or $1000^{\#}$ mg/L.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
3	SP5	5.00*	1.25	741.64	9.53			25.51	0.36	114.40	19.66	3.56	0.12	76.83	10.39
3	SP6	5.00*	1.25	791.33	9.53			22.49	0.36	120.30	19.66	3.59	0.12	75.15	10.39
3	SP7	5.00*	1.25	743.95	9.53			23.15	0.36	110.00	19.66	3.54	0.12	74.19	10.39
3	SP8	5.00*	1.25	665.98	9.53			24.40	0.36	101.60	19.66	3.22	0.12	70.12	10.39
3	SP9	5.00*	1.25	709.98	9.53			22.47	0.36	104.10	19.66	4.11	0.12	68.04	10.39
3	SP10	5.00*	1.25	761.91	9.53			22.34	0.36	106.90	19.66	4.48	0.12	71.15	10.39
4	SS1	25.80	0.31	677.07	14.43	327.90	9.55	9.28	0.13	111.70	1.20	6.88	0.09	93.14	4.59
4	SS2	9.51	0.31	824.29	14.43	68.83	9.55	21.30	0.13	200.60	1.20	11.15	0.09	105.97	4.59
4	SS3	0.39	0.09	819.93	14.43	3.26	0.02	18.12	0.13	130.70	1.20	5.31	0.09	91.12	4.59
4	SS4	49.94	0.31	746.51	14.43	59.79	1.20	17.05	0.13	141.40	1.20	12.14	0.09	106.54	4.59
4	SS5	19.54	0.31	773.95	14.43	49.13	1.20	15.65	0.13	138.10	1.20	16.16	0.09	108.52	4.59
4	SP1	0.99	0.09	737.61	14.43	5.67	0.23	18.10	0.13	133.00	1.20	5.66	0.09	101.66	4.59
4	SP2	5.33	0.31	763.15	14.43	1.05	0.23	23.90	0.13	135.20	1.20	3.78	0.09	93.23	4.59
4	SP3	28.46	0.31	760.60	14.43	2.48	0.23	23.30	0.13	128.10	1.20	5.26	0.09	124.40	0.84
4	SP4	0.12	0.09	768.38	14.43	1.19	0.23	23.12	0.13	130.00	1.20	4.74	0.09	108.91	4.59
4	SP5	0.62	0.09	778.50	14.43	0.49	0.23	15.74	0.13	132.10	1.20	4.33	0.09	100.58	4.59
4	SP6	0.14	0.09	779.29	14.43	0.87	0.23	20.47	0.13	132.80	1.20	4.67	0.09	103.20	0.84
4	SP7	0.53	0.09	763.48	14.43	1.89	0.23	21.17	0.13	119.50	1.20	4.12	0.09	87.68	4.59
4	SP8	0.60	0.09	783.65	14.43	1.65	0.23	27.40	0.13	131.90	1.20	4.01	0.09	96.78	4.59
4	SP9	0.60	0.09	665.82	14.43	8.96	0.23	22.47	0.13	104.00	1.20	7.38	0.09	90.35	4.59
4	SP10	0.44	0.09	776.46	14.43	2.97	0.23	23.31	0.13	127.90	1.20	5.73	0.09	96.12	4.59
5	SS1	32.74	1.25	600.57	13.56	458.80	1.20	11.06	1.20	97.03	1.20	7.81	0.12	102.80	0.84
5	SS2	114.60	1.25	613.10	13.56	730.71	8.34	14.86	1.20	130.00	1.20	14.94	0.12	108.10	0.84
5	SS3	1.59	0.28	745.57	13.56	96.74	1.20	20.11	1.20	98.56	1.20	16.79	0.12	109.80	0.84
5	SS4	155.60	1.25	633.94	13.56	928.90	8.34	14.16	1.20	112.50	1.20	14.92	0.12	107.80	0.84
5	SS5	137.10	1.25	601.24	13.56	724.00	8.34	16.47	1.20	95.56	1.20	13.56	0.12	98.87	0.84

Table A8. (cont.) Shale treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. Value above detection: 100**, 500^{o}, or 1000$^{\#}$ mg/L.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
5	SP1	10.52	1.25	807.46	13.56	33.47	1.20	21.66	1.20	105.60	1.20	15.08	0.12	104.10	0.84
5	SP2	34.40	1.25	729.64	13.56	96.26	1.20	26.09	1.20	114.10	1.20	14.73	0.12	107.80	0.84
5	SP3	0.05*	0.28	729.86	13.56	11.47	1.20	30.46	1.20	144.90	1.20	7.78	0.12	168.40	0.84
5	SP4	106.60	1.25	631.64	13.56	556.19	8.34	23.29	1.20	161.30	1.20	18.29	0.12	219.90	0.84
5	SP5	40.46	1.25	707.66	13.56	201.10	1.20	22.48	1.20	127.80	1.20	19.24	0.12	136.10	0.84
5	SP6	0.44	0.28	797.45	13.56	4.44	0.23	20.41	1.20	127.20	1.20	12.97	0.12	116.30	0.84
5	SP7	1.17	0.28	784.71	13.56	7.76	0.23	24.65	1.20	111.00	1.20	10.36	0.12	104.50	0.84
5	SP8	1.22	0.28	789.07	13.56	1.37	0.23	28.24	1.20	119.90	1.20	6.63	0.12	111.20	0.84
5	SP9	33.03	1.25	679.15	13.56	328.60	1.20	22.56	1.20	102.40	1.20	12.77	0.12	103.70	0.84
5	SP10	63.48	1.25	688.47	13.56	252.90	1.20	21.48	1.20	109.00	1.20	13.80	0.12	130.00	0.84
6	SS1	38.61	0.31	606.68	14.43	587.04	8.34	8.06	0.13	92.53	1.20	7.31	0.09	112.60	0.84
6	SS2	143.60	1.53	584.33	14.43	$1622^{\#}$	8.34	8.08	0.13	105.50	1.20	11.70	0.09	104.60	0.84
6	SS3	159.40	1.53	611.55	14.43	937.13	8.34	11.69	0.13	84.66	1.20	10.24	0.09	113.90	0.84
6	SS4	162.60	1.53	594.62	14.43	$1989^{\#}$	8.34	2.87	0.13	88.88	1.20	10.95	0.09	113.60	0.84
6	SS5	139.80	1.53	587.37	14.43	$1635^{\#}$	8.34	6.63	0.13	77.72	1.20	10.33	0.09	96.01	0.84
6	SP1	157.00	1.53	620.99	14.43	973.35	8.34	11.99	0.13	74.23	1.20	10.83	0.09	101.00	0.84
6	SP2	150.40	1.53	602.03	14.43	1149.6	8.34	14.30	0.13	115.80	1.20	12.20	0.09	127.80	0.84
6	SP3	57.14	0.31	694.10	14.43	260.90	1.20	18.67	0.13	122.90	1.20	12.56	0.09	165.40	0.84
6	SP4	90.14	0.31	565.35	14.43	821.82	8.34	11.60	0.13	106.90	1.20	10.48	0.09	139.20	0.84
6	SP5	151.60	1.53	580.34	14.43	1064.8	8.34	12.87	0.13	115.20	1.20	12.53	0.09	134.70	0.84
6	SP6	177.90	1.53	622.21	14.43	659.03	8.34	12.29	0.13	91.27	1.20	13.37	0.09	111.70	0.84
6	SP7	144.30	1.53	663.05	14.43	627.24	8.34	12.34	0.13	82.39	1.20	10.23	0.09	111.30	0.84
6	SP8	120.40	1.53	605.80	14.43	467.60	1.20	17.43	0.13	94.55	1.20	12.76	0.09	113.60	0.84
6	SP9	125.10	1.53	593.08	14.43	936.49	8.34	12.08	0.13	89.38	1.20	7.75	0.09	100.20	0.84
6	SP10	102.13	0.31	624.62	14.43	939.10	8.34	12.40	0.13	120.10	1.20	10.76	0.09	149.70	0.84
7	SS1	47.51	1.25	558.00	9.30	583.50	6.00	9.76	1.15	89.75	11.30	8.55	0.12	105.70	4.25

Table A8. (cont.) Shale treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. Value above detection: 100**, 500^{o}, or $1000^{\#}$ mg/L.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
7	SS2	131.30	1.25	559.50	9.30	1774.0	6.00	8.83	1.15	97.25	11.30	11.77	0.12	109.00	4.25
7	SS3	105.90	1.25	566.00	9.30	1308.0	6.00	10.57	1.15	83.95	11.30	10.22	0.12	116.20	4.25
7	SS4	94.55	1.25	572.50	9.30	2135.5	6.00	2.55	1.15	57.30	11.30	6.87	0.12	114.05	4.25
7	SS5	95.74	1.25	568.00	9.30	1844.0	6.00	5.77	1.15	46.74	1.30	6.92	0.12	89.95	4.25
7	SP1	125.00	1.25	576.50	9.30	1381.0	6.00	11.30	1.15	66.90	11.30	9.94	0.12	98.75	4.25
7	SP2	132.80	1.25	569.50	9.30	1243.5	6.00	14.60	1.15	123.60	11.30	11.27	0.12	137.85	4.25
7	SP3	64.65	1.25	608.50	9.30	399.20	6.00	15.61	1.15	104.00	11.30	11.11	0.12	140.80	4.25
7	SP4	72.45	1.25	561.50	9.30	1011.5	6.00	10.44	1.15	98.55	11.30	10.03	0.12	125.95	4.25
7	SP5	124.00	1.25	557.50	9.30	1525.5	6.00	12.66	1.15	114.30	11.30	12.67	0.12	150.20	4.25
7	SP6	123.30	1.25	566.00	9.30	1220.5	6.00	9.13	1.15	68.20	11.30	9.97	0.12	101.95	4.25
7	SP7	84.55	1.25	570.00	9.30	930.50	6.00	10.59	1.15	85.95	11.30	9.08	0.12	124.55	4.25
7	SP8	117.40	1.25	564.50	9.30	1034.0	6.00	12.44	1.15	78.40	11.30	9.70	0.12	121.90	4.25
7	SP9	95.38	1.25	555.50	9.30	1036.0	6.00	13.50	1.15	92.95	11.30	10.86	0.12	102.20	4.25
7	SP10	91.14	1.25	571.50	9.30	990.50	6.00	13.84	1.15	107.20	11.30	10.41	0.12	139.80	4.25
8	SS1	48.91	0.31	556.00	9.30	663.00	6.00	9.31	1.15	77.35	11.30	6.00	0.09	117.75	4.25
8	SS2	122.40	7.65	566.50	9.30	1767.0	6.00	8.88	1.15	85.90	11.30	7.56	0.09	111.40	4.25
8	SS3	113.30	7.65	555.00	9.30	1335.0	6.00	8.93	1.15	81.90	11.30	8.31	0.09	113.85	4.25
8	SS4	58.77	0.31	574.00	9.30	1979.0	6.00	1.91	1.15	54.70	11.30	4.03	0.09	115.10	4.25
8	SS5	58.53	0.31	534.50	9.30	1519.0	6.00	4.05	1.15	35.42	1.30	3.46	0.09	85.80	4.25
8	SP1	131.05	7.65	581.50	9.30	1496.5	6.00	6.80	1.15	64.00	11.30	6.94	0.09	98.75	4.25
8	SP2	127.10	7.65	550.50	9.30	1197.0	6.00	10.60	1.15	113.85	11.30	8.71	0.09	128.60	4.25
8	SP3	78.83	0.31	575.00	9.30	698.00	6.00	13.01	1.15	93.20	11.30	7.25	0.09	125.15	4.25
8	SP4	82.81	0.31	556.00	9.30	1233.0	6.00	7.69	1.15	99.00	11.30	8.12	0.09	115.25	4.25
8	SP5	131.70	7.65	584.00	9.30	1615.0	6.00	7.95	1.15	106.45	11.30	8.68	0.09	147.60	4.25
8	SP6	99.22	0.31	570.50	9.30	1302.5	6.00	6.17	1.15	60.10	11.30	6.06	0.09	98.10	4.25
8	SP7	62.12	0.31	554.50	9.30	885.00	6.00	8.37	1.15	81.10	11.30	6.60	0.09	110.20	4.25

Table A8. (cont.) Shale treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. Value above detection: 100**, 500^{o}, or $1000^{\#}$ mg/L.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
8	SP8	84.83	0.31	560.50	9.30	1054.5	6.00	8.62	1.15	94.05	11.30	8.09	0.09	128.55	4.25
8	SP9	100.21	0.31	572.00	9.30	1399.0	6.00	12.78	1.15	93.75	11.30	8.08	0.09	114.10	4.25
8	SP10	87.83	0.31	580.00	9.30	1464.0	6.00	10.41	1.15	102.85	11.30	8.27	0.09	133.15	4.25
9	SS1	79.15	1.25	564^{0}	19.35			8.52	0.36	66.49	19.66	7.20	0.12	110.60	19.66
9	SS2	96.00	1.25	601^{0}	19.35			5.45	0.36	64.68	19.66	7.23	0.12	108.50	19.66
9	SS3	97.92	1.25	550^{0}	19.35			6.66	0.36	60.91	19.66	8.17	0.12	104.00	19.66
9	SS4	56.24	1.25	547^{0}	19.35			0.96	0.36	43.98	19.66	4.56	0.12	108.80	19.66
9	SS5	43.48	1.25	445.10	19.35			2.59	0.36	21.87	19.66	3.10	0.12	81.28	19.66
9	SP1	86.65	1.25	574^{0}	19.35			4.35	0.36	38.16	19.66	5.79	0.12	90.35	19.66
9	SP2	148.00	1.25	588^{0}	19.35			5.27	0.36	110.30	19.66	13.99	0.12	120.20	19.66
9	SP3	109.80	1.25	587^{0}	19.35			12.37	0.36	107.90	19.66	10.59	0.12	154.60	19.66
9	SP4	129.40	1.25	586^{0}	19.35			5.34	0.36	103.40	19.66	13.99	0.12	111.10	19.66
9	SP5	124.90	1.25	597^{0}	19.35			5.62	0.36	83.34	19.66	10.66	0.12	129.00	19.66
9	SP6	74.50	1.25	584^{0}	19.35			3.50	0.36	36.75	19.66	5.36	0.12	91.55	19.66
9	SP7	82.06	1.25	588^{0}	19.35			8.07	0.36	85.07	19.66	11.65	0.12	108.70	19.66
9	SP8	120.20	1.25	591^{0}	19.35			6.46	0.36	97.51	19.66	13.32	0.12	126.70	19.66
9	SP9	136.60	1.25	588^{0}	19.35			8.65	0.36	88.72	19.66	12.17	0.12	114.90	19.66
9	SP10	153.00	1.25	595^{0}	19.35			9.75	0.36	112.00	19.66	13.79	0.12	130.50	19.66
10	SS1	79.07	0.31	542.03	14.43	930.84	11.11	5.00	0.13	46.73	3.69	4.18	0.09	113**	4.59
10	SS2	45.09	0.31	563.86	14.43	$1386^{\#}$	11.11	2.45	0.13	34.71	3.69	2.81	0.09	99.68	4.59
10	SS3	47.65	0.31	462.10	19.63	$1153^{\#}$	11.11	3.66	0.13	34.78	3.69	3.09	0.09	100.92	4.59
10	SS4	25.95	0.31	389.00	19.63	$1150^{\#}$	11.11	0.85	0.09	29.17	3.69	2.01	0.09	102.42	4.59
10	SS5	16.08	0.31	246.30	19.63	800.50	11.11	1.69	0.13	16.31	3.69	1.22	0.09	78.13	4.59
10	SP1	23.75	0.31	388.80	19.63	857.46	11.11	1.84	0.13	20.07	3.69	1.57	0.09	82.74	4.59
10	SP2	108.82	0.31	552.94	14.43	$1554^{\#}$	11.11	2.93	0.13	78.15	3.69	7.19	0.09	123**	4.59
10	SP3	104.94	0.31	547.52	14.43	971.79	11.11	10.24	0.13	108.29	3.69	8.27	0.09	171**	4.59

Table A8. (cont.) Shale treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. Value above detection: 100**, 500^{o}, or $1000^{\#}$ mg/L.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
10	SP4	109.26	0.31	557.23	14.43	$1554^{\#}$	11.11	3.31	0.13	66.56	3.69	5.99	0.09	125**	4.59
10	SP5	69.78	0.31	538.47	14.43	$1431^{\#}$	11.11	3.24	0.13	55.11	3.69	4.05	0.09	132**	4.59
10	SP6	24.23	0.31	381.60	19.63	832.04	11.11	1.15	0.13	19.94	3.69	1.64	0.09	83.55	4.59
10	SP7	103.70	0.31	553.26	14.43	934.14	11.11	4.42	0.13	79.37	3.69	8.12	0.09	104.74	4.59
10	SP8	123**	0.31	546.34	14.43	$1330^{\#}$	11.11	3.31	0.13	76.22	3.69	7.25	0.09	122**	4.59
10	SP9	118**	0.31	541.52	14.43	$1771^{\#}$	11.11	4.80	0.13	74.81	3.69	6.68	0.09	127**	4.59
10	SP10	113**	0.31	543.26	14.43	$1774^{\#}$	11.11	4.82	0.13	66.27	3.69	5.26	0.09	123**	4.59
11	SS1	44.17	0.12	509^{0}	0.64	729^{0}	1.80	5.47	0.10	37.42	0.36	2.82	0.12	132.80	1.14
11	SS2	33.38	0.12	540^{0}	0.64	1026^{0}	1.80	2.30	0.10	37.07	0.36	2.48	0.12	106.00	1.14
11	SS3	32.65	0.12	333.50	0.64	831^{0}	1.80	3.10	0.10	38.04	0.36	2.53	0.12	111.20	1.14
11	SS4	19.30	0.12	257.00	0.64	678^{0}	1.80	1.02	0.10	29.60	0.36	1.63	0.12	103.10	1.14
11	SS5	14.05	0.12	114.80	0.64	608^{0}	1.80	2.45	0.10	17.47	0.36	1.15	0.12	83.68	1.14
11	SP1	15.33	0.12	222.50	0.64	576^{0}	1.80	2.36	0.10	18.38	0.36	1.18	0.12	83.75	1.14
11	SP2	61.68	0.12	549^{0}	0.64	1358^{0}	1.80	2.70	0.10	53.19	0.36	4.52	0.12	127.00	1.14
11	SP3	92.62	1.19	493.70	0.64	680^{0}	1.80	12.50	0.10	91.64	0.36	10.69	0.12	143.70	1.14
11	SP4	40.98	0.12	580^{0}	0.64	1066^{0}	1.80	3.77	0.10	38.07	0.36	2.44	0.12	135.90	1.14
11	SP5	37.27	0.12	464.10	0.64	933^{0}	1.80	2.24	0.10	42.48	0.36	2.70	0.12	126.10	1.14
11	SP6	19.94	1.25	206.30	19.35			1.41	0.36	13.74	19.66	1.62	0.12	82.98	19.66
11	SP7	72.59	1.25	553^{0}	19.35			5.29	0.36	45.33	19.66	4.68	0.12	112.20	19.66
11	SP8	68.12	1.25	570^{0}	19.35			3.18	0.36	53.73	19.66	4.67	0.12	131.20	19.66
11	SP9	58.90	1.25	528^{0}	19.35			5.54	0.36	58.13	19.66	4.60	0.12	149.20	19.66
11	SP10	47.14	1.25	601^{0}	19.35			5.29	0.36	48.20	19.66	3.25	0.12	141.60	19.66
12	SS1	13.39	0.31	390.60	19.63	487.90	9.55	5.36	0.13	30.80	3.69	1.29	0.09	148**	4.59
12	SS2	24.14	0.31	289.30	19.63	842.83	11.11	1.98	0.13	37.60	3.69	1.92	0.09	123**	4.59
12	SS3	15.58	0.31	164.10	19.63	495.60	9.55	2.68	0.13	28.38	3.69	1.39	0.09	116**	4.59
12	SS4	10.92	0.31	159.00	19.63	550.80	11.11	2.96	0.13	21.75	3.69	1.23	0.09	100.68	4.59
12	SS5	7.98	0.31	76.06	19.63	493.90	9.55	2.55	0.13	12.50	3.69	0.83	0.06	75.61	4.59

Table A8. (cont.) Shale treatment cation concentrations in soil leachate each week. Error represents the analytical error calculated from quality assurance standards. *Value below detection, reported as half the detection limit. Value above detection: 100**, 500^{o}, or $1000^{\#}$ mg/L.

		Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
Wk	Sample	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
12	SP1	7.95	0.31	113.30	19.63	441.50	9.55	2.40	0.13	12.57	3.69	0.87	0.06	77.21	4.59
12	SP2	18.33	0.31	521.34	14.43	798.78	11.11	1.94	0.13	26.54	3.69	1.32	0.09	117**	4.59
12	SP3	42.37	0.31	544.79	14.43	584.37	11.11	6.80	0.13	35.80	3.69	2.28	0.09	127**	4.59
12	SP4	11.39	0.31	522.15	14.43	640.71	11.11	2.96	0.13	19.88	3.69	1.13	0.09	109.90	4.59
12	SP5	13.86	0.31	293.20	19.63	590.14	11.11	2.24	0.13	24.97	3.69	1.08	0.09	115**	4.59
12	SP6	12.69	0.31	124.00	19.63	613.05	11.11	2.18	0.13	17.25	3.69	1.07	0.09	83.75	4.59
12	SP7	20.70	0.31	508.40	19.63	678.34	11.11	3.13	0.13	27.94	3.69	1.48	0.09	103.17	4.59
12	SP8	20.59	0.31	485.00	19.63	746.92	11.11	2.19	0.13	30.82	3.69	1.47	0.09	121**	4.59
12	SP9	20.81	0.31	453.50	19.63	823.32	11.11	4.58	0.13	41.86	3.69	1.91	0.09	150**	4.59
12	SP10	16.27	0.31	541.28	14.43	786.75	11.11	3.58	0.13	33.01	3.69	1.49	0.09	126**	4.59
13	SS1	11.33	1.25	246.20	19.35			6.67	0.36	29.33	19.66	1.38	0.12	125.10	19.66
13	SS2	19.82	1.25	183.60	19.35			3.18	0.36	27.48	19.66	1.72	0.12	110.90	19.66
13	SS3	12.19	1.25	95.07	19.35			4.41	0.36	18.75	19.66	1.23	0.12	108.00	19.66
13	SS4	13.64	1.25	156.60	19.35			3.45	0.36	21.05	19.66	1.14	0.12	103.00	19.66
13	SS5	5.00*	1.25	65.60	19.35			3.55	0.36	5.00	19.66	0.43	0.11	77.71	19.66
13	SP1	5.00*	1.25	69.54	19.35			3.59	0.36	5.00	19.66	0.52	0.11	80.00	19.66
13	SP2	13.24	1.25	428.40	19.35			4.78	0.36	21.69	19.66	1.38	0.12	117.30	19.66
13	SP3	34.38	1.25	527^{0}	19.35			8.09	0.36	33.55	19.66	2.07	0.12	126.40	19.66
13	SP4	5.00*	1.25	445.80	19.35			4.82	0.36	14.49	19.66	0.59	0.11	105.10	19.66
13	SP5	12.77	1.25	218.70	19.35			3.55	0.36	18.85	19.66	1.04	0.12	108.60	19.66
13	SP6	11.57	1.25	93.32	19.35			3.10	0.36	11.68	19.66	0.62	0.11	89.38	19.66
13	SP7	17.06	1.25	316.80	19.35			4.11	0.36	24.76	19.66	1.57	0.12	103.10	19.66
13	SP8	15.64	1.25	348.60	19.35			3.31	0.36	23.21	19.66	1.33	0.12	112.10	19.66
13	SP9	17.18	1.25	414.70	19.35			8.25	0.36	42.48	19.66	2.00	0.12	177.70	19.66
13	SP10	13.57	1.25	303.00	19.35			6.70	0.36	24.36	19.66	1.46	0.12	117.10	19.66

***Not all upper and lower detection limits are the same due to differences in standards and dilutions between instrument runs.

Table A9. Exchangeable cation concentration in initial soil for all treatments and final soil for the dissolved Mn treatment. Initial soil samples each had three replicates. Total volume of liquid was 0.019 L per one gram of sampled soil. Error represents the analytical error calculated from quality assurance standards.

	Sample	Al (mg/L)		Ca (mg/L)		Fe (mg/L)		K (mg/L)		Mg (mg/L)		Mn (mg/L)		Na (mg/L)	
		Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
Initial	Control/Dissolved Mn	0.09	0.03	34.61	0.19	<0.01	0.02	3.86	3.86	4.00	0.23	0.02	0.05	1.44	0.08
	Control/Dissolved Mn	0.07	0.03	29.06	0.19	<0.01	0.02	3.08	3.08	3.37	0.23	0.01	0.05	1.15	0.08
	Control/Dissolved Mn	0.07	0.03	30.24	0.19	<0.01	0.02	2.86	2.86	3.53	0.23	<0.01	0.05	1.09	0.08
	Mn-oxide	0.09	0.03	34.04	0.19	<0.01	0.02	2.66	2.66	3.89	0.23	0.72	0.05	1.15	0.08
	Mn-oxide	0.06	0.03	23.83	0.19	<0.01	0.02	2.09	2.09	2.67	0.23	0.63	0.05	0.81	0.03
	Mn-oxide	0.09	0.03	35.46	0.19	<0.01	0.02	2.57	2.57	3.98	0.23	0.76	0.05	1.12	0.08
	Shale	1.97	0.15	31.56	0.19	6.72	0.12	0.78	0.78	3.79	0.23	0.28	0.05	0.81	0.03
	Shale	1.65	0.15	26.79	0.19	6.81	0.12	0.75	0.75	3.42	0.23	0.25	0.05	0.78	0.03
	Shale	1.66	0.15	31.02	0.19	6.25	0.12	0.89	0.86	3.81	0.23	0.30	0.05	0.91	0.03
Final	DMS1	0.25	0.01	47.31	0.18	<0.1	<0.1	0.44	0.02	2.36	0.03	17.41	0.11	3.56	0.03
	DMS2	0.16	0.01	33.74	0.18	<0.1	<0.1	0.19	0.02	1.68	0.03	12.22	0.11	2.25	0.03
	DMS3	0.16	0.01	34.19	0.18	<0.1	<0.1	0.09	0.02	2.04	0.03	13.09	0.11	2.51	0.03
	DMS4	0.13	0.01	40.36	0.18	<0.1	<0.1	0.36	0.02	1.79	0.03	14.02	0.01	2.64	0.03
	DMS5	0.16	0.01	37.18	0.18	<0.1	<0.1	0.22	0.02	1.74	0.03	11.79	0.11	1.92	0.03
	DMP1	0.17	0.01	36.16	0.18	<0.1	<0.1	0.14	0.02	1.82	0.03	11.94	0.11	2.30	0.03
	DMP2	0.22	0.01	44.35	0.18	<0.1	<0.1	0.30	0.02	2.17	0.03	13.65	0.11	2.83	0.03
	DMP3	0.22	0.01	43.89	0.18	<0.1	<0.1	0.21	0.02	1.93	0.03	13.52	0.11	2.46	0.03
	DMP4	0.25	0.01	44.55	0.18	<0.1	<0.1	0.31	0.02	2.29	0.03	14.89	0.11	2.98	0.03
	DMP5	0.20	0.01	30.86	0.18	<0.1	<0.1	0.11	0.02	1.53	0.03	11.66	0.11	2.00	0.03
	DMP6	0.18	0.01	44.67	0.18	<0.1	<0.1	0.27	0.02	2.18	0.03	15.30	0.11	2.45	0.03
	DMP7	0.18	0.01	42.93	0.18	<0.1	<0.1	0.16	0.02	1.87	0.03	12.82	0.11	1.90	0.03
	DMP8	0.18	0.01	36.41	0.18	<0.1	<0.1	0.18	0.02	1.90	0.03	10.10	0.11	2.44	0.03
	DMP9	0.14	0.01	36.16	0.18	<0.1	<0.1	0.19	0.02	1.68	0.03	10.74	0.11	1.90	0.03
	DMP10	0.18	0.01	41.10	0.18	<0.1	<0.1	0.14	0.02	1.91	0.03	10.42	0.11	1.94	0.03

Table A10. Anion concentrations in soil leachate for each treatment. Error represents the analytical error calculated from quality assurance standards.

Week	1				2				6				10				13			
Anion	Cl$^-$ (mg/L)		SO$_4^{2-}$ (mg/L)		Cl$^-$ (mg/L)		SO$_4^{2-}$ (mg/L)		Cl$^-$ (mg/L)		SO$_4^{2-}$ (mg/L)		Cl$^-$ (mg/L)		SO$_4^{2-}$ (mg/L)		Cl$^-$ (mg/L)		SO$_4^{2-}$ (mg/L)	
	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
CS1	102.4	0.2	132.3	0.3	93.0	0.2	78.0	0.3	135.0	0.1	85.4	0.2	141.9	0.1	90.1	0.3	144.2	0.1	85.2	0.3
CS2					86.0	0.2	67.0	0.3	140.5	0.1	85.1	0.2	142.1	0.1	50.8	0.3	174.3	0.1	28.2	0.3
CS3					90.7	0.2	48.1	0.3	140.5	0.1	49.5	0.2	157.4	0.1	76.1	0.3	167.8	0.1	99.4	0.3
CS4					87.9	0.2	45.5	0.3	116.3	0.1	56.9	0.2	136.1	0.1	76.9	0.3	124.5	0.1	88.8	0.3
CS5					89.2	0.2	67.2	0.3	148.3	0.1	66.3	0.2	160.2	0.1	79.0	0.3	146.8	0.1	97.5	0.3
CP1	101.5	0.2	135.3	0.3	95.1	0.2	47.5	0.3	151.2	0.1	65.4	0.2	177.2	0.1	104.3	0.3	183.2	0.1	97.8	0.3
CP2					96.0	0.2	30.8	0.3	136.8	0.1	61.2	0.2	181.2	0.1	155.7	0.3	182.2	0.1	71.2	0.3
CP3					89.5	0.2	34.2	0.3	160.6	0.1	77.0	0.2	163.0	0.1	83.6	0.3	150.8	0.1	101.8	0.3
CP4					90.7	0.2	27.6	0.3	121.6	0.1	61.1	0.2	190.8	0.1	151.3	0.3	185.3	0.1	105.3	0.3
CP5					89.2	0.2	34.6	0.3	117.2	0.1	43.4	0.2	111.9	0.1	53.0	0.3	160.9	0.1	94.9	0.3
CP6					90.6	0.2	29.7	0.3	116.9	0.1	40.6	0.2	125.8	0.1	71.0	0.3	221.9	0.1	71.9	0.3
CP7					95.1	0.2	35.1	0.3	128.6	0.1	31.8	0.2	145.6	0.1	51.2	0.3	144.5	0.1	81.1	0.3
CP8					96.7	0.2	42.2	0.3	144.3	0.1	60.4	0.2	169.5	0.1	63.0	0.3	227.9	0.1	89.7	0.3
CP9					90.0	0.2	31.0	0.3	178.7	0.1	79.5	0.2	170.3	0.1	151.1	0.3	213.2	0.1	232.4	0.3
CP10					89.6	0.2	23.7	0.3	144.9	0.1	45.6	0.2	56.4	0.1	51.2	0.3	213.5	0.1	231.9	0.3
DMS1	86.7	0.2	95.2	0.3	89.8	0.2	63.6	0.3	456.1	0.1	75.3	0.2	420.0	0.1	78.4	0.3	533.0	0.1	108.6	0.3
DMS2					87.1	0.2	52.2	0.3	560.4	0.1	70.4	0.2	587.4	0.1	74.0	0.3	478.8	0.1	118.7	0.3
DMS3									430.3	0.1	83.9	0.2	380.6	0.1	85.7	0.3	388.6	0.1	110.4	0.3
DMS4					88.6	0.2	47.4	0.3	364.8	0.1	55.4	0.2	586.5	0.1	73.0	0.3	643.3	0.1	92.1	0.3
DMS5					86.7	0.2	86.5	0.3	315.6	0.1	82.1	0.2	387.7	0.1	91.9	0.3	595.1	0.1	100.7	0.3
DMP1	88.5	0.2	133.2	0.3	88.1	0.2	31.1	0.3	521.9	0.1	46.8	0.2	722.2	0.1	70.4	0.3	515.7	0.1	113.2	0.3
DMP2					90.0	0.2	47.0	0.3	471.2	0.1	44.1	0.2	699.3	0.1	113.5	0.3	596.3	0.1	113.6	0.3
DMP3					94.9	0.2	59.1	0.3	431.4	0.1	79.8	0.2	358.2	0.1	105.5	0.3	494.2	0.1	133.4	0.3
DMP4					91.7	0.2	38.9	0.3	357.5	0.1	58.9	0.2	453.6	0.1	56.8	0.3	798.1	0.1	85.2	0.3
DMP5					87.6	0.2	44.0	0.3	524.9	0.1	65.3	0.2	829.4	0.1	48.8	0.3	760.1	0.1	90.2	0.3
DMP6					88.4	0.2	35.6	0.4	402.4	0.1	65.4	0.2	402.9	0.1	91.9	0.3	875.0	0.1	107.7	0.3
DMP7					91.0	0.2	21.0	0.4	502.9	0.1	66.7	0.2	363.6	0.1	101.5	0.3	523.1	0.1	92.0	0.3
DMP8					90.0	0.2	24.7	0.4	490.1	0.1	52.3	0.2	947.6	0.1	80.3	0.3	702.9	0.1	86.3	0.3
DMP9					89.8	0.2	28.4	0.4	412.1	0.1	67.8	0.2	1106.8	0.1	90.9	0.3	466.4	0.1	94.3	0.3
DMP10					88.2	0.2	22.6	0.4	384.5	0.1	43.1	0.2	933.0	0.1	53.2	0.3	516.0	0.1	91.4	0.3

Table A10. (cont.) Anion concentrations in soil leachate for each treatment measured with IC. Error represents the analytical error calculated from quality assurance standards.

Week	1				2				6				10				13			
Anion	Cl^- (mg/L)		SO_4^{2-} (mg/L)		Cl^- (mg/L)		SO_4^{2-} (mg/L)		Cl^- (mg/L)		SO_4^{2-} (mg/L)		Cl^- (mg/L)		SO_4^{2-} (mg/L)		Cl^- (mg/L)		SO_4^{2-} (mg/L)	
	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
MOS1	87.4	0.2	98.6	0.3	94.4	0.2	59.0	0.4	133.1	0.1	99.4	0.2	132.2	0.1	50.0	0.2	196.6	0.1	85.2	0.2
MOS2					91.1	0.2	66.7	0.4	121.2	0.1	63.9	0.2	121.2	0.1	57.8	0.2	156.2	0.1	69.6	0.2
MOS3									120.0	0.1	80.6	0.2	128.3	0.1	94.8	0.2	128.0	0.1	80.3	0.2
MOS4					89.1	0.2	75.9	0.4	122.1	0.1	87.3	0.2	128.5	0.1	75.6	0.2	149.8	0.1	71.1	0.2
MOS5					92.7	0.2	60.3	0.4	120.9	0.1	72.6	0.2	115.2	0.1	65.0	0.2	144.8	0.1	56.6	0.2
MOP1									113.4	0.1	46.3	0.2	164.1	0.1	94.4	0.2				
MOP2	83.5	0.2	101.8	0.3	88.0	0.2	33.9	0.4	137.2	0.1	70.6	0.2	185.0	0.1	127.7	0.2	184.1	0.1	111.8	0.2
MOP3					89.5	0.2	42.0	0.4	110.6	0.1	77.7	0.2	121.8	0.1	96.2	0.2	142.2	0.1	120.3	0.2
MOP4					90.2	0.2	33.4	0.4	123.0	0.1	46.2	0.2	173.8	0.1	90.5	0.2	232.1	0.1	86.9	0.2
MOP5					92.3	0.2	55.5	0.4	124.4	0.1	94.2	0.2					205.1	0.1	123.3	0.2
MOP6					88.6	0.2	42.0	0.4	124.8	0.1	46.3	0.2	171.2	0.1	82.2	0.2	201.3	0.1	85.4	0.2
MOP7					87.7	0.2	65.5	0.4	125.7	0.1	52.5	0.2	161.7	0.1	62.9	0.2	247.4	0.1	82.7	0.2
MOP8					88.3	0.2	66.4	0.4	113.0	0.1	46.6	0.2	210.7	0.1	40.3	0.2	245.9	0.1	63.1	0.2
MOP9					90.5	0.2	23.3	0.4	153.4	0.1	98.0	0.2	235.8	0.1	168.2	0.2	176.4	0.1	76.8	0.2
MOP10					90.8	0.2	35.8	0.4	111.6	0.1	64.3	0.2	144.4	0.1	90.5	0.2	179.6	0.1	90.0	0.2
SS1	94.5	0.2	1979	0.3	87.5	0.2	2591	0.4	87.3	0.1	8274	0.2	89.0	0.1	9715	0.2	139.1	0.2	6716	0.2
SS2					75.7	0.2	2093	0.4	53.3	0.1	13911	0.2	60.4	0.1	14686	0.2	121.2	0.2	9052	0.2
SS3					77.9	0.2	2136	0.4	57.6	0.1	9443	0.2	64.0	0.1	14908	0.2	131.5	0.2	7519	0.2
SS4					72.4	0.2	1950	0.4	33.4	0.1	17335	0.2	75.2	0.1	13642	0.2	129.3	0.2	8523	0.2
SS5					81.5	0.2	2035	0.4	40.6	0.1	15860	0.2	73.8	0.1	8941	0.2	96.8	0.2	7655	0.2
SP1	85.4	0.2	1201	0.3	77.7	0.2	2095	0.4	44.2	0.1	9583	0.2	67.0	0.1	11991	0.2	93.9	0.2	7039	0.2
SP2					74.9	0.2	1896	0.4	54.6	0.1	9801	0.2	78.9	0.1	15217	0.2	139.4	0.2	10160	0.2
SP3					80.1	0.2	1728	0.4	105.5	0.1	6530	0.2	108.0	0.1	13364	0.2	130.4	0.2	9577	0.2
SP4					76.8	0.2	1670	0.4	89.8	0.1	9013	0.2	84.3	0.1	15163	0.2	124.2	0.2	9710	0.2
SP5									67.3	0.1	13390	0.2	83.6	0.1	15601	0.2	126.2	0.2	9469	0.2
SP6					78.5	0.2	2155	0.4	59.1	0.1	9183	0.2	76.1	0.1	12332	0.2	104.5	0.2	8103	0.2
SP7					77.3	0.2	1938	0.4	61.2	0.1	8456	0.2	71.3	0.1	12971	0.2	125.4	0.2	8836	0.2
SP8					85.9	0.2	2186	0.4	63.9	0.1	7932	0.2	76.6	0.1	14858	0.2	142.2	0.2	9544	0.2
SP9					13.3	0.2	386	0.4	62.5	0.1	9965	0.2	65.5	0.1	17118	0.2	145.3	0.2	9808	0.2
SP10					76.5	0.2	2026	0.4	99.2	0.1	9925	0.2	62.2	0.1	17014	0.2	130.6	0.2	9916	0.2

Appendix B – Rhizosphere microbial analysis

1. Methods

During sapling harvest, roots and small amounts of attached soil were collected into sterilized 15 mL centrifuge tubes and stored in a -80°C freezer. During later processing, the roots were removed, and the soil was sieved (< 2 mm) to homogenize. DNA was lysed, homogenized, and extracted from 0.25 g of soil using a QIAGEN DNeasy PowerSoil kit, following kit protocol. Extracted DNA was sent to the University of Minnesota Genomics Center for polymerase chain reaction (PCR) and sequencing on the V4 region of the 16s rRNA gene for bacteria and the internal transcribed spacer one (ITS1) region for fungi. Sequenced DNA was processed and figures were compiled (Figures B1-B3) by Dr. Carla Rosenfeld at the Northwestern University Quantitative Bioelement Imaging Center (QBIC). Sequenced DNA was used to identify the relative abundances of bacterial and fungal phyla in soil communities.

2. Results

In all treatments, the relative abundance of bacteria was much higher than archaea, although the shale treatment had particularly low relative abundance of archaea (Figure B1). In all treatments, the non-vegetated soil had a higher relative abundance of archaea (lower relative abundance of bacteria) than the vegetated soil.

Relative abundances for bacteria and fungi were compared at the phylum level. Bacterial phylum relative abundance was drastically different in the shale treatment than the other treatments, which contained higher diversity at the phylum-level (Figure B2). Although 12 different phyla were detected in all treatments, the shale treatment was dominated by two different phyla, while in the other treatments, the relative abundances of all detected phyla were more balanced. The shale treatment had a higher relative abundance of Actinobacteria (36% for non-vegetated, and 28% for vegetated) and Nitrospirae (32% for non-vegetated and 28% for vegetated) than the other treatments. The shale vegetated and non-vegetated relative bacterial abundances were not very different from one another, apart from the Acidobacteria phylum where vegetated relative abundance (18%) was much higher than non-vegetated relative abundance (3%). Not only did the control, dissolved Mn, and Mn-oxide treatments have similar relative abundances regarding bacteria phylum, but they also shared similar patterns between non-vegetated and vegetated bacterial communities. In all three, there was a higher relative abundance of Alphaproteobacteria and Betaproteobacteria in the vegetated soil than the non-vegetated soil.

At the phylum level for fungi, the shale treatment was again very different from the other treatments, with a higher relative abundance of Ascomycota (66% for non-vegetated, 80% for vegetated) (Figure B3). In all treatments, Ascomycota was the most abundant, followed by either Basidiomycota or Mortierellomycota. For Ascomycota, there were slight differences between the control, the dissolved Mn, and Mn-oxide treatments; the vegetated control (41%) and non-vegetated control (48%) had a similar relative abundance to the non-vegetated Mn-oxide (48%), but were all higher than the vegetated Mn-oxide (31%). Both the vegetated dissolved Mn (56%) and the non-vegetated dissolved Mn (59%) had a higher relative abundance of Ascomycota relative to the control and Mn-oxide treatments.

3. Discussion

Microbial communities in the shale had a high relative abundance of Actinobacteria and Nitrospirae, both of which are commonly found in acid mine drainage impacted systems (Chen et al., 2016). Some species of Actinobacteria have been shown to oxidize Mn (Tebo et al., 2004). Nitrospirae, however, are more associated with species that are nitrifiers or magnetotactic

(Daims et al., 2015; Li et al., 2015). Both Actinobacteria and Nitrospirae contain species that have been used for bioremediation in acid mine drainage impacted environments (Villegas-Plazas et al., 2019).

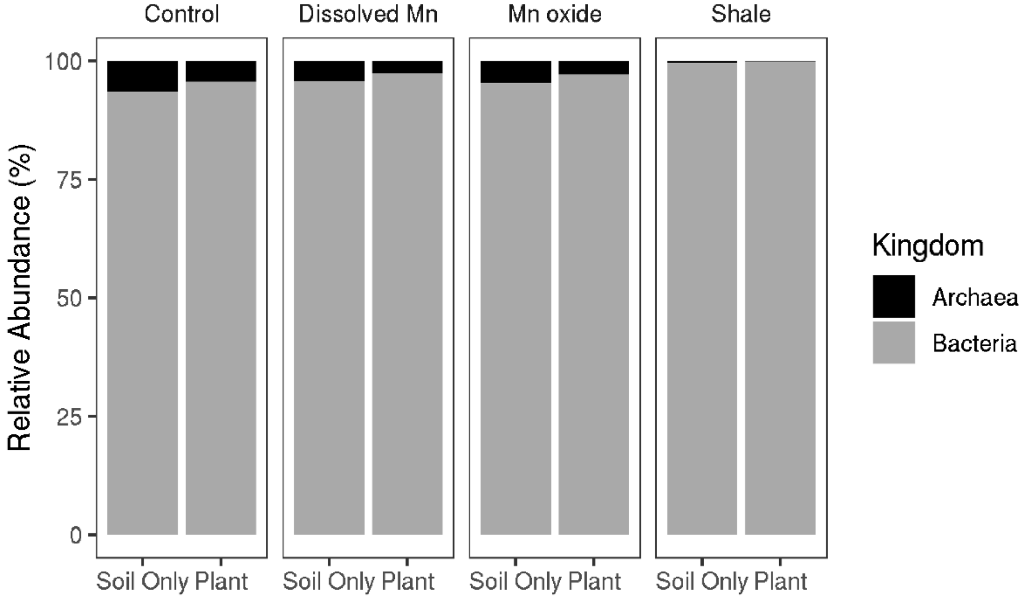

Figure B1. Relative abundances of archaea and bacteria in each treatment. The V4 region was sequenced from DNA extractions taken on samples from the rhizosphere (root-associated soil) for vegetated treatments, and a subsample of homogenized soil for non-vegetated treatments.

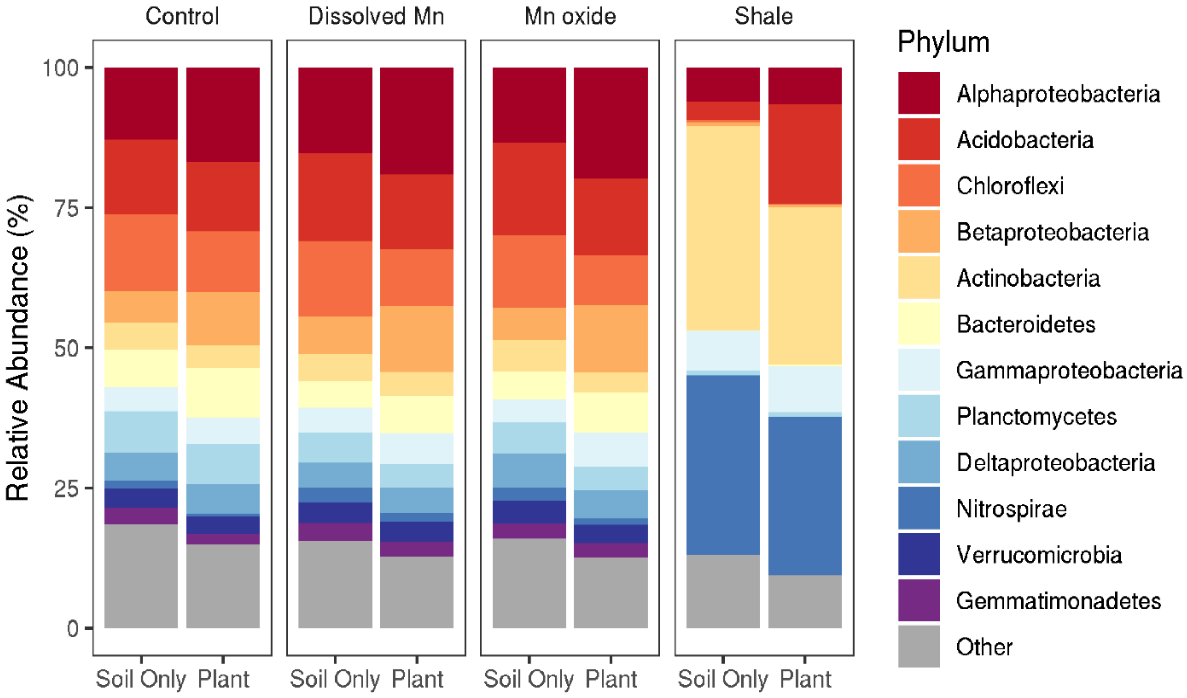

Figure B2. Relative abundances for the bacteria phylum in each treatment. The V4 region was sequenced from DNA extractions taken on samples from the rhizosphere (root-associated soil) for vegetated treatments, and a subsample of homogenized soil for non-vegetated treatments.

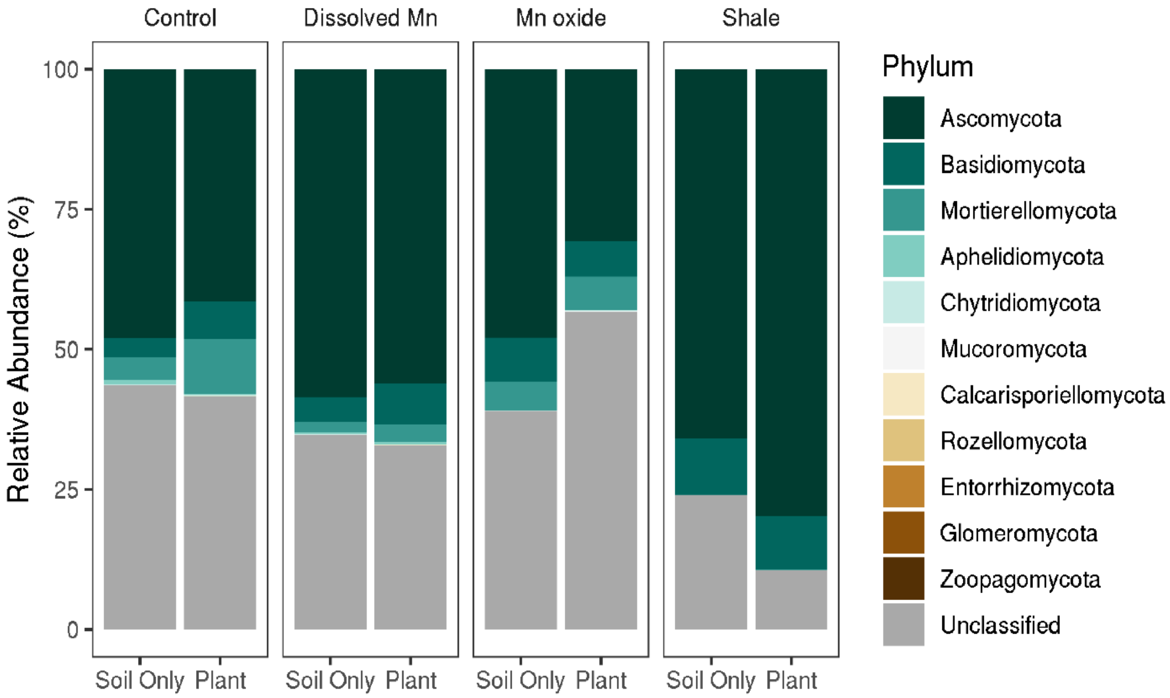

Figure B3. Relative abundances fungal phylum in each treatment. The ITS region was sequenced from DNA extractions taken on samples from the rhizosphere (root-associated soil) for vegetated treatments, and a subsample of homogenized soil for non-vegetated treatments.