Manganese Dynamics in the Third Decade of Forest Ecosystem Experimental Acidification and N Enrichment

Marie-Cécile Gruselle[1], Ivan J. Fernandez[1,2], Cayce Salvino[1], Corianne Tatariw[3]

[1]University of Maine, School of Forest Resources, [2]University of Maine, Climate Change Institute,
[3]University of Maine, School of Biology and Ecology

INTRODUCTION

Manganese (Mn) is a potential modulator of carbon (C), nitrogen (N), and phosphorus (P) cycling in acidic forest ecosystems. This metal and plant micronutrient is involved in several important ecosystem processes such as photosynthesis, organic matter decomposition, mineralization via Mn-depending and Mn-containing enzymes such as arginase, manganese peroxidase, P-transferase (Stevenson 1986), and denitrification (S. Turlapati, pers. comm.). High Mn concentrations, which can occur in acidic soils, may be toxic to certain tree species, threatening forest health and productivity.

Changes in the chemical environment due to N and sulfur (S) atmospheric depositions are known to occur in forest ecosystems. Unlike the N cycle, the Mn cycle is strongly dependent on the local geology and rock weathering. Mn mobilization and availability in soil solution increase with increasing soil acidity. Mn is often not included in research studying the effects of ecosystem acidification and N fertilization on forest ecosystem processes. This study summarizes data on Mn from a long-term soil whole-ecosystem acidification experiment as an initial framework for ongoing research to improve our understanding of the role of Mn in acidic forest soils biogeochemistry.

RATIONALE

In this study, we proposed that Mn dynamics are influenced by chemical (N and S treatment reactions) and biological (mediated by microorganisms and vegetation) processes (Figure 1). Our hypotheses were: (1) Mn is be mobilized and thus more available due to 23+ years of N and S treatment, and (2) high Mn availability fosters organic matter decomposition, to a point, due to the enhancement of lignin-degrading enzyme production but that this Mn effect would be stand type (species) dependent (Berg et al. 2010). To test this hypothesis, we analyzed the Mn data available from the long-term (23+ years) paired watershed experimental acidification and N addition experiment at the Bear Brook Watershed in Maine (BBWM).

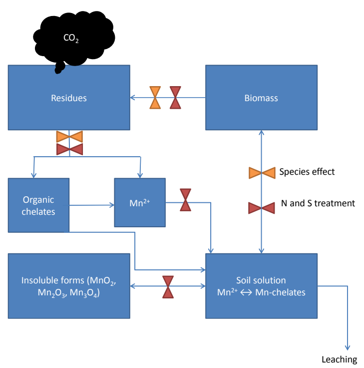
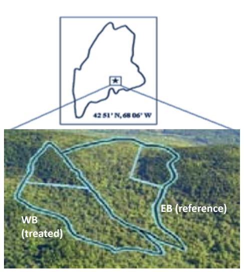


Figure 1. Effects of N and S treatment and vegetation on the Mn cycle (modified after Stevenson 1986).

METHODS

Location of the Bear Brook Watershed in Maine

- Located at 44°52' N. lat. and 68°06' W. long. Maine, USA (Fig. 2)
- Two watersheds; reference East Bear (EB, 10.3 ha) and experimental West Bear (WB, 11.0 ha) treated bimonthly with $(NH_4)_2SO_4$ since 1989.
- Watersheds divided by forest type – hardwoods (HW) and softwoods. (SW).
- Bedrock primarily non-calcareous. Soils are mostly Typic Haplorthods and Haplohumods.



Mn data available

- Quantitative pits of 2010 (organic, B, and C horizons),
- 1998-2000 foliage and litterfall by dominant species (American beech, sugar maple, and red spruce),
- Soil samples extracted with 1 N NH_4Cl and plant samples analyzed with ICP-MS for Mn and other ions.
- Ca/Mn ratios calculated as an index of depletion/mobilization due to acidification.

Figure 2: Location of the BBWM and layout of the watersheds and stand types

MANGANESE BY SOIL INCREMENT

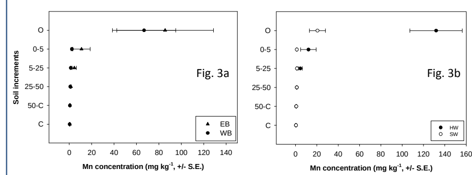


Figure 3. Mn concentration (ppm) in the O, B, and C horizons by (a) watershed, or (b) stand type (2010 soil data) .

Of all soil increments, the O horizon has the highest concentrations of labile Mn in both watersheds. This indicates some combination of strong biorecycling (uplift) by the vegetation (Fig. 3a), but more so in the HW than the SW (Fig. 3b), a higher pool of exchange sites in the O horizon, and Mn^{2+} chelation by organics.

WEATHERING RESULTS AND STOICHIOMETRY

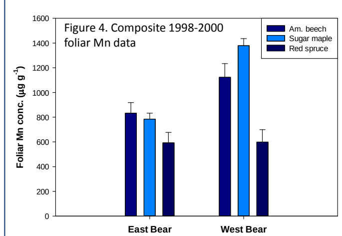
The order of B batch weathering was Al>Fe>Ca>Mn, whereas it was Al>Ca>Fe>Mn for the C batch weathering (Table 1).

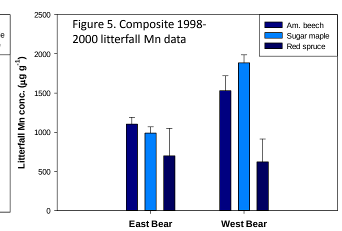
The Ca/Mn of B and C batch weathering solutions were lower in the HW than SW compartments irrespective of treatment (Table 1). This indicates a relative difference in Mn weathering and mobilization by stand type.

Table 1. Mn, Ca, Al, and Fe (mean and S.D., µg kg^{-1}) in and Ca/Mn ratio of the B and C batch weathering solutions by compartment (168 hours, 0.001 M HNO_3, pH 3)

Horizon	Compartment	Mn	Al	Fe	Ca	Ca/Mn
B	EBHW	35.7 (1.8)	4311 (92)	166 (7)	149 (11)	4.2 (0.4)
	EBSW	1.5 (0.1)	3792 (72)	490 (18)	70 (5)	45.6 (6.5)
	WBHW	21.7 (3.9)	4084 (78)	212 (9)	87 (15)	4.1 (0.8)
	WBSW	3.5 (3.2)	4278 (46)	332 (14)	92 (4)	39.7 (19.5)
C	EBHW	11.7 (1.0)	3868 (86)	72 (9)	132 (5)	11.3 (0.9)
	EBSW	1.6 (0.2)	3926 (73)	93 (2)	123 (7)	77.6 (10.6)
	WBHW	7.7 (1.0)	3765 (105)	72 (5)	187 (6)	24.8 (4.3)
	WBSW	2.8 (0.3)	4257 (137)	123 (10)	94 (8)	33.4 (3.5)

MANGANESE IN FOLIAGE AND LITTERFALL





- Foliar and litterfall Mn concentrations were higher in WB compared to EB, except for red spruce (t-tests, Fig. 4 and 5), due to soil mobilization of Mn with watersheds treatment in WB.
- Thus, both treatment and tree species influenced Mn concentrations in foliage and litterfall.
- Mn concentrations increased from foliage to litterfall for all combinations tree species x watershed (treatment). High initial litter Mn concentrations were found to be positively related to high litter limit values (accumulated mass loss) (see Berg et al. 2010). This remains to be tested for mixed northeastern US forest ecosystems.

Ca/Mn IN FOLIAGE AND LITTERFALL

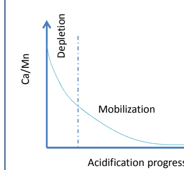


Figure 6. Conceptual model of plant tissue Ca/Mn with the progression of acidification

- Cation depletion and pH dependent Mn mobilization drive plant tissue Ca/Mn due to treatment (Fig. 6).
- We found lower foliar and litterfall Ca/Mn in WB (4-5) compared to in EB (8-10) for the HW but no difference among watersheds for the SW. Ca/Mn between 2-4 and 5-6 for red spruce needles and litter, respectively.

MANGANESE AND O HORIZON MASS

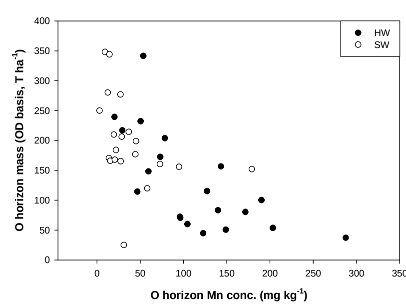


Figure 7. The mass of the fine fraction of the O horizon as a function of Mn concentration by stand type at the Bear Brook Watershed in Maine (from 2010 data, WB and EB pooled).

- Horizon mass decreased with Mn concentration, especially in the HW (Fig. 7), which is consistent with a possible role of Mn in accelerating decomposition.
- This empirical relationship has already been found for pine litter in boreal and temperate forests (see Berg et al. 2010).

CONCLUSIONS

- The O horizon has the highest concentration of available Mn of all soil horizons in all compartments, especially in both HW stands (irrespective of treatment).
- Foliar and litterfall Mn concentrations differed by tree species and watershed, indicating a strong influence of both N and S treatment and forest composition.
- Foliar Mn concentrations are above reported levels of toxicity (500 µg g^{-1} for most plants, Stevenson 1986), especially for sugar maple. Minocha et al. (2013) have found a positive correlation between Mn^{2+} and stress-related compounds (e.g. putrescine) in foliage of the same species at the BBWM.
- The mechanism that potentially links decomposition (O horizon mass) and Mn availability is still poorly understood. Several organic matter degrading enzymes produced by fungi and mycorrhizae may be regulated by Mn^{2+}, and these mechanisms are being studied.
- Given the positive and negative consequences of Mn in forest ecosystem biogeochemistry, this metal deserves further attention relative to organic matter cycling and forest ecosystem health and productivity.

LITERATURE CITED

Berg, B. and others. (2010). Factors influencing limit values for pine needle litter decomposition: a synthesis for boreal and temperate pine forest systems. Biogeochemistry 100: 57-73.

Minocha, R., and others (2013). Species-specific response in foliar physiology of forest trees to elevated N and S additions at the Bear Brook Watershed in Maine. NERC 2013, Saratoga Springs, NY, March 19-20.

Stevenson, F.J. (1986). Cycles of soil carbon, nitrogen, phosphorus, sulfur, micronutrients. John Wiley & Sons, 321-367.

ACKNOWLEDGEMENTS

This research is supported by the National Science Foundation (DEB-1119709) and the University of Maine. Special thanks to Mike Handley and Cheryl Spencer for their assistance in sample analysis and data preparation.