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Metal fate and partitioning in soils under bark beetle-killed trees

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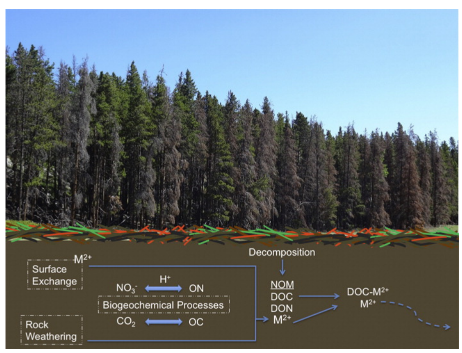
HIGHLIGHTS

- Metal mobility increases in soils under insect-killed trees.
- Zn content increased in all soil fractions, likely from litter inputs.
- Cd increased primarily in the exchangeable and more mobilizable fraction.
- Cu content in soils was redistributed toward the organic fraction.
- Organic carbon complexation controls mobility with tree death in geochemical models.

GRAPHICAL ABSTRACT



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ABSTRACT

Recent mountain pine beetle infestation in the Rocky Mountains of North America has killed an unprecedented acreage of pine forest, creating an opportunity to observe an active re-equilibration in response to widespread land cover perturbation. This work investigates metal mobility in beetle-impacted forests using parallel rainwater and acid leaches to estimate solid–liquid partitioning coefficients and a complete sequential extraction procedure to determine how metals are fractionated in soils under trees experiencing different phases of mortality. Geochemical model simulations analyzed in consideration with experimental data provide additional insight into the mechanisms controlling metal complexation. Metal and base-cation mobility consistently increased in soils under beetle-attacked trees relative to soil under healthy trees. Mobility increases were more pronounced on south facing slopes and more strongly correlated to pH under attacked trees than under healthy trees. Similarly, soil moisture was significantly higher under dead trees, related to the loss of transpiration and interception. Zinc and cadmium content increased in soils under dead trees relative to living trees. Cadmium increases occurred predominantly in the exchangeable fraction, indicating increased mobilization potential. Relative increases of zinc were greatest in the organic fraction, the only fraction where increases in copper were observed. Model results reveal that increased organic complexation, not changes in pH or base cation concentrations, can explain the observed differences in metal partitioning for zinc, nickel, cadmium, and copper. Predicted concentrations would be unlikely to impair human health or plant growth at these sites; however, higher exchangeable metals under beetle-killed trees relative to healthy trees suggest a possible decline in riverine

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ecosystem health and water quality in areas already approaching criteria limits and drinking water standards. Impairment of water quality in important headwater streams from the increased potential for metal mobilization and storage will continue to change as beetle-killed trees decompose and forests begin to recover.

1. Introduction

Forests are important regulators of ecosystem function controlling water, energy, and nutrient fluxes. Natural and anthropogenic disturbances of forest cover set off a ripple effect through the biosphere, lithosphere, hydrosphere and atmosphere of forested mountain ecosystems. Mountain pine beetle (MPB; *Dendroctonus ponderosae*) infestation has resulted in devastating tree death in the Rocky Mountains of the western United States and Canada with important ecological and societal implications. Warming climate and drought conditions have led to the unprecedented severity of the current infestation, as the MPB has impacted forests at higher elevations and latitudes, and attacked trees with weakened defenses (Kaiser et al., 2013; Mitton and Ferrenberg, 2012). The resulting and extensive land cover change impacts not only the esthetic and commercial value of affected forests, but also the water and biogeochemical cycles in these important mountain watersheds (Mikkelson et al., 2013a). Previous biogeochemical research has focused on nutrient cycles in killed stands, and suggests the potential for increased fluxes of dissolved organic carbon (DOC), nitrogen, base cations, and aluminum into soils as trees are killed and decompose (Kaňa et al., 2013; Griffin and Turner, 2012; Clow et al., 2011; Griffin et al., 2011; Huber et al., 2004; Tokuchi et al., 2004; Zimmermann et al., 2000); however results are highly watershed specific (Mikkelson et al., 2013a). Increased nitrification, base cation release from litter or exchange processes, or changes in organic acid inputs may also alter soil pH and ultimately metal mobility. Decreases in soil pH are possible from increased nitrification (Feller, 2005); however, studies of soil chemistry alterations under beetle-killed trees in North America and Europe found increases in soil pH, likely related to exchange-site competition from increased base cation inputs (Kaňa et al., 2013; Xiong et al., 2011). The changing chemistry in soil waters resulting from insect-induced tree death and decomposition may have important implications for trace metal mobility, but has only recently been studied (Mikkelson et al., 2014). In that study, pine needle leachate mobilized metals from soil columns, which consistently eluted higher concentrations of Zn, Cu, and Al than artificial rainwater. Eluted metal concentrations were found to be most strongly correlated with DOC and Ca ions, suggesting the importance of organic complexation and base cation competition in mobilizing metals in beetle-impacted forests and increased metal inputs from decomposing needles (Mikkelson et al., 2014).

Metal mobility in soil water is largely controlled by sorption, complexation, and mineral phase reactions, including ion exchange, specific adsorption, organic complexation, and precipitation (Gong and Donahoe, 1997). These processes depend on pH and soil composition (i.e. iron and manganese oxide, organic matter (OM), and clay content); however, the relative importance of each process may not be consistent for all trace metals. For example, pH-dependent specific adsorption may be the dominant process for Zn, whereas Cu mobility depends on complexation with organic ligands (Gong and Donahoe, 1997; Sauvé et al., 1997; McBride et al., 1997). Metal complexation with OM is likely to increase as forests progress through MPB infestation. Although initial losses of labile carbon in mineral soils were observed as root exudation ceases (Xiong et al., 2011), prolonged carbon fluxes from organic horizons may occur as tree needles and boles continue to decay (Huber et al., 2004; Kaňa et al., 2013). Soil carbon and pH changes may cause different metal mobilization processes to be important with tree death and subsequent regrowth; however the relative importance of each mechanism is unknown. The long-term effects of widespread MPB-induced tree death on metal mobility are also uncertain. As forests recover from widespread lodgepole pine death, regrowth often contains more subalpine fir, Engelmann spruce, and aspen (Pelz and Smith, 2012), which may lead to changes in soil properties with trees species (Andersen et al., 2004), such as greater nutrient availability in new aspen forests (Buck and St Clair, 2012). In addition, if organic matter and metals accumulate in the soil from needle leachate and bole decomposition, metals may continue to be leached as the forest recovers (Brun et al., 2008).

To understand the potential for delayed metal release and improve understanding of mobilization mechanisms, it is important to characterize the solid phase metal concentrations in soil, which may be the source of metals, but wherein different mechanisms are responsible for metal release. Resulting distributions provide a better understanding of how metals are mobilized by identifying where and how metals are sequestered in soils, highlighting the potential for release from environmental perturbations from land cover change, such as changes in pH or water and OM fluxes. The relationship between plants and metal partitioning and mobility in forest soils is complex and often complicated by spatial variability in total metal content and soil composition (Nowack et al., 2010). Specific studies concerning the effect of litter-derived organic matter on metal fractionation are limited; however, humic acids applied as soil amendments have been observed to affect mobility differently for different metals (Janoš et al., 2010). Application of solid humic acid redistributed Zn and Pb to a less mobile phase in moistened soils but increased Cu mobility (Clemente and Bernal, 2006). These effects were more pronounced in acidic soils than in calcareous soil, highlighting the relevance for soils typical of pine forests. Increases in Cu mobility may be attributed to complexation to soluble organic matter or colloids (Clemente and Bernal, 2006), and may also reflect redistribution from residual to OM-bound fractions in soils (Janoš et al., 2010).

The objective of this study is to identify the potential mechanisms of metal mobilization and fractionation in soils collected beneath trees undergoing different stages of MPB-attack. Our approach uses a two-stage leaching procedure to identify the potential for increased metal mobility under dying trees. After identifying potential changes in metal mobility at the first site, a sequential extraction procedure (SEP) is employed to identify where metals are complexed in pine forest soils from an additional sampling event and how that may change as infestation progresses. Laboratory findings are then enriched through geochemical modeling to further identify controls on metal mobility and soils that may be more susceptible to metal leaching from MPB-induced tree death as well as provide generalizable results that transcend tree-scale soil heterogeneities between field samples. Collectively, this study moves toward a better understanding of metal mobilization mechanisms and changes in complex forest soil impacted by the MPB.

2. Methods

2.1. Sample collection

Two soil sampling events were conducted, one for each leaching procedure. Depending on the site, samples were collected from under green, red and gray phase trees. Green phase trees are alive and transpiring and are considered the control in these experiments. Red phase trees have been attacked and cease to transpire by the following growing season. During this phase, trees retain the majority of their needles, which have turned red in color. By three to four years after attack, trees enter the gray phase and have lost almost all needles (Wulder et al., 2006).