Environmental Science Processes & Impacts

Accepted Manuscript

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Environmental Science Processes & Impacts

Formerly Journal of Environmental Monitoring

www.rsc.org/jem

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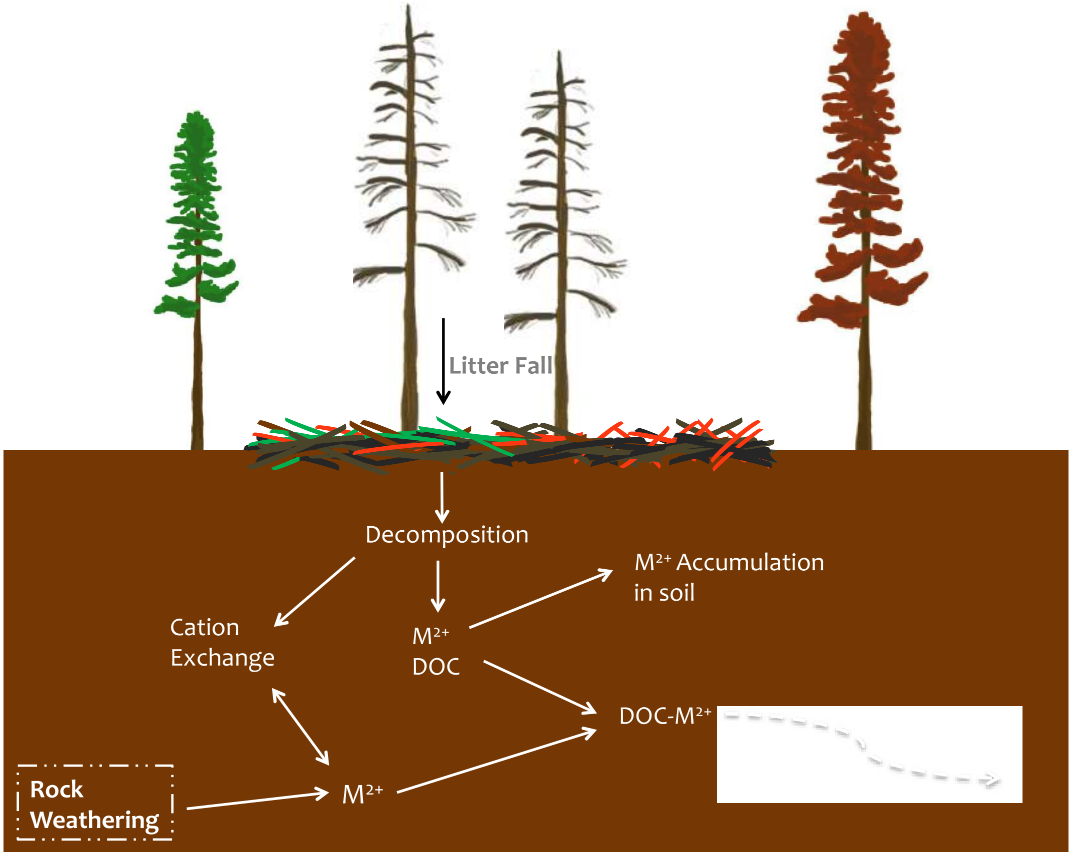

Large-scale tree mortality has the potential to alter subsurface metal mobility and accumulation as demonstrated by laboratory column studies and complimentary field sampling.

Changes in metal mobility associated with bark beetle-induced tree mortality

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Environmental Impact

Large-scale insect infestations have been decimating coniferous forests at unprecedented proportions. Concerns about the impacts of extensive forest mortality have led to numerous studies investigating the effects on water resources. Recent work documenting the mobilization of dissolved organic carbon after tree mortality led to a hypothesis that metals could be mobilized through complexation with organic matter, along with increased deposition from metal accumulation in needles and subsequent decomposition. The work herein employed flow-through column experiments and field observations to determine if tree-death can alter metal mobility in near-surface soils. The findings of this study provide a fundamental baseline needed for future comparison and extrapolation into whether or not large-scale tree mortality will alter metal concentrations in adjacent water bodies.

Abstract

Recent large-scale beetle infestations have caused extensive mortality to conifer forests resulting in alterations to dissolved organic carbon (DOC) cycling, which in turn can impact metal mobility through complexation. This study analyzed soil-water samples beneath impacted trees in concert with laboratory flow-through soil column experiments to explore possible impacts of the bark beetle infestation on metal release and transport. The columns mimicked field conditions by introducing pine needle leachate and artificial rainwater through duplicate homogenized soil columns and measuring effluent metal (focusing on Al, Cu, and Zn) and DOC concentrations. All three metals were consistently found in higher concentrations in the effluent of columns receiving pine needle leachate. In both the field and laboratory, aluminum mobility was largely correlated with the hydrophobic fraction of the DOC, while copper had the largest correlation with total DOC concentrations. Geochemical speciation modeling supported the presence of DOC-metal complexes in column experiments. Copper soil water concentrations in field samples supported laboratory column results, as they were almost twice as high under grey phase trees than under red phase trees further signifying the importance of needle drop. Pine needle leachate contained high concentrations of Zn (0.1mg/l), which led to high effluent zinc concentrations and sorption of zinc to the soil matrix representing a

future potential source for release. In support, field soil-water samples underneath beetle-impacted trees where the needles had recently fallen contained approximately 50% more zinc as samples from under beetle-impacted trees that still held their needles. The high concentrations of carbon in the pine needle leachate also led to increased sorption in the soil matrix creating the potential for subsequent carbon release. While unclear if manifested in adjacent surface waters, these results demonstrate an increased potential for Zn, Cu, and Al mobility, along with increased deposition of metals and carbon beneath beetle-impacted trees.

1. Introduction

Climate change is creating stress on environmental ecosystems throughout the world, altering both water resources and global biogeochemical cycles. One example is through increased temperatures and drought, stressed forests are more susceptible to insect attack, and in the past several decades scientists have witnessed the largest levels of tree mortality ever recorded due to insect infestations[1-4]. In forests that are reaching close to 100% tree mortality due to beetle-kill, biogeochemical cycles are being significantly altered. Beetle mortality has been shown to release larger quantities of carbon into the atmosphere than direct forest fire emissions and can shift forest dynamics from a net carbon sink to a carbon source[5]. Beetle infestation has also been associated with changing water quality; for example, in Colorado the bark beetle infestation has been linked to increases in carcinogenic disinfection byproducts in drinking water, created through chlorination of organic matter-rich waters[6].

As bark beetle infestation can be added to the list of natural and anthropogenic land cover changes that have been shown to influence dissolved organic carbon (DOC) quantity and composition[6,7] it is possible beetle infestations will also influence metal speciation and transport through organic matter complexation[8]. Current literature reviews have predicted changing carbon dynamics in bark beetle-impacted watersheds[9,10], but have not been able to surmise if metal transport will be altered. While others have studied the impact certain types of DOC have on metal transport[11-13], it is not yet known how organic carbon released from these types of dying forests may alter metal mobility.

With large-scale tree die-off, it has been shown that initially there is a rapid loss of carbon from the soil before needle drop due to the cessation of root excretions[14] followed by a prolonged release of DOC into the soil-water and humus efflux associated with increased organic matter decay[15]. One possible source of DOC following a bark beetle infestation is the increased needle deposition on the forest floor and subsequent decomposition[16]. Beetle-killed trees release the majority of their needles faster than the typical annual litterfall as they progress from the red to the grey stage[10]. Increases in soil-water DOC concentrations lead to increased potential for metal-ligand interactions and mobilization to nearby water supplies[17,18] during or after this red-grey transition. Metal concentrations may also increase from needle leaching, as evergreen needles can bioaccumulate heavy metals (*i.e.* Pb, Cu, Zn and Cr) through atmospheric uptake, especially in high pollution areas.[19] Therefore it is possible soil metal concentrations will increase as the metal-rich needles decompose, which could prove problematic especially in areas already laden with legacy mines and high soil metal contentrations typical of beetle-killed areas in the Rocky Mountains of Colorado[20].

Changes in DOC composition (rather than total concentration) may also alter metal mobility. Recent findings suggest that DOC composition and characteristics are being altered as a result of the bark beetle epidemic, specifically the relative fractions of hydrophobic and hydrophilic material[6]. The hydrophobic fraction of DOC consists mostly of acidic products formed from lignin degradation[21] and consequently contains aromatic and reactive moieties[22]. It has previously been observed that the longer pine needles collected from under bark-beetle infested trees degrade the more hydrophobic they become,[23] indicating that as needles degrade in a forest, the leaching of hydrophobic DOC is likely to increase. Changes in the composition of DOC can alter its metal binding capacity as the hydrophobic and hydrophilic fractions have different metal binding characteristics depending on the size fractionation and source of the organic matter[24]. Hydrophobic and hydrophilic fractions of organic matter also sorb differently to soil, as typically the hydrophobic fraction has a stronger affinity for soils and is preferentially adsorbed[25]. Overall, it is important to consider the composition of DOC leached from degrading pine needles as its transport and metal-binding capacity depend largely on the fractionation between hydrophobic and hydrophilic proportions.

By using a combined approach of field pore-water sampling complemented by the controlled introduction of needle-derived carbon to field-derived soil columns, this study set out to explore the effect of pulsed needle drop associated with bark beetle infestation on metal mobility. It is hypothesized that metal release and sorption from near-surface soils under bark beetle impacted trees will be altered by (1) increased release of metals that readily complex with pine needle-derived DOC, (2) increased deposition of metals derived from pine needle leachate, and (3) varied temporal trends for different metals due to preferential carbon and metal sorption processes and differences in carbon composition.

2. Materials and Methods

2.1 Field sites and soils

The soils used in the column experiments were gathered in September 2012 from Keystone Gulch, Keystone, CO. The soil belongs to the Frisco and Peeler formations and is derived from glacial till[26]. Soil was collected from under red phase beetle-killed lodgepole pine trees (0-30cm bgs) in which the needles on the tree were dead and red in color. Soil was sampled from this stage of mortality, as it is the most representative of the soil that would be found right before needle drop. Soil was taken from under three red phase trees where three holes were dug around each tree, approximately 100g of soil taken from each hole and homogenized with all other samples (9 samples total) to reduce spatial soil variability. The homogenized soils were sieved through a coarse mesh (5.66mm) to remove stones and woody debris, while preserving most of the micropore structure within the soil aggregates, and stored in an airtight container at -4°C until use. The soil had an average pH of 4.74 (measured using a 0.01M $CaCl_2$ solution), moisture content of 9.5% (dried overnight at 105°C), organic carbon content of 159 g kg^{-1} (determined by loss on ignition) and a loamy sand texture with 85% sand, 9% silt and 6% clay. The soil total metal content for Al, Zn, Cu, Fe and Mn was 55,500; 143; 16; 34,600; and 786 mg/kg respectively (XRF, Thermo Scientific Niton XL3t GOLDD+). The easily exchangeable metal content of the soil (performed in triplicate) was determined from digestion with $MgCl_2$ according to Tessier *et al* (1979)[27]. The exchangeable Al, Zn and

Cu contents of the soil were found on average to be 7.78 (± 0.87) mg/kg, 4.91 (± 0.71) mg/kg and 0.18 (± 0.09) mg/kg respectively.

Soil-water samples were collected under late red and early grey phase lodgepole pine trees (needles had recently fallen to the ground) at Chimney Park, WY in the spring and summer of 2011 and 2013. Additional site characteristics can be found in Biederman et al. (2012)[28]. The soil surrounding the lysimeters at Chimney Park is similar to the soil obtained for the column studies and is a coarse loamy texture[29] with an average pH of 4.44. Twenty-four samples were collected using a vacuum hand pump to pull suction on lysimeters installed at various depths (9-74 cm below ground surface). Samples were collected in 20ml glass amber vials for DOC analysis and acid-washed 15ml plastic vials for metal analysis, transported back to the laboratory in a cooler and stored at 4°C until analysis. Samples were filtered and acidified as described below for respective analyses.

2.2 Column set-up

Four acid-washed borosilicate glass soil columns (Kontes, 4.8 cm diameter and 15 cm long) were packed 10 cm high with 170 g of soil added in 50 g increments. Uniform packing was ensured by tapping the sides of the column a consistent number of times between each incremental addition to settle the soil. All columns had 1.5 cm of glass wool on the bottom to prevent clogging and 2.5 cm of glass wool on top to help uniformly disperse the influent over the top of the soil. The bulk density and pore volume of the soil columns was 0.94 g cm^{-3} and 116 cm^3 respectively. To maintain unsaturated flow (chosen to best mimic soil-water contact and redox conditions created during infiltration events in field conditions), 15 cm of tension was applied at the column base with a hanging water column.

Two different influents were applied to duplicate columns: artificial rainwater (RW) and pine needle tea (PNT). Artificial rainwater was created according to Davies et al. (2004).[30] The following inorganic salts were added per liter of deionized water to prepare artificial rainwater: $NaNO_3$, 4.07 mg; NaCl, 3.24 mg; KCl, 0.35 mg; $CaCl_2 \cdot 2H_2O$, 1.65 mg; $MgSO_4 \cdot 7H_2O$, 2.98 mg; and $(NH_4)_2SO_4$, 3.41 mg. The resulting solution had an ionic strength of 0.3 mM and a pH of 5.9. The RW composition and pH was typical of many reported in the literature for studies carried out in both the northern and southern hemispheres[30]. PNT was made by leaching 12.5 g of pine needles per liter of artificial rainwater in 3L glass amber bottles placed in natural sunlight for 48 hours (modified from Beggs et al.[23]) Pine needles were collected from under trees that had just transitioned to the grey phase, indicating the majority of needles had fallen within the last year. See Table 1 for RW and PNT characteristics.

Two column variations were run in duplicate (4 columns total). Two columns were established as controls and received artificial rainwater as influent while the two test columns received PNT as influent. Influent was applied to all columns at a steady rate of 1mm/min for 32 pore volumes until concentrations began leveling off.

Columns utilized Tygon® tubing and an Ismatec® 8 channel peristaltic pump for influent flow. Column effluent was collected manually in 40ml acid-washed glass amber vials, filtered through a 0.45 μm polyethersufone filters and stored at 4°C until analysis. Analysis occurred within one week of collection. Samples collected for metal analysis were acidified to pH<2 using trace metal grade concentrated nitric acid, while samples collected for DOC analysis were acidified to pH<2 using concentrated phosphoric acid. Samples collected for specific UV absorbance (SUVA) and nitrate analysis were filtered but not acidified.

2.3 Sample Analysis and Calculations

Samples were analyzed for DOC using a Shimadzu TOC-550A Total Organic Carbon Analyzer. The amount of carbon sorbed or released in columns was calculated by equation 1:

$$C_{sorbed/released} = ([DOC]_{PNT/RW} - [DOC]_i)*Q \qquad (1)$$

Where: $[DOC]_{PNT/RW}$ = DOC concentration of the influent (PNT or RW)

$[DOC]_i$ = DOC concentration at time *i*

Q = The flow rate

SUVA has been shown to be strongly correlated to the percent aromaticity of the organic carbon[31]. Absorbance scans were run at 254 nm and 260 nm for SUVA (DU 800 spectrophotometer) and the hydrophobic fraction of DOC respectively. The SUVA values were calculated by dividing the absorbance at 254 nm by DOC concentration and reported in units of L mg^{-1} m^{-1}. The hydrophobic fraction of the DOC was calculated by using the directly proportional relationship between light absorbance at 260 nm and the concentration of the hydrophobic fraction for pine trees[32]. This method is applicable for water samples of low nitrate (< 25 mg/l) and low iron (<5 mg/l)[32]. The column influent and effluent met both of these criteria at all points throughout the experiment.

Metal concentrations were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) in the laboratories at the Colorado School of Mines and all reported metal concentrations are the total aqueous concentrations. Detection limits were all an order of magnitude below sample measurements (detection limits for copper = 0.1µg/l, aluminum = 0.7 µg/l and zinc = 0.2 µg/l). Standard checks were performed every ten samples (five times total in the ICP-AES run for the column effluent results) and the low metal standard concentrations remained consistent throughout the entire run with five duplicate checks (Cu = 7.2 ± 1.1 µg/l, Al = 20.2 ± 6.2 µg/l, Zn = 2.8 ± 0.0 µg/l). Nitrate was measured using colorimetric test kits (Hach).

The PNT was analyzed for the hydrophobic and hydrophilic fractions of DOC using XAD-8 resin chromatography[33]. The XAD8 resin columns confirmed the relationship between light absorbance at 260 nm and the hydrophobic portion of DOC.

2.4 Geochemical Modeling

The program Visual MINTEQ version 3.0[34] was used to calculate the metal speciation in the column effluent using the non-ideal competitive adsorption (NICA) model[35] with the assumption of continuous distribution of site affinity. Input parameters included metal concentrations, DOC concentrations, solution pH and Ca^{2+} concentrations measured in the column effluent. When other ions were added to model runs (Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-} and Cl^{-}) no major changes to species distributions were found. When modeling the RW columns, generic parameters for fulvic acid (FA) were used for proton binding and metal complexation assuming that 50% of the dissolved organic matter (DOM) is C by weight and 100% of the active humic substances are FA[36]. However, when modeling the PNT columns, both the generic parameters and the measured proportions of humic and fulvic acids were used (89% FA and 11% HA as the ‘active’ humic substances) to best represent the mobilized soil organic carbon and the DOC from the PNT.

3. Results and Discussion

To better understand how a bark beetle infestation might impact metal mobility and transport, leached PNT was passed through duplicate, homogenized soil columns. To compliment this laboratory experiment, field soil-water samples were also collected beneath beetle-impacted trees. Three metals, Cu, Zn and Al, were chosen for in-depth analysis with relation to needle-derived DOC. Cu is important to monitor as it readily complexes with DOC[13], and Zn has been found in high concentrations in pine needles[37]. Prior field studies have also seen an increase in Al mobility after beetle infestation[15,38,39] often correlated to NO_3^- levels, which have implications for potential shifts in nitrogen cycling. It is also important to take into account these metals with regard to bark beetle infestations as metal contamination is already common in many mountain streams of Colorado located in beetle-killed watersheds, with Zn and Cu often exceeding ecotoxicity limits[40]. For clarity only the average concentrations from the duplicate experiments are shown in the representative figures and tables. Effluent concentrations were on average within ± 7% (DOC) and ± 21% (metals) of their respective duplicate columns and error bars can be seen in figures S1 and S2.

3.1 DOC Mobility in Column Experiments

Figure 1 shows the average Cu, Al and Zn effluent concentrations for both the PNT and RW columns, along with the average effluent DOC concentrations for the respective column. The PNT influent DOC concentration was 96 mg/l (representative of peak concentrations of forest floor leachate in a lodgepole pine dominated forest)[16] and the RW influent DOC concentration was 2 mg/l. The PNT columns effluent DOC concentration was at a maximum within one pore volume, while the RW columns did not reach maximum DOC levels until around five pore volumes. The PNT columns experienced an increase in DOC concentrations around the eighth pore volume, but the DOC slowly tapered off for the remaining experimental duration. However, it is clear that the influent DOC was immobilized in the soils of the PNT column within the first several pore volumes (Figure 2, red shaded area). This behavior could be attributed to the interaction of dissolved organic compounds with DOM sorbed to the soil, thus inhibiting the mobility[41] or the interaction of DOC with Fe and Al oxyhydroxides[42]. In total, an average of 50.0 (± 11.5) mg of carbon sorbed to the PNT columns, while the RW column actually released 50.2 (± 8.6) mg of carbon from the soil (32 pore volumes in total were eluted). Overall, the PNT effluent contained 303.7 (± 9.2) mg of carbon (in addition to 50.0 mg of C sorbing to the soil), which is 6 times more than the amount of carbon in the RW column effluent.

The column experiments indicated that low influent DOC concentrations (*i.e.* rainwater infiltrating into bare soil) mobilize organic carbon from the soil matrix (Figure 2, blue shaded area). This phenomenon has been observed in field and laboratory experiments where DOM mobilization and transport is coupled with rain events[43]. However, when the influent contains large concentrations of DOC (*i.e.* rainwater infiltrating through a large decomposing needle layer before entering the soil matrix), a portion of the carbon transported through the soil matrix will sorb to the soil (Figure 2, red shaded area). This leads to the potential for future desorption of the newly deposited soil carbon after the thick needle layer is removed or has leached much of its carbon through the soil matrix, creating a potentially large mobile carbon pulse that could travel to adjacent surface and groundwaters.

3.2 Metal Mobility in Column Experiments

The addition of DOC from needle leachate may influence metal speciation and transport, particularly due to the low percentage of metals in the exchangeable pool of the soils when compared to soils utilized in previous studies[eg. 44]. Both columns experienced their maximum Cu and DOC concentrations concurrently (Figure 1) and have a positive correlation between the effluent DOC and Cu concentrations (Table 2), consistent with other soil column experiments[13,45]. This phenomenon was explored more in the field samples and is described below (section 3.3). In the PNT columns, Cu was rapidly released in approximately the first twelve pore volumes in association with the high flux of DOC running through the columns followed by tapering (Figure 1A). The RW columns exhibited a similar trend, as the effluent Cu tracked well with DOC concentration (Figure 1B). Overall, the PNT columns eluted an average of 31.5 (± 0.7) µg of Cu, 9.4 (± 0.7) of which were desorbed from the soil. The RW columns released an average of 18 (± 0.7) μg of Cu, all attributed to soil desorption. Given the RW columns had a larger quantity of desorbed Cu, it appears that the concentration of Cu in the PNT (0.006 mg/l) is inhibiting soil desorption, leaving the possibility for additional subsequent release. In previous studies, Cu mobility has shown initial enhancement from DOC followed by subsequent retardation attributed to the formation of ternary complexes between the aquifer material, Cu and DOC or changes in the electrostatic potential at the solid-phase surface[41]. This may be the case in the PNT columns, as the PNT significantly enhanced Cu mobility in the beginning of the column experiments, but then the fractional increase in mobility tapered off. Cu also has a positive correlation to aqueous Ca effluent concentrations suggesting competitive DOM sorption occurred in these soil columns[46].

Aluminum effluent concentrations exhibit a different trend than was observed for Cu. Effluent Al concentrations in the PNT columns increased until around the twelfth pore volume, despite decreasing DOC concentrations (Figure 1C). When the influent DOC was low (*i.e.* the RW columns), the effluent Al concentrations appeared to follow the same trend as Cu and were positively correlated to effluent DOC, hydrophobic DOC and Ca concentrations (Table 2); however, in the PNT columns Al concentrations appear to be closely correlated with only the hydrophobic portion of DOC. This is markedly different than Cu and Zn, as only the Cu concentrations in the RW columns appeared to have any correlation with the hydrophobic portion of DOC concentrations (Table 2). Aluminum mobility appeared to be enhanced throughout the entire duration of the column run, with the maximum enhancement occurring in the first eight pore volumes. This observed trend could be attributed to desorption of Al from the exchangeable pool of metals or related to the initial rapid solubilization of reactive solid phase Al followed by the slower dissolution of less reactive minerals in the soil, assuming kinetically controlled dissolution of inorganic soil Al compounds is the main supply for organically bound Al as has been suggested by other studies[47,48]. Overall, the PNT column effluent contained 4.1 (± 0.9) mg of Al, 3.2 (± 0.9) of which were desorbed from the soil. This suggests that Al soil desorption is enhanced more than Cu desorption by the addition of DOC, possibly because the additional Al in the PNT does not inhibit Al desorption as is possible in the case of Cu. In comparison, the RW column only released a total of 2.0 (± 0.3) mg of Al, less than half that of the PNT column.

Zinc effluent concentrations followed a similar trend as the Cu effluent concentrations where the PNT and RW columns displayed fairly strong correlations with DOC and Ca concentrations (Figure 1E & 1F, Table 2). However, from the fifth to the ninth pore volume, the average Zn concentrations in the PNT columns increased despite a decreasing DOC concentration (Figure 1E). Zn was also positively correlated with Ca concentrations (Table 2) suggesting that when carbon sorbs to the soil matrix it replaces Zn and Ca ions. This trend has been observed before, where Zn is strongly correlated to Ca and to a lesser extent DOC[49]. In these experiments, the concentration of Zn in the PNT was high enough that a large portion of the zinc sorbs to the soil matrix instead of transporting in the aqueous phase. Throughout the duration of the column experiment (except for the first pore volume), the concentration of Zn in the PNT was 2-3 times higher than the concentration of Zn in the effluent. In total, out of the 319 µg of Zn entering the PNT columns an average of 220 (± 14.8) µg of Zn sorbed to the soil matrix. This indicates that the soil possessed a large capacity to sorb Zn ions. Even with the large amount of Zn sorption, the effluent in the PNT columns contained a total of 119 (± 10.6) µg of Zn, which is almost twice that of the RW column.

3.3 Metal and Carbon Association in the Field Under Beetle-Impacted Trees.

Field correlations often corroborated column results although field correlations were reported from only from under late-red phase trees (Table 2), as they were the majority of the samples, and only a few early-grey phase trees were available for comparison. In complimenting the column results, Cu and DOC concentrations were strongly correlated in field measurements under red phase beetle-impacted trees (Table 2), suggesting the potential for higher concentrations of Cu after increased DOC flux from needle decomposition. Furthermore, the average soil-water Cu concentration under grey phase trees (6.5 ± 4.3 µg/l, n = 8) was almost twice as high as under red phase trees (3.6 ± 2.0 µg/l, n = 16) suggesting an association between the pulsed needle drop that occurs as the trees progress from the red to the grey stage.

In the field samples, Al exhibited a strong correlation with both DOC and Ca, which were not observed in the PNT columns (Table 2); however, trends observed in the field were also seen in the RW columns. Al concentrations in soil-water samples from under red and grey trees were not significantly different (red phase: 0.60 ± 0.53mg/l, n =16; grey phase: 0.58 ± 0.84mg/l, n = 8). This suggests there might be other processes occurring in the field that are not completely mimicked by the columns. Soil-water aluminum levels have also been observed to correlate with NO_3^- concentrations in field studies after beetle attack[15,38,39]. Laboratory results confirmed a weak correlation between Al and NO_3^- in the PNT columns (r = 0.40) and RW columns (r = 0.38); however, the column duration was brief enough that it might not have had sufficient time to capture the microbial assemblages responsible for nitrogen cycling often observed in the field. On the other hand, the field samples from this study displayed a negative correlation (r = -0.60) with nitrate, although NO_3^- field data was limited and the sample size small (n = 4).

In the field, Zn had a weak negative correlation with DOC, which was not observed in the soil columns. The samples also showed a negative correlation between Zn and Ca, possibly due to Zn sorption to the soil and the release of Ca. Comparison of these field and column results supports previous observations of the opposing behavior of Zn with regards to DOC that has been observed in previous column and field studies[49-51]. However, field observations confirmed the hypothesis that zinc-saturated needle decomposition will lead to higher soil-water Zn concentrations as the samples from under grey phase trees that had recently lost their needles were on average 50% higher (40.5 ± 33μg/l, n = 8) than the Zn concentrations under red phase trees (28.6 ± 33μg/l, n = 16).

3.4 Metal Mobility and pH in Column Experiments.

The pH of the effluent averaged 7.4 ± 0.4 and 6.4 ± 0.3 for the RW and PNT columns respectively (Figure S3). The DOC effluent concentrations in the PNT column had very little correlation with pH (r=0.11) and the RW columns had a weak positive correlation (r=0.34). The effluent pH concentrations were higher than the soil pH (measured in batch) in both the PNT and RW columns by about 1.5 and 2 pH units respectively which suggests that ion exchange may have decreased proton concentrations in the effluent. Effluent pH does not appear to explain any of the metal concentrations or DOC concentrations except in the PNT column with regard to Cu (Table 2) as DOC-metal complexation dominates at high pH[13] as compared to lower pH values where there are less deprotonated acidic functional groups available in the DOM for metal binding[52].

This was verified with geochemical modeling, which found all metal species in the PNT column to be complexed to DOC (Table S1) until the last measured time step where 0.5% of the aqueous Al was $[Al(OH)_4]^-$. The effluent from the RW columns was oversaturated with respect to gibbsite ($Al(OH)_3$) for the entire column duration, while the PNT column effluent was under-saturated with respect to gibbsite until the last three pore volumes where it reached equilibrium followed by slight oversaturation. The metal species in the RW columns were more varied for Zn and Al, but aqueous Cu was always complexed with DOC. Zn^{2+} and $[Al(OH)_4]^-$ were the other dominant species in the RW columns besides Zn-DOM and Al-DOM (Table S1).

3.5 Influence of DOC Composition on Metal Mobility

Along with the transport and sorption, the composition of DOC was important in determining metal mobility. The PNT was found to contain 41.4% hydrophobic DOC through XAD8-resin chromatography, and the directly proportional relationship between absorbance at 260 nm and DOC concentration found the PNT to be 40% hydrophobic DOC. During the column experiments, the proportion of hydrophobic DOC relative to the total DOC increased in the first 7 pore volumes in the PNT column reaching a maximum of 66% hydrophobic DOC, while the RW column showed an increase in the hydrophobic portion of DOC throughout most of the experimental duration, approaching 100% hydrophobic DOC after 20 pore volumes (Figure 3). As the proportion of hydrophobic DOC in the RW experiment eventually approached 1, it appeared that initially both the hydrophilic and hydrophobic fractions of soil-bound DOC were mobilized; however, with a longer duration continuous rain event, eventually all the hydrophilic DOC is mobilized. This behavior supports previous observations that the hydrophilic fraction of DOC is more mobile than the hydrophobic fraction[53]. Specifically, the hydrophobic fraction of DOM (of which DOC is a component) has been shown to interact strongly with Al and Fe oxides and hydroxides[54] slowing down their transport. Thus, the hydrophilic fractions of DOM are likely to travel faster in hydrologic systems than the hydrophobic fractions[55]. On the other hand, the opposite trend was observed in the PNT columns as the proportion of hydrophobic DOC was higher in the effluent than the influent after the first few pore volumes. This indicates that either the soil had a higher affinity for hydrophilic DOC sorption than hydrophobic DOC sorption or additional hydrophobic DOC was desorbing (Figure 3). As the proportion of hydrophobic DOC appeared to tail off in the final pore volumes, it is probable that once steady state is reached the effluent DOC will closely resemble the influent PNT composition of 41% hydrophobics, 19% hydrophilics and 40% neutral compounds.

Along with differences in transport, the composition of DOM can change its metal-binding capacity. Hydrophilic acids represent the more mobile fraction of DOM in the soil column[25] and in some studies have been shown to bind Cu more effectively than hydrophobic acids[53]. However, more recent studies have found no difference in the binding characteristics of the two fractions of DOM from leaf litter with regard to Cu binding[56]. In the experiments reported herein, Al was the only metal strongly correlated to a specific fraction of DOC (the hydrophobic fraction; Table 2). This strong correlation combined with the absence of correlation to overall DOC concentration, indicates a strong preference for Al binding with the hydrophobic fraction of pine needle leachate. The longer tailing of increased Al concentrations (Figure 1C) and the later dominance of the hydrophobic fraction of DOC in the PNT columns (Figure 3) further supports the hypothesis that hydrophobic DOC plays a primary role in Al complexation.

4. Conclusions and Environmental Implications

A combined interpretation of field and laboratory data suggests that a large needle pulse after bark beetle-induced tree mortality and subsequent decomposition has the potential to enhance soil-water concentrations of Cu, Zn and Al. Increased DOC release resulting from the decomposition of the pine needles forms complexes with these metals enhancing their transport through the soil matrix while also increasing carbon sorption to the soil matrix that could result in a subsequent carbon release. It is expected that there will be an initial pulse of Cu released from pine needle leachate due to its affinity for organic complexes, but the duration of this pulse is unknown as DOM can inhibit Cu transport over longer periods. The addition of large amounts of Zn from the pine needle leachate creates higher soil-water concentrations along with additional sorption of zinc to the soil matrix possibly prolonging impacts even after the needles are leached as the recently sorbed Zn is subsequently released from soils. Aluminum appears to have a high affinity for hydrophobic DOC complexation, which indicates that the pine needle leachate will mobilize large amounts of Al due to its high proportion of hydrophobic acids.

In beetle-impacted watersheds, water treatment facilities have experienced increases in disinfection byproducts associated with an increased proportion of hydrophobic acids, indicating that the hydrophobic acids are an important component of organic matter originating from beetle-impacted trees[6]. If this portion of organic matter is increasing in association with beetle-impacted trees and has a propensity to complex with aluminum, ecotoxicity levels in surrounding waters may be surpassed. Field collected soil-water samples consistently had concentrations above EPA aquatic life criteria levels for Al and Zn (CMC for Al = 750 µg/l and Zn = 120 µg/l) but not for Cu[57], which would exacerbate existing water quality issues in Colorado where streams often exceed ecotoxicity levels for Al, Cu and Zn[40]. The enhanced mobilization of the three metals from pine needle leachate could also create ecological toxicity issues for plants as well as inhibit regrowth beneath the dead canopies[58].

Thus, it appears that as bark beetle infestations alter carbon dynamics, water quality may be degraded not only through increased potential for the formation of disinfection byproducts[6] but also through increased aqueous metal concentrations (particularly those metals with an affinity for the hydrophobic fraction of organic matter) that could have an ecological impact on localized regrowth or adjacent water bodies. This contrasts with climate-change projections of reduced surface-water metal concentrations in lowland catchments[59] which do not account for forest mortality due to insect infestations. It is uncertain how large the magnitude of response will be in beetle-impacted catchments with regard to trace metals, as some watershed-scale biogeochemical responses (particularly NO^{3-}) in beetle-impacted watersheds have been predicted to be large but observations have only indicated a weak response[60]. It would be insightful to determine the temporal trend of metal mobilization beneath degrading pine needles and whether or not the increased soil-water concentrations will be seen in adjacent surface and groundwaters creating ecological or human health concerns.

Supporting Information

Additional tables and figures can be found in the Supporting Information.

Acknowledgements

This material was based in part upon work supported by the U.S. National Science Foundation (EAR-1204787, CBET-1055396), Office of Science (BER) in the U.S. Department of Energy (DE-SC0006997), U.S. Geological Survey (G-2914-1) and the U.S. Environmental Protection Agency (EPA) STAR Fellowship no. FP91735401. Although the research described in the article was funded in part by the U.S. EPA STAR program, it has not been subjected to any EPA review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. The authors wish to thank Paul Brooks and Joel A. Biederman for field access and additional field samples, Brent Brouillard for data compilation and Brad E. Burback for laboratory and field assistance.

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Tables

Table 1: Influent pH values, DOC and metal concentrations. All units are mg/l except SUVA which is (L/mg/m).

	pH	DOC	SUVA	Zn	Cu	Al	Ca
PNT	5.56	96.0	2.13	0.095	0.006	0.234	4.14
RW	5.94	1.8	2.84	0	0	0	1.64

Table 2: Pearson's correlation coefficients (r) for Cu, Zn and Al with effluent DOC concentrations, hydrophobic DOC concentrations, pH and Ca concentrations in column and field studies. The coefficient ranges from -1 to 1 with values close to 1 or -1 signifying stronger positive or negative correlations respectively and is based off of the averages from the duplicate column runs. The field correlations are from under late-red phase trees. The grey highlighted cells indicate correlations > |0.60|.

	DOC	Hydroph. DOC	pH	Ca
Cu				
RW	0.86	0.59	-0.14	0.65
PNT	0.64	0.10	0.62	0.69
Field	0.82	N/A	N/A	0.47
Zn				
RW	0.67	0.40	-0.25	0.70
PNT	0.74	-0.31	0.28	0.61
Field	-0.23	N/A	N/A	-0.68
Al				
RW	0.82	0.79	-0.42	0.53
PNT	0.06	0.60	0.13	0.32
Field	0.91	N/A	N/A	0.69

Figures

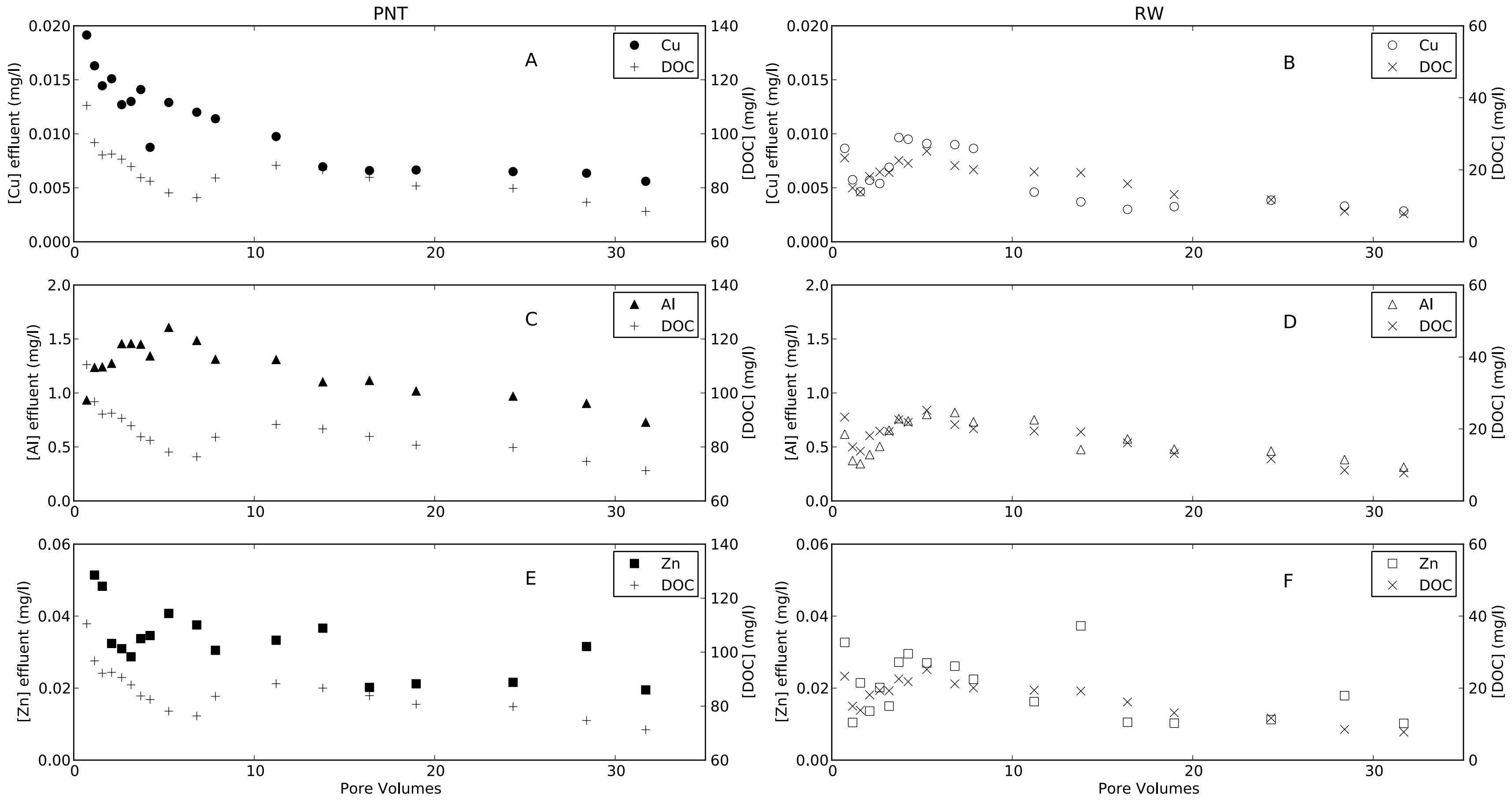

Figure 1: Average effluent metal (Cu, Al, Zn) and DOC concentrations from duplicate columns of PNT (A,C,E) and rainwater (B,D,F) influents. For RW, the initial metal concentrations were zero and $[DOC]_{RW}$ = 1.8 mg/l. The influent PNT concentrations were: $[DOC]_{PNT}$ = 96.0 mg/l , $[Cu]_{PNT}$ = 6.2 µg/l, $[Al]_{PNT}$ = 0.23 mg/l and $[Zn]_{PNT}$ = 0.95 mg/l. The first pore volume [Zn] = 0.25 mg/l and is not shown due to scale. Note scale differences for [DOC] in PNT and RW graphs. Associated error bars can be found in the supplementary information, Figure S1.

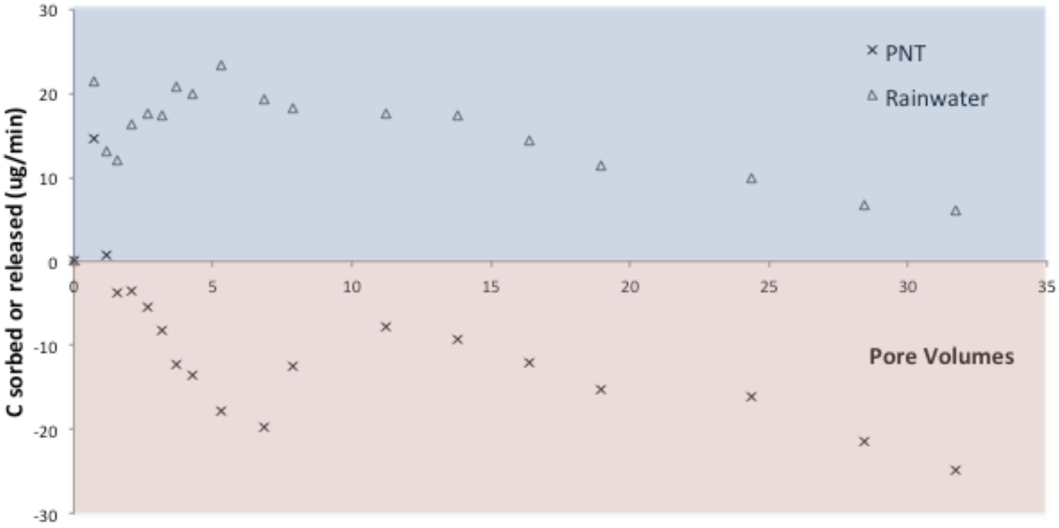

Figure 2: Average carbon balance from the duplicate columns contrasting PNT and rainwater. The blue shaded area indicates carbon is desorbing from the soil column and the red shaded area indicates that carbon is being sorbed to the soil column as the influent travels through the soil matrix.

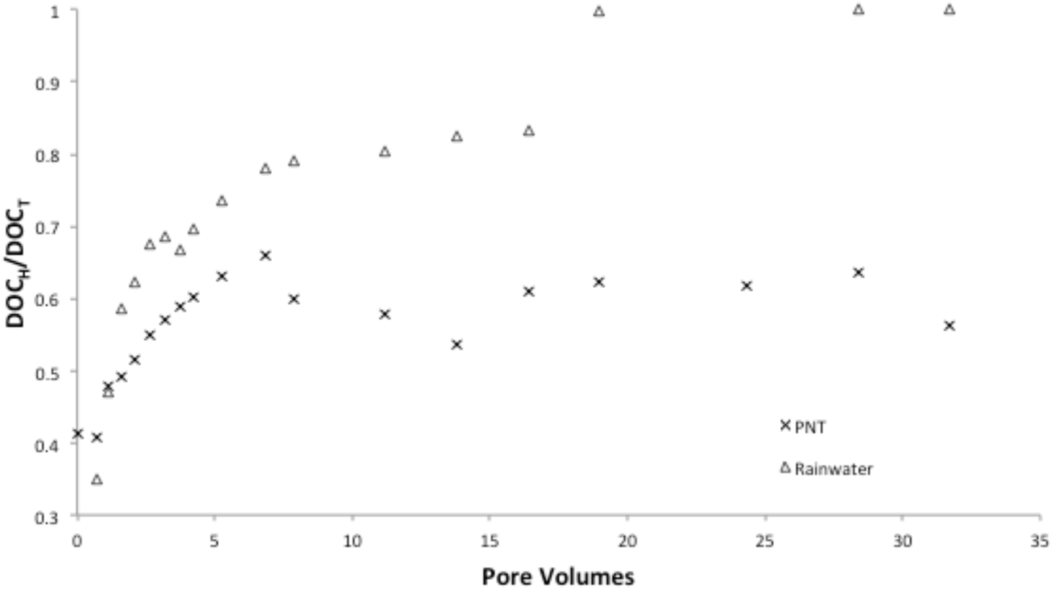

Figure 3: The average proportion of DOC_H (hydrophobic DOC) to DOC_T (total DOC) in duplicate column effluents for both PNT and rainwater (control) columns.