EFFECTS OF MINE DRAINAGE ON BREAKDOWN OF ASPEN LITTER IN MOUNTAIN STREAMS

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Abstract. Rates of aspen litter breakdown were measured at 40 sites in streams of the Rocky Mountains of Colorado, U.S.A. The sites encompassed a range of effects of mine drainage, from pristine (no effects) to highly stressed. The pH, concentrations of dissolved zinc, and deposition rates of metal oxides (the three main stresses from mine drainage) were measured in each stream. Rates of litter breakdown were estimated from changes in mass of aspen leaves in litterbags. The biological communities associated with litter breakdown also were evaluated by measuring the biomass of shredding invertebrates in litterbags and the rate of microbial respiration on litter. Of the stresses from mine drainage, concentration of zinc and deposition rate of metal oxides were most closely related (negatively) to rate of litter breakdown. Biomass of shredding invertebrates was also negatively related to concentration of dissolved zinc and deposition of metal oxides. Microbial respiration was negatively related to deposition rate of metal oxides and positively related to concentration of nutrients. Both shredder biomass and microbial respiration were positively related to litter breakdown rate and, together, accounted for 79% of its variation. Recovery of litter breakdown in streams affected by mine drainage requires remediation that limits both dissolved and deposited metals.

Keywords: decomposition, litter breakdown, microbial respiration, mine drainage, mountain streams, multiple stresses, shredding invertebrates, zinc

1. Introduction

Many streams throughout the world are affected by acidic, metal-rich water from active or abandoned mines. Mine drainage is a complex agent of stress in that it incorporates several individual stresses, any one of which can affect aquatic ecosystems. The stresses include acidity, high concentrations of dissolved metals, and deposition of precipitated metal oxides such as iron hydroxides. We studied the effects of mine drainage on the breakdown of leaf litter, an important ecological process, in streams of the Rocky Mountains of Colorado, U.S.A.

Acid rock drainage is caused by the weathering of pyrite, which involves a series of reactions that produce sulfuric acid when pyrite is exposed to oxygen and water. Oxidation of pyrite occurs naturally, but the rate of oxidation often is accelerated by mining, which increases the exposure of pyrite to oxygen and water, thereby

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producing acid mine drainage. Other metals, including aluminum, zinc, copper, and cadmium, are subject to weathering reactions and dissolution by acidic water. Thus, mine drainage can have high concentrations of these metals, which can be toxic to aquatic biota (Kelly, 1988; Clements, 1994). Most metals are very soluble at low pH and less soluble at circumneutral pH. As acidic drainage enters a stream, its pH usually increases because of dilution and buffering, and the solubility of some metal oxides, especially those of iron and aluminum, can be exceeded. In such cases, these metal oxides precipitate and form particles that are deposited onto the streambed. This deposition of metal oxides can affect stream biota (Letterman and Mitsch, 1978; Sode, 1983). Overall, the stresses from mine drainage can be considered chemical (low pH, dissolved metals) or physical (deposition of metal oxides), and can affect stream biota in different ways (McKnight and Feder, 1984; Niyogi *et al.*, 1999).

Several studies have shown that litter breakdown in aquatic environments is affected by mine drainage. Carpenter *et al.* (1983), Gray and Ward (1983), Maltby and Booth (1991), and Bermingham *et al.* (1996) all noted reduced rates of litter breakdown in such systems. Niyogi *et al.* (2001) analyzed breakdown of willow litter at 27 sites with varying degrees and types of stress from mine drainage in an effort to isolate the effects of the different stresses from mine drainage. In that study, litter breakdown was negatively affected by high concentrations of zinc and the deposition of metal oxides, mainly through their effects on shredding invertebrates. The effects of dissolved zinc were especially apparent in that study; sites with zinc greater than 0.5 mg L^{-1} had slow breakdown of litter and no shredding invertebrates.

This study was designed to extend the conclusions of Niyogi *et al.* (2001). In the present study, we examined breakdown of aspen litter at 40 sites with varying degrees of the three individual stresses described above. The biotic mechanisms underlying the effects of mine drainage on litter breakdown were examined by analysis of shredding invertebrates and microbes (fungi and bacteria). We hypothesized that mine drainage would affect the rate of breakdown through its effects on both shredding invertebrates and microbial activity. From our previous study, we predicted that streams lacking shredders because of mine drainage would have low breakdown rates.

2. Study Sites and Methods

2.1. Study sites

All study sites were located on low-order streams at high elevation (2800–3400 m a.s.l.) in the Rocky Mountains of Colorado, U.S.A. This study included 13 sites that were studied by Niyogi *et al.* (2001), but also included 27 additional sites. The new sites were predominantly located in the Upper Animas River basin in southwestern

Colorado. For most sites affected by mine drainage, we monitored at least one pristine site either upstream of the mine drainage or in a neighboring watershed. Streams in this region have hydrographs dominated by snowmelt, which occurs predominantly during May and June. Study streams usually had slopes of 2–8%, and streambeds were composed mainly of cobble. Riparian vegetation at the sites included willows (*Salix* spp.), aspen (*Populus tremuloides*), pine (*Pinus* spp.), fir (*Abies* spp.), and spruce (*Picea* spp.).

2.2. Abiotic Characteristics of Streams

The study began in late September 1998 and ended in December 1998. Methods for analysis of abiotic and biotic variables closely follow those of Niyogi *et al.* (2001), which was conducted in the autumn of 1997.

Data on stresses from mine drainage include pH, concentrations of dissolved metals, and deposition rates of metal oxides for all streams near the start of the study (September to early October), during baseflow. pH was measured on at least two samples from each site with an ion-specific electrode. Water samples for analysis of dissolved metals were filtered through cellulose nitrate filters (0.45 μm pore size), acidified with ultrapure nitric acid, and analyzed by ICP-AES or AA spectroscopy (Kimball *et al.*, 1994). Of the dissolved metals that were measured (aluminum, iron, copper, cadmium, lead, manganese, zinc), zinc was most closely related to biological variables (invertebrate biomass, rate of litter breakdown). Similarly, other studies in the area have shown that zinc is the major toxicant to aquatic life (Roline, 1988; Clements, 1994; Clements and Kiffney, 1995). Consequently, dissolved zinc was taken as the index of stress related to metals in the data analyses reported here. An average of at least two samples per site was used as the concentration of dissolved zinc in data analyses. Replicate samples were usually within 10% of each other, as expected during the baseflow conditions of the study.

The rate of metal oxide deposition was estimated as the rate of accumulation of mass (expressed as ash weight) on cobbles placed in the stream for known periods of time. Cobbles to be used for this purpose were removed from the stream, brushed clean, and placed in areas of moderate stream velocity (surface velocity 10–30 cm sec^{-1}). The cobbles were removed from the stream after 4 to 8 weeks and placed in plastic bags. In the laboratory, deposits on the cobbles were brushed into a tared weighing boat for determination of dry and ash mass. Chemical analyses of metal oxides were conducted as described by Niyogi *et al.* (1999) to confirm that the deposits were metal oxides; the analyses showed that the 'metal oxides' referred to here were indeed iron or aluminum oxides (or a mixture) that resulted from mine drainage. Deposition rates of metal oxides were calculated as the average ash mass per unit of surface area per unit time for 3–10 replicates.

Stream width (average of width at 5 transects) for each site was used in data analyses as an index of stream size. Stream temperature was recorded during the study with recording thermometers at 3 sites from different watersheds. Nutrient concentrations were measured in all streams following standard protocols (Lewis *et al.*, 1984). Filtered samples were analyzed for soluble reactive phosphorus (SRP) by an acid molybdate procedure, for ammonium by a phenol hypochlorite test, and for nitrate and nitrite by ion chromatography. Dissolved inorganic nitrogen (DIN) was calculated as the sum of ammonium N and nitrate N; nitrite N was not a significant component at any site.

2.3. Rates of Litter Breakdown

Rates of litter breakdown were measured with litterbags (Benfield, 1996). The litterbags consisted of plastic tubes (10 cm long, 5 cm in diameter) that had 1-mm nylon mesh covering both ends. Litterbags were oriented in the streams parallel to the current, and the mesh on the upstream side was perforated in several places with holes sufficiently large (8 mm) to allow invertebrates to enter.

Each litterbag contained 1 g dry mass of aspen leaves (*Populus tremuloides*) that had been collected just prior to abscission the previous autumn and air-dried. Litterbags were placed in streams during the start of litterfall (near the end of September) and were collected over several months. Three litterbags were retrieved at each of 3–5 sampling dates per site. The ash-free dry mass (AFDM) of remaining litter was measured by standard protocols (Benfield, 1996). The dry mass of litter was measured after oven-drying (60 °C) to a constant mass, and ash mass was determined after combustion in a furnace (540 °C for 8 hr). Decline of AFDM was quantified by use of an exponential equation:

$$M_t = M_o e^{-kt}$$

where

t	=	time in days;
M_t	=	AFDM at time t;
M_o	=	initial AFDM;
k	=	the breakdown coefficient per day (Petersen and Cummins, 1974).

There was an initial period of leaching from the dried litter, as has been reported in other studies (Short *et al.*, 1980). This loss was excluded from estimates of breakdown. Instead, the initial AFDM for analysis was set to 0.67 g, which was the AFDM of 1 g dry mass of aspen litter following 3 days of leaching in sterile stream water.

2.4. Biological Communities

Invertebrates were separated from litter and pooled from replicate litterbags during each sampling. Invertebrates were preserved in 70% ethanol, and sorted to genus or species, except for chironomids, which were not identified beyond the family level. Biomass of invertebrates was calculated from lengths of individuals and converted to AFDM by use of regression equations developed for Rocky Mountain populations of these taxa (McCutchan, 1999). The average biomass of shredding invertebrates (as classified by Merritt and Cummins, 1984) was computed from data on litterbags that had been in the stream for 3 to 10 weeks (2–3 sampling dates).

Respiration rates for decomposing litter were used as a measure of microbial activity. Oxygen consumption was measured on cores taken from the litter following the protocols of Niyogi *et al.* (2001). Three cores of 1 cm diameter were enclosed in a 26 mL vial that contained filtered stream water. The incubations were performed at 10 °C and lasted 18 to 24 hr. Each vial was gently stirred during the incubations. The average respiration rate was computed from data on litter that had been in the stream for 3 to 10 weeks (2–3 sampling dates). Microbial respiration is reported as μg O_2 consumed per cm^2 of litter per hour.

2.5. Data Analyses

Multiple regression was used to determine the effects of the three stresses (pH, dissolved zinc, and deposition rate of metal hydroxides) on rates of litter breakdown. Similarly, multiple regression was used to examine the roles of invertebrate biomass and microbial activity in affecting breakdown rates. Variables were log-transformed as necessary to meet assumptions of parametric statistics. Statistics were performed with SAS software (SAS Version 6.12).

3. Results

3.1. Abiotic Characteristics of Streams

The temperatures that were recorded at three sites in different watersheds were very similar. The mean daily temperature was approximately 3 °C during the first three weeks of the study (late September to early October), and the maximum temperature was 7–8 °C during warm days. Temperature varied from 0–2 °C throughout the rest of the study (mid-October to December), during which ice began to cover the stream. Other sites, where temperature was not recorded, had similar climates and are assumed to have had similar temperatures during the study to the sites that were measured. Stream width varied from 0.4 to 10.2 m.

Pristine sites all had circumneutral pH (7.1 to 7.8); the pH of sites affected by mine drainage ranged from 2.7 to 7.9. Concentrations of dissolved zinc ranged from <0.01 to 76 mg L^{-1}. Most sites in the study had intermediate concentrations of dissolved zinc (0.1 to 2.0 mg L^{-1}, as seen in Figure 1). The deposition rate of metal oxides ranged from <0.01 to 1.6 g m^{-2} d^{-1}. As with zinc, most sites had an intermediate rate of deposition (0.02 to 0.2 g m^{-2} d^{-1}, as seen in Figure 2).

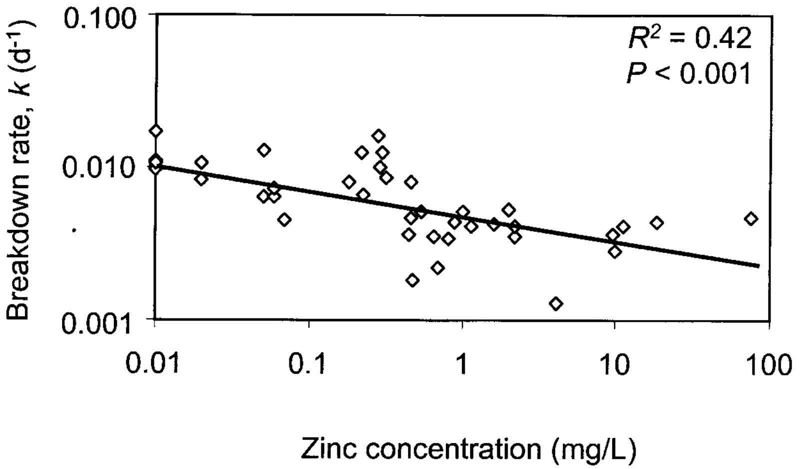

Figure 1. Rate of litter breakdown versus concentration of dissolved zinc.

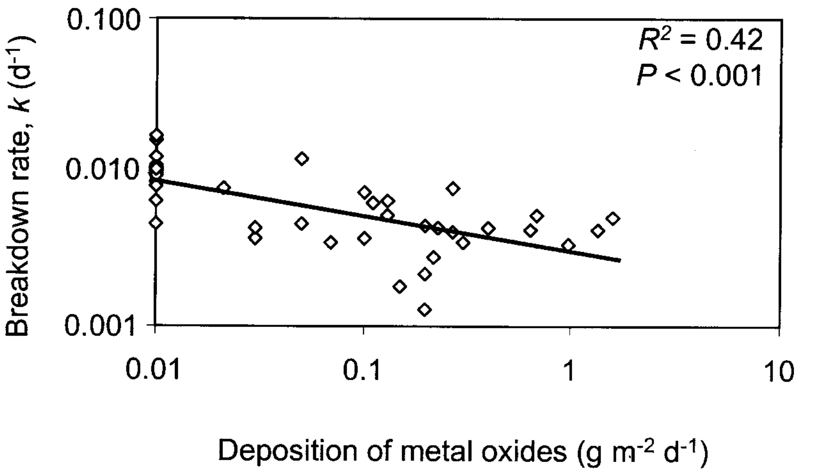

Figure 2. Rate of litter breakdown versus deposition rate of metal oxides.

3.2. Rates of Litter Breakdown

Rates of litter breakdown (as estimated by breakdown coefficient, k) ranged from 0.001 to 0.017 d^{-1}. Pristine reference sites had breakdown rates that ranged from 0.008 to 0.017 d^{-1} (mean = 0.011 d^{-1}). Sites affected by mine drainage usually, but not always, had lower rates ($k = 0.001$ to 0.016 d^{-1}, mean = 0.006 d^{-1}). Breakdown rate was closely related to both concentration of dissolved zinc (Figure 1) and deposition rate of metal oxides (Figure 2). Sites with zinc concentration greater than 0.5 mg L^{-1} all had breakdown rates less than 0.006 d^{-1}. Zinc and deposition rate accounted for 55% (overall R^2) of the variation in breakdown rates (Table I). pH, concentrations of nutrients (DIN, SRP), and stream width were not significant

TABLE I

Multiple regression analysis of rate of litter breakdown, shredder biomass, and microbial respiration in relation to abiotic and biotic variables

Dependent variable	df	Overall R^2	Overall *P* value	Independent variable	Standardized Regression Coefficient	*P* value
Breakdown rate (*k*)	2, 37	0.55	<0.001	Zn concentration	–0.42	0.002
				Rate of deposition	–0.44	0.002
Breakdown rate (*k*)	2, 37	0.79	<0.001	Shredder biomass	+0.51	<0.001
				Microbial respiration	+0.47	<0.001
Shredder biomass	2, 37	0.54	<0.001	Zn concentration	–0.46	<0.001
				Rate of deposition	–0.39	0.004
Microbial respiration	3, 36	0.63	<0.001	Rate of deposition	–0.73	<0.001
				DIN	+0.42	0.002
				SRP	+0.33	0.014

All variables log transformed except for microbial respiration.

when added to a regression incorporating zinc and deposition rate. The lowest rates of litter breakdown ($k < 0.004$ d^{-1}) were measured at sites with stress from both high concentrations of zinc and high deposition of metal oxides.

3.3. Invertebrate Biomass

Shredder biomass ranged from 0 to 3.1 mg AFDM/litterbag. A total of 21 streams affected by mine drainage had no shredding invertebrates. For those sites with shredders, stonefly nymphs of the genus *Zapada* (family Nemouridae) and families Capniidae and Leuctridae were the most common in the litterbags. Shredder biomass was closely related to both concentration of dissolved zinc and deposition rate of metal oxides. Sites with high zinc concentration usually had low shredder biomass; shredders were absent at all 17 sites with zinc >0.5 mg L^{-1}. Concentrations of dissolved zinc and deposition rates of metal oxides accounted for 54% of the variation in shredder biomass (Table I). Other variables were not significant if added to a regression incorporating zinc and deposition rate.

3.4. Microbial Respiration

Rates of microbial respiration ranged from 0.3 to 1.3 μg O_2 cm^{-2} hr^{-1}. Respiration rate on litter was most closely related to deposition rate of metal oxides; neither pH nor concentration of zinc was significantly related to respiration rate after the effects of metal oxide deposition were taken into account. Multiple regression showed that deposition rate of metal oxides and nutrient concentrations

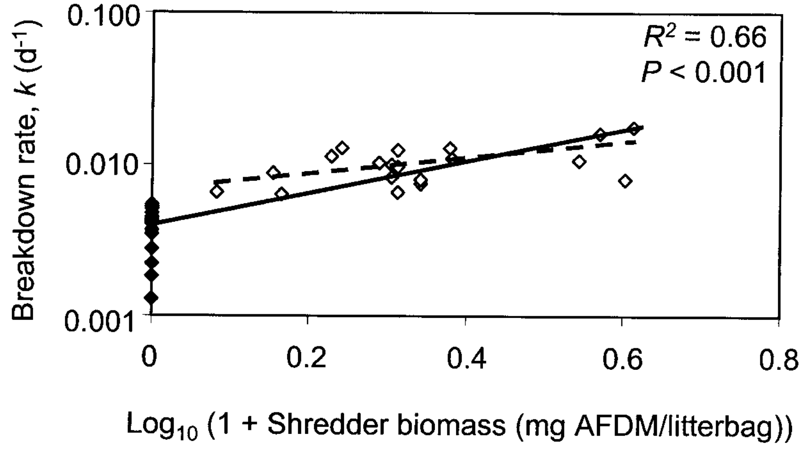

Figure 3. Rate of litter breakdown versus shredder biomass. Open symbols represent sites with shredders; closed symbols represent sites without shredders. The solid regression line and statistics on graph are for all data points. The dashed line is the regression for only those sites with shredders ($R^2 = 0.29$, $P < 0.05$).

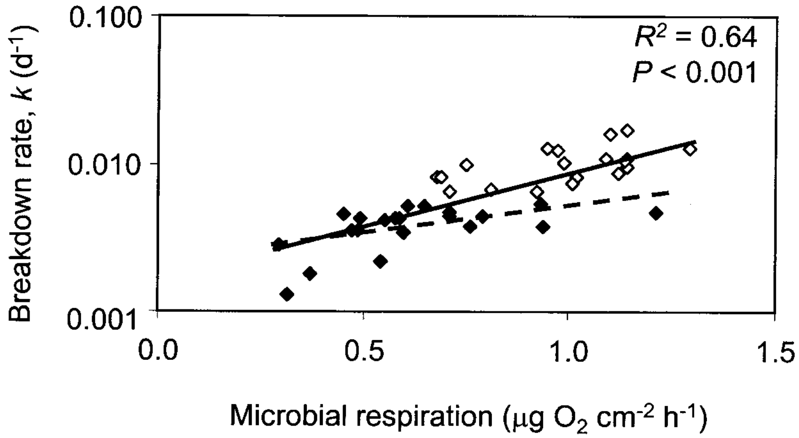

Figure 4. Rate of litter breakdown versus rate of microbial respiration. Open symbols represent sites with shredders; closed symbols represent sites without shredders. The solid regression line and statistics on graph are for all data points. The dashed line is the regression for only those sites without shredders ($R^2 = 0.33$, $P < 0.01$).

(DIN and SRP) were significantly related to respiration rate (Table I). These three variables accounted for 63% of the variation in respiration rate across streams. Other variables were not significant if added to a regression incorporating metal oxide deposition, DIN, and SRP.

3.5. Effects of Invertebrates and Microbes on Litter Breakdown

Breakdown rate was closely related to both shredder biomass (Figure 3) and microbial respiration (Figure 4). Shredders were found at all pristine sites and some stressed sites, and these sites all had high breakdown rates (>0.006 d^{-1}, mean = 0.010 d^{-1}). Sites without shredders all had low breakdown rates (<0.006 d^{-1}, mean = 0.004 d^{-1}). For sites with shredders, shredder biomass was still closely related to breakdown rate (dashed line in Figure 3). For sites without shredders, breakdown rate was significantly related to microbial respiration (dashed line in Figure 4). Several sites had high rates of microbial respiration (>0.8 μg O_2 cm^{-2} hr^{-1}) but low rates of litter breakdown (<0.006 d^{-1}); these sites lacked shredders because of the effects of mine drainage. Shredder biomass and rate of microbial respiration together accounted for 79% of the variation in breakdown rates (Table I).

4. Discussion

4.1. Rates of Litter Breakdown in Streams Affected by Mine Drainage

The present study was designed to complement the results of Niyogi *et al.* (2001), which examined breakdown of willow litter in 27 sites with varying effects of mine drainage. Sites in the present study covered a broader geographic range than Niyogi *et al.* (2001) and included sites along larger streams (up to 10 m in width). Overall, the results from the present study were similar to those of Niyogi *et al.* (2001), and suggest that our reported mechanisms of effects of mine drainage on litter breakdown may apply to streams elsewhere.

Breakdown of aspen litter was expected to be slower than that of willow litter (Short *et al.*, 1980). The rate of litter breakdown for aspen litter at pristine sites in the present study was slightly lower (mean k = 0.011 d^{-1}) than for willow litter in Niyogi *et al.* (2001) (mean k = 0.013 d^{-1}). Zinc was more closely related to rate of litter breakdown in Niyogi *et al.* (2001) (R^2 = 0.64) than the present study (R^2 = 0.42). Part of this difference may be related to the greater number of sites with intermediate concentrations of zinc in the present study. The highest residuals in the regression (Figure 1) occur near 0.5 mg L^{-1} zinc, where there appears to be a step relation: sites with zinc less than 0.5 mg L^{-1} usually have high breakdown rates, and sites with zinc greater than this threshold have low breakdown rates. Thus, there appears to be a threshold response at this zinc concentration of 0.5 mg L^{-1}, which is probably related to the tolerance of shredding invertebrates, as described below.

Rates of litter breakdown usually are low in waters affected by mine drainage (Carpenter *et al.*, 1983; Bermingham *et al.*, 1996; Schultheis *et al.*, 1997). Sites in our study that were affected by mine drainage usually had low breakdown rates, except in cases where mine drainage did not significantly affect biota (see below).

Our results were very similar to those of Niyogi *et al.* (2001) in that both zinc and deposition of metal oxides affected litter breakdown. The rate of breakdown was usually low at sites with either of these two stresses. Similarly, Gray and Ward (1983) reported that litter breakdown in a stream affected by mine drainage remained depressed even after improvements in water quality. They attributed the lack of recovery to the continued effects of metal oxide deposition.

4.2. Effects of Mine Drainage on Biological Communities

Shredder biomass and rate of litter breakdown were affected similarly by mine drainage, and were most closely related to concentrations of dissolved zinc and deposition rate of metal oxides. Zinc and other dissolved metals often affect community structure in streams affected by mine drainage (Kelly, 1988; Clements, 1994). We conducted our analyses using zinc because its concentrations often exceeded levels known to affect invertebrates (e.g., Clements, 1994). However, other metals such as copper were present at a few sites and could have acted in combination with zinc to affect biota.

Although pH affects invertebrate communities in many acidified streams (Kelly, 1988; Courtney and Clements, 1998), pH did not have a significant effect on biomass of shredding invertebrates that was independent of the effects of zinc and deposition of metal oxides. Several of our sites with low pH actually had high biomass of Nemourid stoneflies, as has been found in other studies (McKnight and Feder, 1984; Ledger and Hildrew, 2000).

The deposition of metal oxides negatively affected both shredder biomass and breakdown rate. Although these effects have been noted in other studies (Gray and Ward, 1983; McKnight and Feder, 1984), the mechanisms for metal oxide effects on invertebrates are not well understood. Toxic metals such as zinc and copper can be present in metal oxides or associated with leaf litter, but their concentrations were not related to breakdown rates at our sites (D.K. Niyogi, unpublished data) or in another study (Schultheis and Hendricks, 1999).

Microbial activity appears to have a higher threshold than invertebrate biomass to stress from pH and zinc. Low pH can affect microbial communities associated with litter breakdown in streams (e.g., Mulholland *et al.*, 1987; Thompson and Bärlocher, 1989). In the present study, however, neither low pH nor high zinc was statistically related to microbial respiration rate after the effect of metal oxide deposition was accounted for. High rates of microbial respiration (>1 $\mu g\ O_2\ cm^{-2}\ hr^{-1}$) were measured at sites with pH as low as 2.7 and concentrations of zinc as high as 76 mg L^{-1}. Similarly, Miersch *et al.* (1997) found that the growth of some aquatic fungi (hyphomycetes) was inhibited only at very high concentrations of metals. In both the present study and Niyogi *et al.* (2001), microbial activity was related negatively to deposition of metal oxides and positively to concentration of nutrients (DIN and SRP). The negative effect of deposition may be related to the coating of metal oxides on the litter or microbes, especially fungal hyphae (D.K.

Niyogi, personal observation). The positive effect of nutrients is not surprising as microbial communities on litter are often influenced by concentrations of nutrients (e.g., Suberkropp and Chauvet, 1995).

4.3. Roles of Invertebrates and Microbes in Litter Breakdown

Litter breakdown in streams is affected by physical (leaching, mechanical breakdown) and biological processes (shredding, decomposition). Results from this study suggest that both shredders and microbes control breakdown rates in mountain streams. Sites without shredders always had low breakdown rates. At these sites without shredders, breakdown rate was significantly related to microbial activity. Thus, mine drainage can affect litter breakdown through effects on invertebrates, microbial activity, or both.

The important role of invertebrates in litter breakdown has been documented in other systems under stress (e.g., Tuchman, 1993). For example, Griffith and Perry (1993) and Dangles and Guerold (1998) attributed low rates of litter breakdown in acidic streams to the loss of amphipods, although other shredders were still present. Wallace *et al.* (1982) found that the rate of litter breakdown was greatly reduced in a stream treated with an insecticide, which reduced the abundance of shredding invertebrates.

Niyogi *et al.* (2001) concluded that zinc acts as an insecticide to shredders above a threshold near 0.5 mg L^{-1}. Breakdown rates of willow litter were always depressed ($k < 0.008$ d^{-1}) at sites with zinc concentrations greater than 0.5 mg L^{-1} in that study. In the present study, shredding invertebrates were again absent above this threshold of 0.5 mg L^{-1}, and these sites had slow breakdown of aspen litter ($k < 0.006$ d^{-1}). Several sites in both studies that were affected by mine drainage had concentrations of dissolved zinc below this threshold, and these sites had shredders and high breakdown rates ($k > 0.008$ d^{-1}) if they were not affected by deposition of metal oxides. Similarly, Nelson (2000) showed that the rate of litter breakdown was not depressed at two sites affected by mine drainage that had concentrations of zinc less than 0.5 mg L^{-1} and still had shredding stoneflies.

5. Conclusions

Mine drainage is a challenging problem for scientists and managers because it can impose several different stresses on aquatic systems. However, the stresses from mine drainage (low pH, dissolved metals, metal oxide deposition) are well understood from a geochemical perspective and can be modeled in streams (Kimball *et al.*, 1994; Runkel *et al.*, 1999). The effects of mine drainage on ecological processes such as litter breakdown are becoming well understood, and the combined knowledge of abiotic and biotic conditions in streams can help guide remediation at such sites. Both high concentration of dissolved metals (zinc above 0.5 mg L^{-1}

in the streams of our study) and deposition of metal oxides can decrease the rate of litter breakdown compared to pristine streams. For the recovery of litter breakdown, remediation must decrease concentrations of dissolved metals such as zinc below the threshold for survival of shredding invertebrates, and also must prevent high rates of metal oxide deposition, which can limit both shredders and microbes.

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