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LITTER BREAKDOWN IN MOUNTAIN STREAMS AFFECTED BY MINE DRAINAGE: BIOTIC MEDIATION OF ABIOTIC CONTROLS

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Abstract. Breakdown of plant litter in streams was studied as an example of a major ecological process subject to change through multiple stresses associated with mine drainage. Rates of litter breakdown were measured at 27 sites in streams of the Rocky Mountains of Colorado, USA. Eight of the sites were pristine, and 19 were affected to varying degrees by mine drainage. The pH, concentrations of dissolved zinc, and deposition rates of metal oxides were measured in each stream. Rates of litter breakdown were estimated from changes in mass of willow leaves in litterbags. Biomass of shredding invertebrates in litterbags was monitored at each site, as was microbial respiration on litter. Of the abiotic variables, increased concentrations of zinc and increased deposition rates of metal oxides were most closely related to decreased rates of litter breakdown. Biomass of shredding invertebrates was negatively related to concentration of dissolved zinc and deposition of metal oxides and was more closely related to breakdown rates than was microbial respiration. Microbial respiration was related negatively to deposition rates of metal oxides and positively to nutrient concentrations. Shredder biomass and microbial respiration together accounted for 76% of the variation in breakdown rates. Remediation schemes for streams affected by mine drainage should take into account the distinct ecological effects of the multiple stresses caused by mine drainage (pH, high concentrations of dissolved metals, deposition of metal oxides); remediation of a single stress is likely to be ineffective.

Key words: acidification; Colorado (USA); decomposition; litter breakdown; metal toxicity; microbial respiration; mine drainage; multiple stresses; shredding invertebrates; streams, Rocky Mountain.

INTRODUCTION

Mine drainage affects many aquatic ecosystems in regions with a history of mining (see Plate 1). Mine drainage is a complex agent of stress in that it incorporates several distinct mechanisms of stress, any one of which can affect aquatic ecosystems. The stresses include: (1) acidity, (2) high concentrations of dissolved metals, and (3) deposition of precipitated metal oxides, such as iron hydroxides (McKnight and Feder 1984, Kelly 1988). The geochemistry of waters affected by mine drainage has been studied extensively, and models allow researchers to predict changes in water quality that can be expected following remediation (e.g., Walton-Day et al. 1999). In contrast, the effects of mine drainage on aquatic biota and ecosystem processes are poorly understood, as are the ecological benefits of various degrees of remediation. We report here connections between the multiple stresses of mine drainage and the breakdown of leaf litter, an important ecological process, in streams of the Rocky Mountains of Colorado.

Acid rock drainage is caused by the weathering of pyrite, which produces 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 exposes pyrite to oxygen and water. In the subsurface, low pH enhances mobility of other metals, including aluminum, zinc, copper, and cadmium, which are also subject to weathering reactions. Mine drainage and receiving streams consequently may have high concentrations of these metals, which can be toxic to aquatic biota (Kelly 1988). Certain metals such as iron and aluminum often are dissolved in mine drainage but can precipitate upon entering streams. Most metals are very soluble at low pH, as would be typical of acidic mine drainage, and less soluble at circumneutral pH. As acidic drainage enters a stream, pH usually increases because of dilution and buffering. If the pH required for solubility of hydrous oxides of iron and aluminum is exceeded, these metals will precipitate. Colloidal metal oxides may aggregate to form larger particles that will be deposited onto the streambed. The deposition of metal oxides can affect stream biota (Sode 1983, McKnight and Feder 1984, Wellnitz and Sheldon 1995, Niyogi et al. 1999).

The effects of mine drainage on invertebrate communities, especially as related to dissolved metals, have been documented in many studies (e.g., Kelly 1988, Clements 1994, Clements and Kiffney 1995, Nelson and Roline 1996). Fewer studies have examined litter

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PLATE 1. Acidic drainage flows from an abandoned mine into St. Kevin Gulch, near Leadville, Colorado, USA.

breakdown in aquatic environments 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. These studies, however, included only one or a few sites that were stressed by mine drainage. The work reported here included many sites with varying degrees of stress from mine drainage, and the sites had varying degrees of the three individual stresses described above. Specifically, sites affected by mine drainage had a range in pH from acidic to neutral, zinc concentrations spanning three orders of magnitude, and varying rates of metal oxide deposition. The range in site characteristics enabled us to separate the effects of the different stresses caused by mine drainage. These stresses, which can be considered chemical (low pH, dissolved metals) or physical (deposition of metal oxides), can affect stream biota in different ways (McKnight and Feder 1984, Niyogi et al. 1999).

The biotic mechanisms underlying the effects of mine drainage on litter breakdown were examined by analysis of the biological communities that cause the breakdown of litter: shredding invertebrates and microbes (fungi and bacteria). Recent research suggests that aquatic fungi are the dominant microbial decomposers during the early stages of litter breakdown (Baldy et al. 1995, Weyers and Suberkropp 1996). Several studies have dealt with the roles of invertebrates and microbes in litter breakdown (reviewed in Maltby [1992]). In streams affected by mine drainage, the roles of shredders and microbes may be altered if they have different sensitivities to the stresses from mine drainage. Many invertebrates are sensitive to low pH (Courtney and Clements 1998), dissolved metals (Clements 1994), and deposition of metal oxides (McKnight and Feder 1984). Microbial activity on decomposing litter also can be affected by low pH (Thompson and Bärlocher 1989), high concentrations of dissolved metals (Abel and Bärlocher 1984), and deposition of metal oxides (Maltby and Booth 1991).

The biotic studies of litter breakdown are based on two questions: (1) how do stresses from mine drainage affect invertebrates and microorganisms involved in litter breakdown, and (2) how are changes in the communities related to changes in rates of litter breakdown? The rate of litter breakdown was measured by use of litterbags at 27 stream sites, 19 of which were affected by mine drainage and 8 of which were pristine. The three possible stresses from mine drainage outlined above (pH, dissolved metals, and deposition of metal hydroxides) were quantified. The biomass of invertebrates in litterbags was quantified, as was microbial activity (by measurement of oxygen consumption associated with litter). The objective of the work was to elucidate the mechanisms by which a complex stress (mine drainage) affects a biotically-driven process (breakdown of litter).

METHODS

Site descriptions

All study sites were located on low-order streams at high elevation (2800–3400 m above sea level) in the Rocky Mountains of Colorado, USA (Fig. 1). A de-

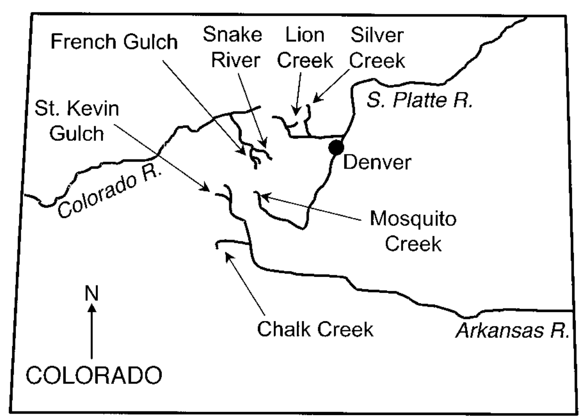

FIG. 1. Map of Colorado showing study areas.

TABLE 1. Physicochemical and biological characteristics of stream sites in seven study regions in Colorado.

Region Site	Elev. (m)	Width (m)	pH	Zn (mg/L)	MOH ($g \cdot m^{-2} \cdot d^{-1}$)	DIN (μg/L)	SRP (μg/L)	Shr (mg/bag)	Resp (μg $O_2 \cdot cm^{-2} \cdot h^{-1}$)	Breakdown rate, k (d^{-1})	SE	R^2
St. Kevin Gulch												
Site 1†	3230	1.0	7.4	0.01	0.01	6	21	4.8	1.11	0.014	0.0027	0.90
Site 2† (Shingle Mill Gulch)	3140	0.5	7.3	0.01	0.01	5	27	4.1	1.08	0.013	0.0008	0.98
Site 3† (Porcupine Gulch)	3080	1.6	7.2	0.01	0.01	7	12	3.3	1.20	0.009	0.0011	0.93
Site 4	3120	1.0	4.5	3.3	0.06	10	2	0	0.41	0.003	0.0005	0.91
Site 5	3110	1.5	4.8	3.5	0.31	11	2	0	0.50	0.002	0.0004	0.87
Site 6	3103	1.4	3.7	10	0.45	26	2	0	0.59	0.003	0.0003	0.94
Site 7	3017	1.6	3.8	10	0.23	26	2	0	0.44	0.003	0.0007	0.82
Site 8	3115	0.3	2.7	80	0.01	27	82	0	1.24	0.004	0.0004	0.95
Snake River												
Site 1† (Deer Creek)	3276	3.5	7.0	0.01	0.01	57	1	5.3	1.13	0.013	0.0012	0.97
Site 2	3275	4.4	3.8	0.45	0.02	62	2	7.3	0.93	0.010	0.0008	0.95
Site 3	3260	5.7	5.2	0.27	0.31	50	2	1.2	0.30	0.004	0.0011	0.85
Site 4	3140	6.2	6.2	0.25	0.12	49	2	0.6	0.50	0.005	0.0008	0.90
Site 5 (Peru Creek)	3155	5.1	5.2	1.5	0.27	47	2	1.2	0.67	0.005	0.0013	0.83
French Gulch												
Site 1† (UFG-97 in Fig. 8)	3110	3.1	7.7	0.01	0.01	58	2	3.9	1.00	0.012	0.0012	0.96
Site 1† (UFG-98 in Fig. 8)	3110	3.1	7.7	0.01	0.01	55	2	3.0	1.05	0.013	0.0015	0.93
Site 2 (LFG-97 in Fig. 8)	3078	3.2	7.5	1.0	0.01	50	3	0	1.40	0.005	0.0011	0.94
Site 2 (LFG-98 in Fig. 8)	3078	3.2	7.4	0.30	0.01	52	3	2.1	1.10	0.016	0.0020	0.92
Site 3	3087	0.9	7.3	0.65	0.59	51	4	0	0.66	0.005	0.0008	0.89
Mosquito Creek												
Site 1† (N. Mosquito Creek)	3368	4.1	7.7	0.01	0.01	43	1	3.9	1.30	0.008	0.0005	0.98
Site 2 (S. Mosquito Creek)	3383	3.5	7.9	1.1	0.08	74	1	2.0	1.26	0.006	0.0008	0.94
Site 3	3125	8.8	7.9	0.26	0.03	47	1	0.3	1.13	0.005	0.0007	0.93
Chalk Creek												
Site 1†	3185	4.1	7.6	0.03	0.01	52	2	4.0	1.01	0.010	0.0012	0.97
Site 2	3170	4.2	7.5	0.33	0.01	46	1	3.0	1.11	0.010	0.0004	0.98
Site 3	3190	1.1	7.1	20	0.05	42	2	0	1.07	0.004	0.0011	0.89
Silver Creek												
Site 1†	3185	1.7	7.0	0.01	0.01	10	2	7.1	1.02	0.021	0.0036	0.95
Site 2	3165	1.7	7.0	0.02	0.05	17	4	6.7	0.90	0.011	0.0017	0.95
Lion Creek												
Site 1	2835	1.4	3.2	0.78	1.05	41	8	0	1.11	0.006	0.0008	0.89
Site 2	2845	1.6	3.1	0.88	1.15	40	3	0	0.56	0.006	0.0006	0.91

Notes: Region refers to study areas in Fig. 1. MOH is rate of deposition of metal oxides. ''Shr'' is biomass of shredding invertebrates. ''Resp'' is rate of respiration of microbes on litter. The detection limit for Zn and MOH measurements was 0.01.

† Site was considered pristine.

scription of the sites is presented in Table 1. 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 3–8%; streambeds were composed mainly of cobble. Riparian vegetation at all sites was dominated by willows (*Salix* spp.), but included some aspen (*Populus tremuloides*), pine (*Pinus* spp.), and spruce (*Picea* spp.). Further descriptions of the study regions can be found in McKnight and Feder (1984) for the Snake River area, Kimball et al. (1994) and Niyogi et al. (1999) for the St. Kevin Gulch area, and Clements and Kiffney (1995) for French Gulch, Chalk Creek, and Mosquito Creek watersheds.

Abiotic characteristics of streams

The study began in late September 1997 and ended in December 1997. Stream width (average bank-to-bank width at five 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 three sites.

Data on stresses from mine drainage include pH, concentrations of dissolved metals, and deposition rates of metal hydroxides for all streams near the start of the study (September to early October), during baseflow. Procedures for measurement of abiotic variables are described by Niyogi et al. (1999). Streamwater 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 inductively coupled plasma–atomic emission spectroscopy or atomic absorption spectrometry (Kimball et al. 1994). Of the dissolved metals 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 revealed that zinc is the major toxicant to aquatic life (Roline 1988, Clements and Kiffney 1995). Consequently, zinc was the main dissolved metal that was included as a stress in the data analyses reported here. An average of at least two samples per site was used to generate the concentration value of dissolved zinc in data analyses.

The rate of metal oxide deposition was estimated as the rate of accumulation of ash mass 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/s). The cobbles were removed from the stream after 4–8 wk 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.

Nutrient concentrations were measured in all streams. Water samples for nutrient analysis were filtered through Whatman GF/F filters (nominal pore size 0.7 μm). Ammonium nitrogen was measured by a phenol hypochlorite colorimetric test, nitrate nitrogen was measured by ion chromatography, and soluble reactive phosphorus (SRP) was measured by an acid molybdate colorimetric procedure (Lewis et al. 1984). Dissolved inorganic nitrogen (DIN) was estimated as the sum of ammonium N and nitrate N (nitrite N was not a significant component at any site).

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 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 willow leaves (*Salix* spp.) 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 three to six sampling dates per site. The ash-free dry mass (AFDM) of remaining litter was measured by standard protocols (Benfield 1996). Decline of AFDM was quantified by use of an exponential equation: $M_t = M_0 e^{-kt}$ where t is time in days, M_t is AFDM at time t, M_0 is initial AFDM, and k is the litter-breakdown coefficient, expressed as mass loss 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, Gessner and Schwoerbel 1989). This loss was excluded from estimates of breakdown. Instead, the initial AFDM for analysis was set to 0.65 g, which was the AFDM of 1 g dry mass of litter following 3 d of leaching in sterile stream water.

Biomass of shredding invertebrates

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 3–10 wk (two to four sampling dates).

Microbial respiration

Respiration rates for decomposing litter were used as a measure of microbial activity. Oxygen consumption was measured on cores taken from the litter. Litter in litterbags was gently rinsed with filtered stream water drawn from the site from which the litterbag had been collected. 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 18–24 h. Each vial was gently stirred during the incubations. Preliminary trials revealed that oxygen uptake was linear during the course of the incubations. Additional treatments of vials containing only stream water or stream water and metal oxides were run to insure that oxygen uptake by these control treatments was not significant compared to that of litter samples. The average respiration rate was computed from data on litter that had been in the stream for 3–10 wk (two to four sampling dates). Microbial respiration is reported as micrograms of O_2 consumed per square centimeter of litter-core surface area per hour.

Data analyses

Multiple regression was used to determine the effects of the three stresses (pH, dissolved zinc, and deposition

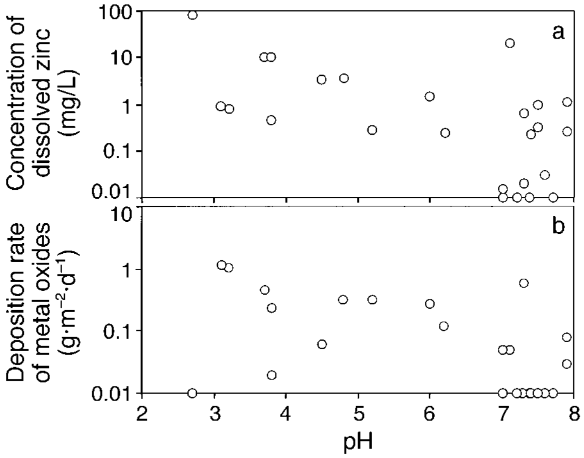

FIG. 2. (a) Relation between pH and concentration of dissolved zinc (plotted on log scale) and (b) relation between streamwater pH and deposition rate of metal oxides (plotted on log scale) across Colorado stream sites.

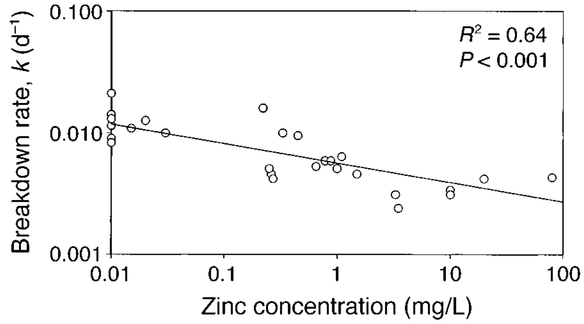

FIG. 3. Rate of litter breakdown (plotted on log scale) vs. concentration of dissolved zinc (plotted on log scale).

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). Results were considered significant if $P < 0.05$, and weakly significant if $P = 0.05$–0.10.

RESULTS

Abiotic characteristics of streams

Table 1 presents abiotic and biotic data associated with each site. The temperatures that were recorded at three sites in different watersheds were very similar. The mean daily temperature was 3–4°C during the first 3 wk of the study (late September to early October), with a maximum temperature of 6–8°C during warm days. The temperature range was 0–1°C throughout the rest of the study (mid October to December), during which ice began to cover the stream. All other sites (where temperature was not recorded) had similar climates and most likely had a range in temperature during the study similar to the sites that were measured.

The streamwater pH of study sites ranged from 2.7 to circumneutral. Pristine sites all had circumneutral pH; sites affected by mine drainage had pH that ranged from 2.7 to 7.8. Mine drainage may have circumneutral pH if it is buffered by basic minerals (e.g., carbonates), as was the case for some study sites.

The concentration of dissolved zinc was negatively related to pH, especially at low pH (Fig. 2a). Sites with low pH consistently had high concentrations of zinc (>0.25 mg/L); this trend was not unexpected, as the geochemical mechanisms producing these stresses are related. Sites with circumneutral pH had an especially wide range of zinc concentrations (<0.01–20 mg/L). Zinc is highly mobile once dissolved (usually in acidic groundwater) and was often present in high concentration in mine drainage of neutral pH. The deposition rate of metal oxides also varied with pH (Fig. 2b). Some sites with low pH (<4) had low rates of deposition because most metal oxides are soluble at low pH. Sites with pH between 4.5 and 6.5 had consistently high deposition rates; such sites usually occurred where acidic and neutral waters mix, and metals from acidic waters often precipitate as pH increases during mixing. Sites with circumneutral pH had a large range of deposition rates (<0.01–$0.6\ g \cdot m^{-2} \cdot d^{-1}$).

Rates of litter breakdown

Rates of litter breakdown (as estimated by the breakdown coefficient, k) ranged from 0.002 to 0.021 d^{-1}. Pristine reference sites had breakdown rates that ranged from 0.008 to 0.021 d^{-1} (mean = 0.013 d^{-1}). Sites affected by mine drainage usually had lower rates (k = 0.003–0.016 d^{-1}, mean = 0.006 d^{-1}). Breakdown rate was most closely related to concentration of dissolved zinc (Fig. 3). Sites with zinc concentration >0.5 mg/L all had breakdown rates <0.010 d^{-1}. The deposition rate of metal oxides had the next highest correlation with breakdown rate and explained added variance in multiple regression after zinc was taken into account (Table 2). Streamwater pH, concentrations of nutrients (inorganic N, SRP), and stream width were not significant when added to a regression incorporating zinc and deposition rate. Zinc and deposition rate accounted for 72% of the overall variation in breakdown rates (Table 2). 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.

Invertebrate biomass

Invertebrate densities ranged from zero to 41 individuals per litterbag. Shredder biomass ranged from zero to 7.3 mg AFDM/litterbag. Shredding stoneflies were dominant in most streams. Stonefly nymphs of the genus *Zapada* (family Nemouridae) and family Capniidae were the most common. Shredder biomass was most highly correlated with concentration of dis-

TABLE 2. Multiple regression analysis of rate of litter breakdown (log transformed), shredder biomass, and microbial respiration in relation to abiotic variables (all log transformed) in Colorado streams.

Dependent variable	df	Overall R^2	Overall P value	Independent variable	Standardized regression coefficient	P value
Breakdown rate, k	2, 24	0.72	0.0001	Zn concentration	−0.64	0.0001
				Rate of deposition	−0.32	0.0159
Shredder biomass	2, 24	0.64	0.0001	Zn concentration	−0.62	0.0002
				Rate of deposition	−0.28	0.0582
Microbial respiration	2, 24	0.54	0.0001	Rate of deposition	−0.69	0.0001
				DIN + SRP	+0.25	0.0831

solved zinc (Fig. 4). Sites with increased zinc concentration usually had low shredder biomass; shredders were absent at most sites with zinc >0.5 mg/L. Concentrations of dissolved zinc (P = 0.0002) and deposition rates of metal oxides (P = 0.058) were significantly related to shredder biomass (Table 2). Other variables were not significant if added to a regression incorporating zinc and deposition rate.

Microbial respiration

Rates of microbial respiration ranged from 0.30 to 1.40 μg O_2 cm^{-2} h^{-1}. Deposition rate of metal oxides was most closely related to respiration rates on litter (Fig. 5). Multiple regression showed that deposition rate of metal oxides was highly significant (P = 0.0001) and nutrient concentration (log DIN + log SRP) was weakly significant (P = 0.08) for predicting respiration rate (Table 2). These two variables accounted for 54% of the variation in respiration rate among streams. Other variables were not significant if added to a regression incorporating metal oxide deposition and nutrients.

Effects of invertebrates and microbes on litter breakdown

Breakdown rate was more closely related to shredder biomass (Fig. 6) than to microbial respiration (Fig. 7). Shredders were common (>4 mg AFDM/litterbag) at all pristine sites and some stressed sites, and these sites all had breakdown rates >0.008 d^{-1} (Fig. 6) Sites with few or no shredders all had slow breakdown rates (<0.006 d^{-1}). Several sites had high rates of microbial respiration but low rates of litter breakdown (Fig. 7). Shredder biomass and rate of microbial respiration together accounted for 76% of the variation in breakdown rates (Table 3).

Interannual variability of litter breakdown

Litter breakdown was measured at several sites in a second year (1998). For most sites, there was no significant difference in the rate of litter breakdown between the two years (*data not shown*), but there was a significant difference between years for one site in French Gulch, near Breckenridge, Colorado. In 1997 this site (LFG) had a high concentration of zinc (1.0 mg/L), whereas an upstream site (UFG) had a very low concentration of zinc (<0.01 mg/L). In 1997 the rate of litter breakdown was significantly lower at LFG than at UFG (Fig. 8a). Shredding invertebrates were absent at LFG but present at UFG (Fig. 8b). Microbial respiration was significantly higher at LFG than at UFG in 1997 (Fig. 8c). In 1998, the concentration of zinc at LFG was 0.3 mg/L, and there were no significant differences in shredder biomass, microbial respiration, and rate of litter breakdown between the two sites (Fig. 8).

DISCUSSION

Rates of litter breakdown in streams affected by mine drainage

Pristine reference sites in the present study had breakdown rates (mean breakdown coefficient k = 0.013 d^{-1}) that were similar to those measured previously for willow litter in Rocky Mountain streams

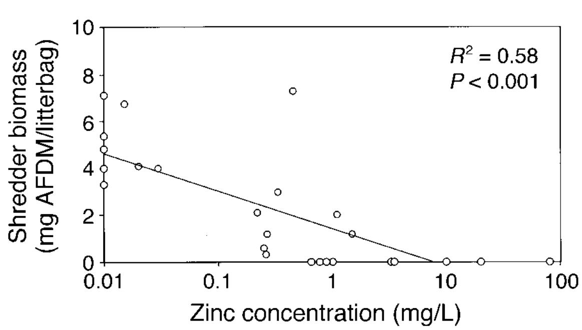

FIG. 4. Shredder biomass vs. concentration of dissolved zinc (plotted on log scale).

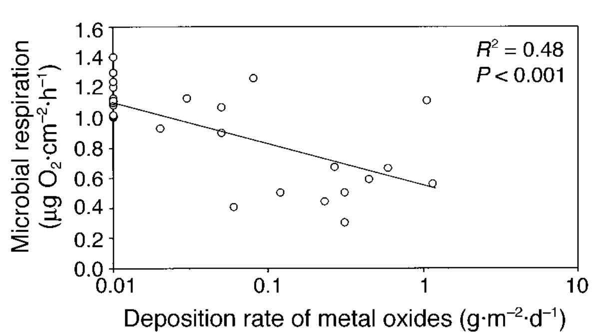

FIG. 5. Microbial respiration vs. deposition rate of metal oxides (plotted on log scale).

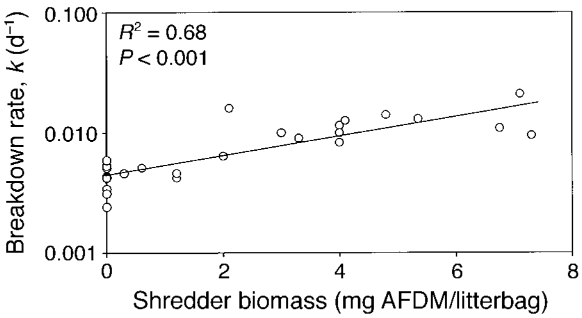

FIG. 6. Rate of litter breakdown (plotted on log scale) vs. shredder biomass.

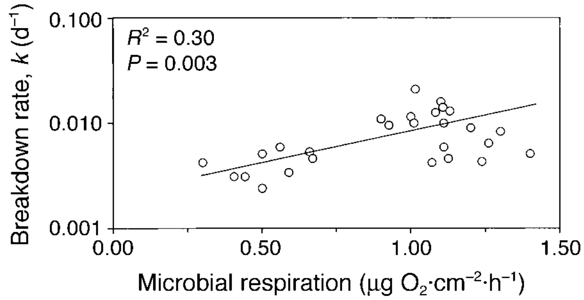

FIG. 7. Rate of litter breakdown (plotted on log scale) vs. rate of microbial respiration.

(Short et al. 1980, Mutch and Davies 1984). Sites affected by mine drainage usually had lower rates. Concentrations of dissolved zinc and deposition rate of metal oxides were most closely related to breakdown rate, and together accounted for 72% of the variation in breakdown rates. Rates of litter breakdown usually are low in waters affected by acid mine drainage (Carpenter et al. 1983, Bermingham et al. 1996, Schultheis et al. 1997, Arp et al. 1999). Gray and Ward (1983) found that litter breakdown in a stream affected by mine drainage remained depressed even after improvements in water quality, including lower concentrations of metals. They attributed the lack of recovery to the continued effects of metal oxide deposition. The results of the present study are consistent with their findings. In fact, several sites that had high rates of metal oxide deposition had slow rates of breakdown even though they had low concentrations of dissolved zinc.

Effects of mine drainage on shredding invertebrates and microbes

Shredder biomass and rates 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. All but two sites with zinc concentrations >0.5 mg/L lacked shredders (Fig. 4) and had depressed rates of litter breakdown (Fig. 3). Some sites with <0.5 mg/L zinc also had very low biomass of shredders, probably because of deposition of metal oxides (Table 2). Concentrations of dissolved zinc affect invertebrate communities in many streams receiving mine drainage, but may not eliminate invertebrates. Some shredding invertebrates, such as stoneflies of the genus *Zapada*, are not as sensitive to zinc as other taxa, including most mayflies (Clements 1994, Clements and Kiffney 1995). Although other dissolved metals can affect invertebrates, zinc was more closely related to shredder biomass and rate of breakdown than copper, iron, or aluminum in our study streams (*data not shown*). It is possible, however, that these metals acted in combination to affect invertebrates in some cases.

Streamwater pH also affects invertebrates, including shredders, in many streams (Mackay and Kersey 1985, Griffith and Perry 1993, Courtney and Clements 1998). In the present study, however, pH was not significantly related to shredder biomass after consideration of zinc and deposition rate. In fact, *Zapada* was abundant at a site where pH was 3.8, and is often found in acidic streams affected by acid rock drainage (D. K. Niyogi, *personal observation*).

Microbial respiration, in contrast to shredder biomass, was most closely related to the deposition rate of metal oxides and the concentrations of dissolved nutrients (Table 2). Low pH often affects microbial communities associated with litter breakdown in streams (e.g., Chamier 1987, Mulholland et al. 1987, Jenkins and Suberkropp 1995). 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 μg O_2 cm^{-2} h^{-1}) were measured at sites with pH as low as 2.7 and concentrations of zinc as high as 80 mg/L. Thus, microbial activity appears to have a higher threshold of response than does invertebrate biomass to stress from pH and zinc. Similarly, Miersch et al. (1997) found that the growth of some aquatic fungi (hyphomycetes) was inhibited only at very high concentrations of metals. High

TABLE 3. Multiple regression analysis of rate of litter breakdown (log transformed) in relation to biotic variables (shredder biomass and microbial respiration on litter) in Colorado streams.

Dependent variable	df	Overall R^2	Overall P value	Independent variable	Standardized regression coefficient	P value
Breakdown rate, k	2, 24	0.76	0.0001	Shredder biomass	+0.73	0.0001
				Microbial respiration	+0.29	0.0118

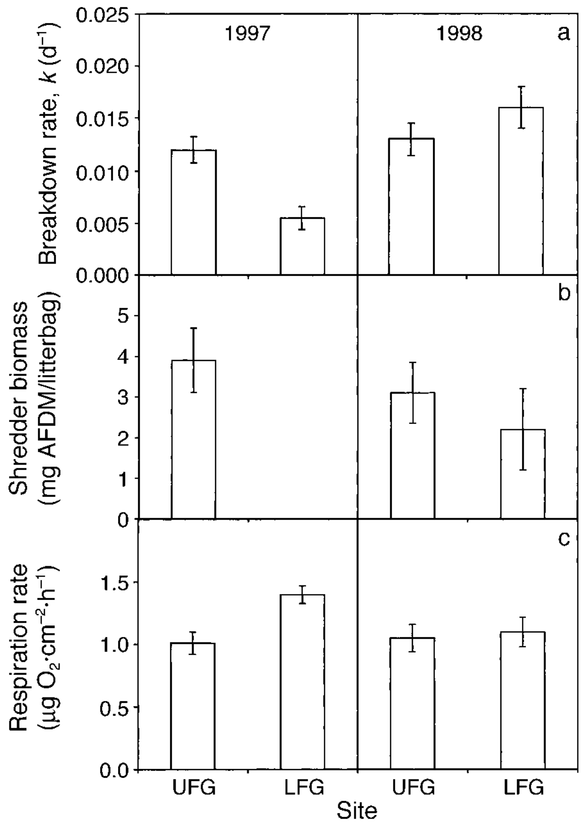

FIG. 8. Comparison of (a) rate of litter breakdown, (b) shredder biomass, and (c) microbial respiration for two sites in French Gulch in 1997 and 1998. UFG (Upper French Gulch) is a pristine reference site; LFG (Lower French Gulch) is a site affected by mine drainage. Differences are significant ($P < 0.05$) in 1997, but not in 1998. Values are means ± 1 SE.

rates of microbial respiration at some stressed sites was probably related to the loss of shredding invertebrates (Niyogi 1999). Invertebrates may constrain microbial biomass and metabolism by direct consumption and by competing with microbes for a limiting resource (litter) (Bärlocher 1980).

Roles of invertebrates and microbes in litter breakdown

Mine drainage and other stresses often affect both shredders and microbes associated with leaf litter; in such cases, it can be difficult to determine the biological mechanisms underlying changes in rates of litter breakdown. Results from this study (Tables 2 and 3) suggest that when present, shredders have an important effect on breakdown rates both in pristine streams and in streams affected by mine drainage of the Colorado Rocky Mountains. In fact, several sites with high rates of microbial respiration had low rates of litter breakdown ($k < 0.010$ d^{-1}, Fig. 7). These sites had few if any shredding invertebrates, probably because of high concentrations of zinc. For example, site LFG in 1997 (Fig. 8) had a high rate of microbial respiration (1.4 μg O_2 cm^{-2} h^{-1}), but no shredders and a low rate of breakdown (0.005 d^{-1}).

There are two other lines of evidence that also suggest that invertebrates play an important role in litter breakdown in these streams. Our respiration measurements can be used to estimate loss of mass from litter due to microbial metabolism. Microbial activity at site LFG in 1997 (when shredders were absent, Fig. 8) would result in a breakdown rate of ~0.007 d^{-1}, which is similar to the field estimate of 0.005 d^{-1} (our respiration measurements were conducted at 10°C whereas average stream temperatures were 1–2°C). We also have estimates of litter consumption by shredding invertebrates (*data not shown*). The dominant stonefly in these streams, *Zapada oregonensis*, consumed enough litter in laboratory trials (~0.5 mg AFDM of litter per individual per day) to account for the differences in litter breakdown between sites with and without shredding invertebrates (based on densities of shredders found in litterbags). These data reinforce the idea that microbial communities alone did not break down litter as fast alone as with shredders at our study sites.

The important role of invertebrates in litter breakdown has been documented in other systems under stress. Tuchman (1993) found that a decrease in abundance of shredding invertebrates led to greatly decreased rates of litter breakdown in acidic lakes. Similarly, Kok and Van der Velde (1994) reported fewer shredders and slower litter breakdown in acidic ponds than in neutral ponds. Griffith and Perry (1993) and Dangles and Guerold (1998) attributed decreased rates of litter breakdown in acidic streams to the loss of amphipods, although other shredders were still present. In contrast, other studies suggest that the suppression of microbes can be more important than effects on invertebrates in reducing the rates of litter breakdown in some stressed systems (Allard and Moreau 1986, Mulholland et al. 1987).

In a classic study, 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. For streams in the present study, shredding invertebrates were usually absent above 0.5 mg/L dissolved zinc. Thus, zinc may have acted as an insecticide to shredders above this threshold. Rates of litter breakdown were always depressed ($k < 0.010$ d^{-1}) at sites with zinc concentrations >0.5 mg/L. Several sites that were affected by mine drainage had concentrations of dissolved zinc less than this threshold, and these sites had high breakdown rates ($k > 0.010$ 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 <0.5 mg/L and still had shredding stoneflies. The importance of the zinc threshold was also clear at site LFG, where the breakdown rate was 3× higher in

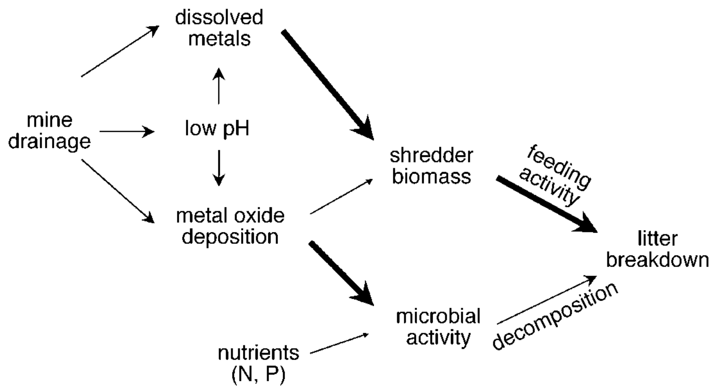

FIG. 9. Conceptual model of the effects of mine drainage on breakdown of leaf litter (loss of mass from litterbags), as mediated by shredder and microbial communities. The thickness of a line indicates the significance of the effect.

1998 than in 1997 (Fig. 8). In 1997 shredders were absent at LFG, probably because of high zinc concentrations (1 mg/L). In 1998 the zinc concentration was lower (<0.5 mg/L), and shredders, including *Zapada,* were present.

Irons et al. (1994) suggested that invertebrates may have a larger role than microbes in litter breakdown for streams at high latitude, where low temperatures limit microbial activity. Streams at high elevation, such as those of the Rocky Mountains, may follow the same pattern. For example, invertebrates played a dominant role in litter decomposition in a mountain stream in Alberta, Canada (Mutch and Davies 1984). Furthermore, microbial communities involved in litter breakdown can be limited by nutrients such as phosphorus and nitrogen (Elwood et al. 1981, Suberkropp and Chauvet 1995). Unpolluted Rocky Mountain streams typically have low concentrations of nutrients (SRP usually <5 μg/L; DIN usually <60 μg/L for the present study, Table 1). The role of microbial communities may be more important in warm streams or in streams with high concentrations of nutrients.

Loss of litter from litterbags containing shredders may occur mostly as fine particulate organic matter (FPOM) rather than as a result of mineralization (Suberkropp 1998, Gessner et al. 1999). In laboratory microcosms, 60–90% of the mass lost from litter exposed to the dominant shredder in our streams (*Zapada oregonensis*) could be accounted for in FPOM production, most of which was fecal pellets (D. K. Niyogi, *unpublished data*). As shredders are lost in streams affected by mine drainage, there may be less FPOM production from litter and less transport of FPOM downstream (Cuffney et al. 1990).

CONCLUSIONS AND IMPLICATIONS FOR REMEDIATION

The mechanisms by which mine drainage affects litter breakdown in Colorado mountain streams are summarized in Fig. 9. Concentration of zinc appeared to be the primary abiotic control on shredding invertebrates. Because shredders, through feeding and FPOM production, were primarily responsible for breakdown of litter, concentration of dissolved zinc was in turn the best abiotic predictor of breakdown rate (Table 2). Other dissolved metals, such as copper, can play a similar role in other streams affected by mine drainage (e.g., Leland and Carter 1985, Schultheis et al. 1997). Deposition rate of metal oxides also was detrimental to shredding invertebrates, and was the main control on activity of microbial communities. Microbial communities were more tolerant than shredders to dissolved zinc, and were positively affected by concentrations of nutrients (N, P). Although pH did not have an independent effect on litter breakdown or the biological communities, it is indirectly significant through geochemical mechanisms. For example, most sites with low pH had high zinc concentrations, and pH controls the solubility of metal oxides (Fig. 9).

Mine drainage is a complex agent of stress (Fig. 9). Components of stress (low pH, dissolved metals, metal oxide deposition) are well understood from a geochemical perspective, and their effects on stream conditions such as dissolved and deposited metals can be modeled (Kimball et al. 1994, Broshears et al. 1996, Runkel et al. 1999*a, b*). Furthermore, models can be used to predict stream conditions following remediation of mine drainage sources (Walton-Day et al. 1999). The relative importance of stresses from mine drainage may shift as geochemical conditions change either downstream or with remediation. For example, dilution of acid mine drainage will raise pH and decrease concentrations of dissolved metals downstream, thereby relieving the effects of these stresses. The increase in pH, however, may increase the deposition rate of metal oxides, thus increasing this physical stress.

The present work shows that ecological processes, such as litter breakdown, also can be predicted, but only if the specific mechanisms of response are taken into account (Fig. 9). Remediation must decrease concentrations of dissolved metals such as zinc below the threshold for survival of shredding invertebrates, but also must prevent high rates of metal oxide deposition, which can limit both shredders and microbes. A more complete understanding of mine drainage, including its geochemistry and its effects on biotic components of ecosystems, is now emerging and can be used in the design of remediation schemes.

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