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RESPONSE OF A NEW ZEALAND MAYFLY (*DELEATIDIUM* SPP.) TO ACID MINE DRAINAGE: IMPLICATIONS FOR MINE REMEDIATION

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Abstract—Investigating the toxicity of acid mine drainage (AMD) on benthic communities in receiving waters can be highly challenging because of the difficulty in unraveling the effects of acidity, dissolved metals, and precipitates. Furthermore, the survival of different species may vary depending on any natural adaptation they may have acquired to low pH, metals, or sedimentation. We investigated the effect of different pHs and AMD on the survival of a common New Zealand leptophlebiid mayfly (*Deleatidium* spp.) in 96-h laboratory trials. Our results indicate that the primary driver of toxicity in AMD was pH, although some mortality could be attributable to the presence of dissolved heavy metals at low pH (≤ 3.6). Mayflies sourced from three naturally acidic streams (pH $\approx$ 5.7–6.5) had a distinctly higher tolerance to AMD and low pH (3.5–4.0) compared to mayflies sourced from three circumneutral streams (pH $\approx$ 7.0–7.4). This indicates that the chemistry of the natal stream strongly influences the sensitivity of mayflies to AMD, which, in turn, could have consequences for the successful remediation of a given AMD-impacted stream. Furthermore, the water chemistry of unimpacted streams that could be sources of potential recolonists might provide ecologically relevant water-quality targets for remediation of AMD-damaged streams. Understanding the variable tolerances of common lotic benthic taxa can provide ecologically relevant water-quality criteria for mine remediation.

Keywords—Benthic invertebrates Acid mine drainage Toxicity Remediation

INTRODUCTION

Acid mine drainage (AMD) is a long-term, global issue affecting almost all countries with abandoned or active coal mines [1,2]. Acid mine drainage is produced when water mixes with mineral deposits containing sulfides, such as iron disulfide (FeS_2, pyrite) in an oxidizing environment. Sulfuric acid is formed, lowering the pH of receiving waters while reacting with elevated dissolved metal concentrations (predominantly iron and aluminum ions). Changes in pH, which might result from dilution of waters from tributary streams or heavy rainfall, can cause the precipitation of metals (e.g., iron hydroxide). Metal precipitate smothers the streambed substrate, reducing the habitat for stream fauna [3]. Acid mine drainage frequently is persistent and extreme in its effects on water chemistry and biotic communities [4]. Toxicity can arise from the increased acidity as well as from the presence of soluble and particulate metals. The interplay between pH and metals in solution makes these systems complex to investigate and manage. Consequently, environmental agencies dealing with the mining sector currently rely on generic water-quality criteria to predict the potential toxicity of AMD on stream communities. These generic criteria usually do not account for any specialized or adaptive characteristics of species inhabiting the receiving-water environments of concern. This aspect is of particular interest in New Zealand, because naturally acidic streams, usually with a pH of approximately 4 [5], frequently occur on the west coast of the South Island.

In New Zealand, many freshwater benthic invertebrates have highly variable tolerances to pH and AMD [5–11]. Furthermore, several studies have indicated that organisms in streams of naturally low pH also may tolerate anthropogenically acidic waters better than the same taxa in streams of higher natural pH [5,7,11,12]. This variability in tolerances of the same taxa creates complexity in determining what constitutes successful remediation of an AMD-impacted stream and, where new mining operations are being considered, establishing appropriate water-quality criteria to avoid significantly impacting the existing ecosystem.

The aim of the present study was to evaluate the survival of a common indigenous freshwater invertebrate to a range of mine-impacted waters in New Zealand. Specifically, we used the leptophlebiid mayfly (*Deleatidium* spp.) as a representative organism to evaluate the effect of dilution and pH modification on AMD toxicity, to delineate pH tolerance in the presence and absence of AMD-associated metals, and to investigate the influence of natal stream chemistry on sensitivity to AMD.

MATERIALS AND METHODS

Test organism

We selected the leptophlebiid mayfly (*Deleatidium* spp. [Ephemoptera: Leptophlebiidae]) as a representative organism for the evaluation of AMD tolerances. Although not widely used as a toxicity-testing organism, this mayfly has proved to be useful in other New Zealand studies [13,14]. It is endemic to New Zealand and is among the most abundant taxa collected in New Zealand streams [15,16], thus allowing large numbers to be collected as required for use in replicated toxicity tests. Ephemoptera, which have a reported sensitivity to acidic conditions [17], commonly are used in biotic indices of stream condition, including receiving waters in the vicinity of mines [18,19]. Frequently, it is one of the earliest colonizers of streams [20] and could be an important indicator of ecosystem recovery in remediated mine streams.

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Midinstar nymphs of *Deleatidium* spp. were collected using a hand-net and transported in the source stream water at 10 to 15°C in insulated, aerated containers to the laboratory. When possible, organisms were collected within 24 h of the start of each experiment. Nymphs with dark wing pads were excluded to reduce the possibility of nymphs emerging as adults during the experiments.

The AMD dilution and pH manipulation experiments were performed on nymphs collected from a single, naturally acidic stream (Carton Creek [171°50.666′E, 42°08.526′S], Reefton, New Zealand) with a background pH of 5.7. Variations in tolerance to AMD also were examined in mayflies sourced from five additional New Zealand streams (Cust River [172° 37.609′E, 43°22.327′S], Donegals Stream [171°14.727′E, 42°43.240′S], Soldiers Creek [171°51.126′E, 42°7.974′S], Lankey Creek [171°54.057′E, 42°8.866′S], and Otira Spring [171°33.865′E, 42°49.006′S]).

Test water

All AMD water samples used in the present study were sourced from West Sullivan Mine on the Denniston Plateau north of Westport, on the west coast of South Island, New Zealand. Natural stream water upstream of the mine discharge (pH 4.6) was used for dilution water and control treatments.

To simulate the effect of simple remediation measures, such as dilution and neutralization, AMD water collected from the mine discharge point was manipulated. Initial pH of the AMD was recorded (Mettler Toledo™ SevenEasy pH meter; Mettler Toledo International, Schwerzenbach, Switzerland) before making a series of dilutions (i.e., 0.5×, 0.25×, 0.125×, and 0.0625×) to simulate natural dilution of AMD waters. A duplicate dilution series was then modified with alkali (NaOH) to neutralize the pH up to background levels (pH 4.6). Samples were filtered through a 0.45-μM membrane filter to remove precipitated material and then assessed for toxicity, pH, conductivity, and total and dissolved metals.

To differentiate between metal and pH toxicity, additional tests were conducted using uncontaminated water that had been acidified (with HCl) to match the pH of the unmodified dilution series described above.

Variations in AMD tolerance were then examined in mayflies sourced from three circumneutral and three naturally acidic streams. The mayflies were exposed to AMD dilutions that gave low pH (i.e., 3.3), medium pH (i.e., 3.5), and higher pH (i.e., 4.0). The pH varied between 3.2 and 3.3 in the low-pH samples on different experimental occasions. Therefore, it is reported as a range in figure legends. These dilutions represented the range of pH found above the AMD discharge point and in the receiving waters of Sullivan Mine. No mortality occurred in the source water (i.e., the water from where the mayflies were collected) controls (data not shown).

Toxicity testing

Toxicity tests were conducted in the laboratory on active mayfly nymphs ($n \geq 5$). Nymphs were randomly assigned to replicate plastic, 200-ml containers ($n = 8$ unless otherwise stated), each with 100 ml of treatment water. Air was supplied to the containers from an electric aerator for 15 min twice daily. Mayflies were checked every 24 h for mortality and evidence of molting. Individuals lacking vitality and independent mobility were considered to be dead, and dead mayflies and exoskeletons were removed daily. During the experiment, the pH of the test samples ($n \leq 8$ per treatment) was recorded every 24 h (i.e., five times). Experiments were run for 96 h in a environment-controlled room set to simulate summer stream conditions at 15°C with a 16:8-h light:dark photoperiod.

Chemical analysis

Water samples were analyzed for heavy metals (aluminum, arsenics, iron, manganese, nickel, and zinc), pH, and electrical conductivity by R.J. Hills Laboratories (Hamilton, New Zealand). Total and dissolved metals were filtered and analyzed by digesting samples through boiling in nitric acid and then analyzed using inductively coupled plasma–mass spectrophotometry according to American Public Health Association method 3125 [21]. Method detection limits were as follows: Iron, 0.02 g/L; aluminum, 0.003 g/L; arsenic and zinc, 0.001 g/L; and manganese and nickel, 0.0005 g/L. Electrical conductivity and pH were measured according to American Public Health Association methods 2510 and 4500, respectively [21].

Statistical analysis

The proportion of mayfly nymphs surviving after 96 h were square-root arcsin transformed to normalize error variance [22]. Data were analyzed using the statistical package S-PLUS® (Ver 6.2; Insightful, Seattle, WA, USA). Differences between treatments after 96 h of exposure were assessed using one-way analysis of variance, with a significance level of $p < 0.05$. Tukey's multiple-range post hoc test was used to determine when significant differences occurred.

The influence of AMD metals on the proportion of mayflies surviving at various pH was analyzed using binomial regression analysis of pH versus the transformed survival data in AMD and non-AMD water [23]. The difference between the slopes of the two lines was compared using analysis of deviance (Genstat™ 8th ed; VSN International, Hempstead, UK) at a significance level of $p < 0.05$.

To evaluate the importance of their natal stream water chemistry, the proportion of mayflies surviving from either acidic or circumneutral streams was modeled with a generalized linear model using binomial errors (Genstat). Data collected at the lowest pH were excluded, because no animals survived at this pH.

RESULTS

Both undiluted (pH 3.0) and 0.5× AMD (pH 3.2) resulted in 100% mortality in mayflies sourced from streams of naturally low pH, but with each subsequent dilution, mayfly survival increased (Fig. 1A). Significantly greater survival occurred with dilutions of fourfold or greater ($F_{5,42} = 72.8$, $p < 0.0001$), which corresponds to pH ≥ 3.5 (Fig. 1A and Table 1). Mayfly survival of 80% or greater was observed in 0.125× AMD or lower (i.e., pH ≥ 3.8) (Table 1). Dilution also markedly reduced metal concentrations, with iron and aluminum effectively reduced by 50% with each dilution (Table 1) and remaining largely in a dissolved form despite the progressive increase in pH up to background levels (data not shown).

Following modification to pH 4.6, most of the iron and up to 39% of the aluminum in the AMD was precipitated. Mayfly survival was high (≥77%) in all pH-modified AMD dilutions, and no significant difference was found between any of the AMD samples or the control ($F_{5,42} = 1.39$, $p = 0.25$) (Fig. 1B).

Other metals analyzed (manganese, arsenic, nickel, and zinc) existed as dissolved ions in both unmodified and pH-modified samples, indicating that these metals are most likely

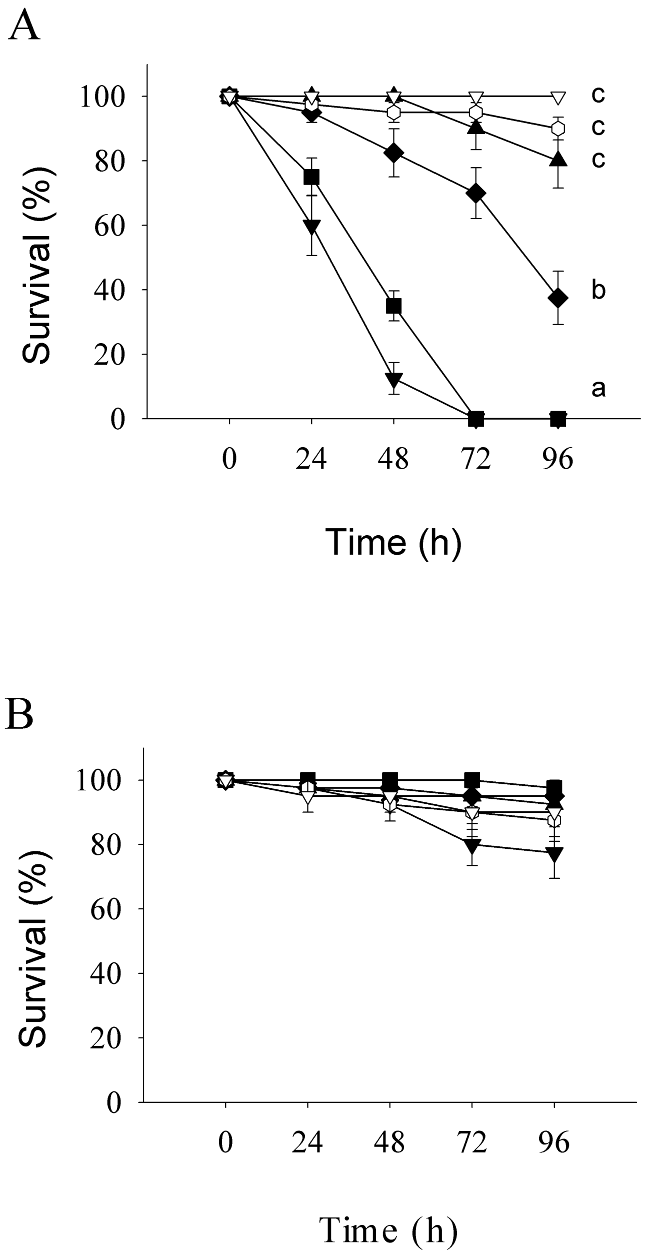

Fig. 1. Survival of mayflies (sourced from stream with low pH) in (**A**) differing dilutions of unmodified acid mine drainage (AMD) and (**B**) AMD dilutions where pH was modified to background level (pH 4.6). Values are presented as the mean ± standard error (n = 8 replicates). Letters denote significantly different groups at 96 h. ▼ = undiluted AMD; ■ = 0.5× AMD; ◆ = 0.25× AMD; ▲ = 0.125× AMD; ○ = 0.062× AMD; ▽ = control water.

to exist in a soluble form in both diluted and undiluted AMD samples.

Neutralization of AMD reduces its acute toxicity (Fig. 1B), suggesting that low pH is driving toxicity in the unmodified AMD samples (Fig. 1A). Modification of pH, however, also causes precipitation of iron and aluminum; therefore, the contribution of these metal ions to the toxicity observed in the unmodified samples cannot be dismissed entirely. Mayflies exposed to non-AMD water that had been artificially acidified to the same range of pH as in the first trial showed comparatively greater survival at lower pH (Fig. 2, compare to Fig. 1B). Survival at pH 3.3 was low (≈40%) but significantly greater than survival at pH 3.1 ($F_{7,32}$ = 15.66, $p < 0.01$) (Fig. 2). Survival at pH > 3.3 (≈90%) was not significantly different from survival in control water (Fig. 2). Furthermore, the slopes of the lines derived from pH versus survival data at 96 h for mayflies exposed to AMD and non-AMD water were significantly different ($F_{1,116}$ = 14.90, $p < 0.001$). An increased mortality in the AMD-contaminated samples occurred at pH ≤3.6 (p = 0.05), indicating higher toxicity in the metal-rich AMD water at these lower pH levels.

Preadaptation to low pH based on water chemistry in natal streams was evaluated in mayflies sourced from three circumneutral and three naturally acidic streams (Fig. 3). A significant difference in the response to different AMD dilutions of mayflies sourced from different streams was observed ($F_{4,78}$ = 5.62, $p < 0.001$). These differences were explained by significantly lower survival in AMD water ($F_{1,78}$ = 188.22, $p < 0.001$) observed in mayflies sourced from circumneutral streams (Fig. 3A–C) compared to mayflies from streams with naturally low pH (Fig. 3D–F). After the 96-h exposure period, mayflies sourced from circumneutral streams showed 100% mortality at pH ≤ 3.5. At pH 4.0, markedly higher numbers survived, although mortality was still considerable (between 62.5 and 82.5%) (Fig. 3A–C), whereas mayflies sourced from naturally acidic streams had a higher tolerance to AMD-contaminated water. In these trials, mayfly mortality was still 100% at pH ≤ 3.3, but survival improved in all treatments with pH ≥ 3.5, with no mortality occurring at pH 4.0 (Fig. 3D–F).

DISCUSSION

Mayfly survival improved with progressive dilutions of AMD and mayflies were able to tolerate 96-h exposures to AMD diluted to less than 0.125 (i.e., at pH ≥ 3.8), with no statistically significant mortality occurring. Modifying to pH 4.6 (equivalent to the background pH of naturally acidic streams) abrogates the toxicity observed in the unmodified AMD samples, despite the continued presence of metals in solution. Our findings indicate that pH probably is the main factor causing mortality in these mayflies. Low pH may hinder osmoregulatory processes in these animals, disturbing the cellular ionic balance. In particular, significant losses of sodium, calcium, potassium, and chloride ions may occur [24].

Evaluating the role of metal ions in AMD toxicity is complex at lower pHs where dissolved metals may exist. The results of the present study show that mayflies can tolerate lower pH if the water is free of metals, suggesting that dissolved metals contribute additional toxicity at lower pH. Elevated iron and aluminum concentrations are common in AMD [25], but information on the toxicity of dissolved iron to freshwater invertebrates is limited. Water-quality criteria for the protection of aquatic life range from 0.3 to 1.5 mg/L of iron [26–29] (http://www.ccme.ca/publications/ceqg_rcqe.html and http://www.environment-agency.gov.uk/). Although iron is not considered to be an overtly toxic or priority pollutant, these criteria are still below the concentration of iron in the AMD samples that we tested, in which concentrations of dissolved iron of up to 2.29 mg/L had no adverse influence on the survival of *Deleatidium* spp. Some suggest that the presence of iron can reduce the toxicity of other metals to aquatic invertebrates. Soucek et al. suggest the mechanism may be via the formation of iron oxyhydroxides and its coprecipitation of or absorption to other metals [30]. Furthermore, it has been suggested that iron additions (up to 3.9 mg/L) increased survival of *Deleatidium* and *Zealandiobus* spp. at low pH (i.e., pH 3) (M.K. Anthony. 1999. Masters thesis. University of Canter-

Table 1. pH and dissolved metal concentrations (mg/L) in acid mine drainage (AMD)

Treatment[a]	Sample	pH	Fe	Al	As	Mn	Ni	Zn
U	AMD	3.1	22.4	8.9	0.005	0.291	0.066	0.381
D	0.5× AMD	3.2	11.2	4.56	0.001	0.152	0.034	0.202
D	0.25× AMD	3.5	3.87	2.24	<0.001	0.077	0.017	0.108
D	0.125× AMD	3.8	2.29	1.22	<0.001	0.045	0.010	0.066
D	0.062× AMD	4.0	1.05	0.631	<0.001	0.026	0.005	0.040
U, P	AMD	4.6	0.07	5.44	<0.001	0.263	0.063	0.351
D, P	0.5× AMD	4.6	0.09	2.50	<0.001	0.144	0.031	0.192
D, P	0.25× AMD	4.6	0.11	1.35	<0.001	0.076	0.016	0.110
D, P	0.125× AMD	4.6	0.12	0.80	<0.001	0.043	0.009	0.067
D, P	0.062× AMD	4.6	0.12	0.24	<0.001	0.023	0.004	0.040
—	Dilution water	4.6	0.05	0.11	<0.001	0.008	0.001	0.018

[a] D = diluted; U = undiluted; P = pH modified to 4.6.

bury, Christchurch, New Zealand). This finding is contrary to our results, in which we observed a higher toxicity at low pH in the presence of dissolved Fe at concentrations greater than approximately 3.0 mg/L; however, we cannot overlook the presence of dissolved Al, as well as that of other dissolved metals, in our samples.

Aluminum also occurred at a significant concentration in the AMD, and a considerable proportion remains in solution even in pH-modified samples. International water-quality criteria (intended to protect freshwater aquatic life) range from 87 to 150 μg/L of aluminum [26,27,29]. Lower criteria for aluminum have been suggested for pH < 6.5 (i.e., 0.8–5 μg/L) [26,27]. Even in the greatest dilution used in our tests, the aluminum concentration exceeded these criteria. Although aluminum is reportedly not as toxic to aquatic invertebrates as it is to fish [31], acute effects have been reported between 2.3 and 36.9 mg/L [26].

The dissolution status of all other metals that we measured (i.e., arsenic, manganese, nickel, and zinc) were not noticeably influenced by pH and remained primarily in solution even at pH 4.6. The concentrations of dissolved manganese and arsenic were at very low levels and were unlikely to be influencing toxicity in the AMD sample. Both nickel and zinc concentrations exceeded generic water-quality criteria of 0.011 and 0.008 mg/L, respectively [26], and, therefore, may contribute to any observed toxicity in the AMD sample. *Deleatidium* spp., however, have been reported to be particularly tolerant to significantly higher concentrations of zinc [13], and Havas and Hutchison [9] found that only aluminum (20 mg/L) and iron (30 mg/L) had any influence on toxicity to *Daphnia middendorffiana* at pH 4.5. Those authors concluded that aluminum was the key additional factor in the toxicity of pH (H^+ ions). These amendments [9] were within a concentration range similar to that of our AMD samples.

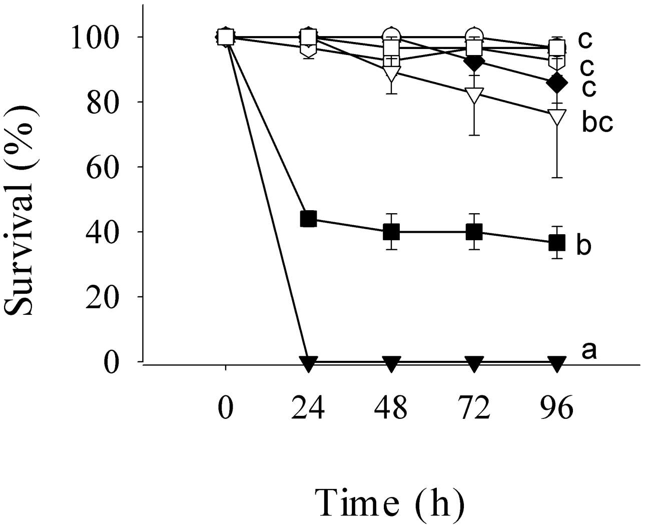

Fig. 2. Survival of mayflies (sourced from stream with low pH) in uncontaminated stream water that was artificially acidified to various pH levels with the addition of HCl. Values are presented as the mean ± standard error (*n* = 5 replicates). Letters denote significantly different groups at 96 h. ▼ = pH 3.1; ■ = pH 3.3; ◆ = pH 3.5; ▲ = pH 3.8; ○ = pH 4.0; ◇ = pH 4.2; ▽ = pH 4.5; □ = pH 5.7.

Our experiments comparing mayflies sourced from circumneutral and naturally acidic streams indicated that depending on the water-quality conditions in their natal streams, mayflies may be more or less tolerant of changing water chemistry. Previous studies of New Zealand stream invertebrates have shown that taxa can have highly variable tolerances to differing water-quality conditions [5,6,8,10]. Specifically, many catchments within the west coast of South Island have naturally acidic, brown waters [6]. These naturally low-pH systems receive fluvic and humic acids generated by percolation of rainfall through organic soils and surface vegetation [6]. Healthy communities of benthic fauna that exist in these low-pH systems exhibit a degree of tolerance to acidic conditions, and taxonomic richness can be similar to that of circumneutral streams [5]. Intraspecific variability in tolerances to acidic conditions between populations has been shown in stream invertebrates [7], amphibians [32], and fish [33]. Mackie [12] observed that populations of both *Hyalella azteca* and *Amnicola limosa* sourced from low-alkalinity waters could tolerate lower pH compared with populations sourced from high-alkalinity waters. France and Stokes [7] also showed that populations of the Canadian amphipod *H. azteca* sourced from acidic lakes in Ontario survived longer at lethal pH than did conspecifics from circumneutral lakes. Furthermore, those authors suggested that acid tolerance could be determined genetically. Most acid-tolerant species have physiological adaptations that result in an enhanced ability for osmoregulation at low pH, such as a greater buffering capacity of the hymolymph or a lower permeability of the cuticle or gill epithelium to hydrogen ions [34]. Collier et al. [5] suggested that intraspecific variation in acid tolerance may be widespread in some parts of New Zealand. Our mayfly data strongly support this contention.

Identification to the species level would have allowed more certainty regarding whether differences in sensitivity to AMD were the result of varied species compositions at the six different locations where mayflies were sourced. Taxonomically,

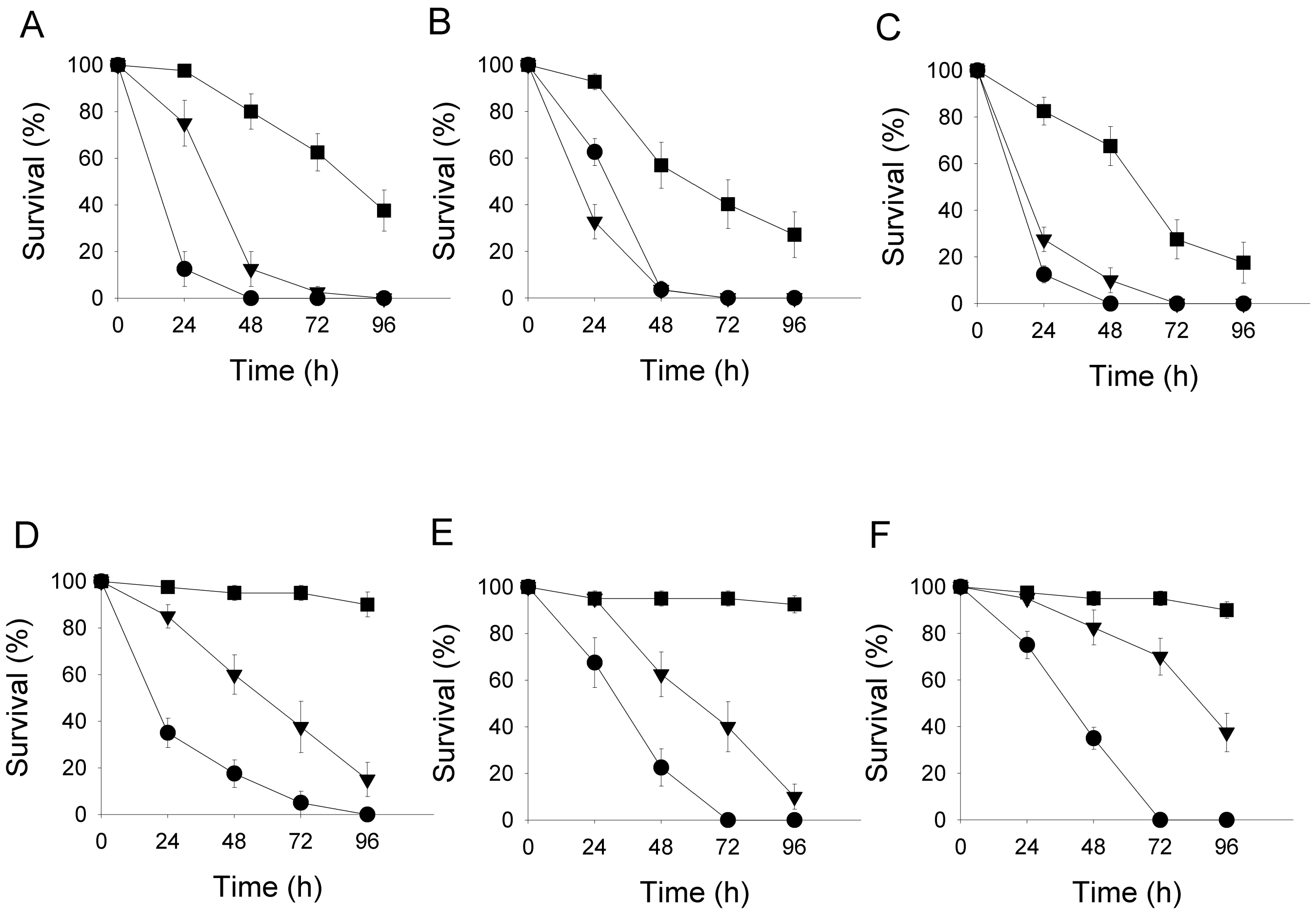

Fig. 3. Mayflies from three circumneutral and three acidic streams exposed to acid mine drainage waters diluted to give low-pH (3.2–3.3), medium pH (3.5), and higher pH (4.0) levels. Survival in mayflies sourced from (**A–C**) circumneutral streams (pH 7.0–7.4) and (**D–F**) acidic streams (pH 5.7–6.5). Values are presented as the mean ± standard error (*n* = 8 replicates). ● = pH 3.2–3.3; ▼ = pH 3.5; ■ = pH 4.0.

Deleatidium spp. are difficult to identify confidently to the species level, and it is standard biomonitoring practice in New Zealand not to distinguish this taxa below the genus level [35]. The time-consuming nature of species identification in the field would make running the laboratory-based toxicity tests reported in the present study unfeasible. Retrospective species identification at the six streams may provide further confirmation; however, there does appear to be a definite increased pH tolerance in *Deleatidium* spp. sourced from acidic streams.

The longer-term sublethal impacts of heavy metals contained in AMD were not evaluated in the present study, which only looked at one kind of AMD from a single source. Based on these 96-h mortality tests, we cannot attempt to draw conclusions regarding the chronic effects on organisms inhabiting the receiving waters of all kinds of AMD. For the type of AMD that we studied, however, our acute toxicity data do indicate that pH probably is the main factor underpinning acute toxicity to mayflies, but overall tolerance to AMD appeared to be strongly influenced by the chemistry of their natal stream. This has important consequences in setting water-quality criteria for remediation and rehabilitation of AMD-affected systems. If the aim of AMD remediation is to improve water quality to an extent that it supports healthy biotic communities, then remediation thresholds should reflect the likely water chemistry of streams that may act as sources for recolonists of a restored stream. The water chemistry of nearby unimpacted streams could provide an ecologically relevant water-quality target for remediation of AMD-damaged streams.

For a population to be successful, organisms need to be able to survive all life stages, reproduce successfully, and have access to adequate food resources. Although the mayfly survival assays reported here only indicate acute toxicity, they have allowed us to differentiate toxicity and have provided critical information regarding mayfly tolerances according to where mayflies were sourced. These kinds of data can provide valuable information regarding the likelihood of remediated waters to support aquatic invertebrate life. Understanding the variable tolerances of common lotic benthic taxa can provide ecologically realistic water-quality criteria for mine remediation.

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