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Disentangling the effects of low pH and metal mixture toxicity on macroinvertebrate diversity[☆]

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A B S T R A C T

One of the primary goals of biological assessment of streams is to identify which of a suite of chemical stressors is limiting their ecological potential. Elevated metal concentrations in streams are often associated with low pH, yet the effects of these two potentially limiting factors of freshwater biodiversity are rarely considered to interact beyond the effects of pH on metal speciation. Using a dataset from two continents, a biogeochemical model of the toxicity of metal mixtures (Al, Cd, Cu, Pb, Zn) and quantile regression, we addressed the relative importance of both pH and metals as limiting factors for macroinvertebrate communities. Current environmental quality standards for metals proved to be protective of stream macroinvertebrate communities and were used as a starting point to assess metal mixture toxicity. A model of metal mixture toxicity accounting for metal interactions was a better predictor of macroinvertebrate responses than a model considering individual metal toxicity. We showed that the direct limiting effect of pH on richness was of the same magnitude as that of chronic metal toxicity, independent of its influence on the availability and toxicity of metals. By accounting for the direct effect of pH on macroinvertebrate communities, we were able to determine that acidic streams supported less diverse communities than neutral streams even when metals were below no-effect thresholds. Through a multivariate quantile model, we untangled the limiting effect of both pH and metals and predicted the maximum diversity that could be expected at other sites as a function of these variables. This model can be used to identify which of the two stressors is more limiting to the ecological potential of running waters.

1. Introduction

One of the primary goals of biological assessment of streams is to identify which of a suite of chemical stressors is limiting their ecological potential. Quantitative relationships between species richness and environmental gradients are needed to better predict biodiversity patterns, to develop increasingly accurate biotic indices, and to set environmental quality standards. However, describing these relationships is not straightforward, because species richness is typically dependent on a multitude of environmental gradients (Friberg et al., 2011; Ormerod et al., 2010) such as water pollution (Kail et al., 2012), nutrient supplies (Wagenhoff et al., 2012), habitat quality (Dunbar et al., 2010) and changes in climate and land use (Kuemmerlen et al., 2015).

Elevated concentrations of metals are common in streams draining mineralized and especially mined basins (Clements et al.,

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2000; Malmqvist and Hoffsten, 1999; Runnells et al., 1992). Metals transported into aquatic habitats cause metal-sensitive populations to decline. Resultant communities are less diverse and dominated by metal-tolerant species (Clements, 1994; Schmidt et al., 2012a). However, most of the studies on this subject focus on the effect of metals in mined basins (Solà et al., 2004; Van Damme et al., 2008), while the effects of metals in naturally acid and metal-rich streams are less studied (Andrén and Eriksson Wiklund, 2013; Annala et al., 2014; Petrin et al., 2007a; Schmidt et al., 2012b). Low pH can increase the bioaccumulation of metals and enhance the toxicity of a given metal to aquatic macroinvertebrates (U.S. Environmental Protection Agency, 1986; Wren and Stephenson, 1991).

The bioavailability of metals to aquatic organisms is largely dependent on the physical-chemical characteristics of the medium. Alkalinity (Spry and Wiener, 1991), hardness (Pagenkopf, 1983; Playle et al., 1992; Sprague, 1985), dissolved organic carbon (Playle et al., 1993), and pH (Pagenkopf, 1983; Playle et al., 1992) all play important roles in determining the speciation and bioavailability of metals. These same physical-chemical characteristics influence the competition between dissolved metals and other ions for binding to receptive biological tissues. Considering these multiple factors and their potential interactions, it is not surprising that metal concentrations (either dissolved or total) alone are typically only weakly related to variation in composition of biological communities along gradients of contamination (Iwasaki et al., 2013; Schmidt et al., 2010).

We used the U.S. Environmental Protection Agency environmental quality standards for metals, expressed as metal concentrations, as a starting point to assess metal mixture toxicity and to evaluate their toxicity on stream macroinvertebrate communities. Understanding the importance of pH and concentration of metals is challenging in field studies because of their typically high correlation. The relative importance of pH and metal concentration on biological communities has been addressed in only a few studies with conflicting results (Balistrieri et al., 2015; Gerhardt, 1993; Gerritsen et al., 2010; Stockdale et al., 2010).

The bioavailability of any metal can be determined by assessing the relationship between exposure and accumulation by the animal (Hare, 1992). The Biotic Ligand Model (BLM, Di Toro et al., 2000) predicts the lethality of a metal based on the amount of metal and protons accumulated in the organism, as a function of free metal ion species in the water based on measurements of dissolved metal concentration and other physical-chemical characteristics of the water. The model is based on experimental evidence of short-term accumulation of metals by fish and their associated mortality (e.g., (MacRae et al., 1999; Playle et al., 1993; Smith et al., 2015). Nevertheless, the biotic ligand model approach is conceptually applicable to all freshwater animals (Niyogi and Wood, 2004; Paquin et al., 2002a). Indeed, ionoregulation is a relevant cause of mortality for many freshwater organisms, and the biochemical pathways underpinning this process are similar across non-air-breathing animals (Buchwalter and Luoma, 2005; Kikuchi, 1983). An assumption of biotic ligand models is that the ionoregulatory surface can be considered as a chemical ligand in equilibrium with the aqueous solution and accumulation of metals and protons on this surface is related to lethality. This assumption does not take into account the ability of organisms to increase or decrease uptake and elimination of metals, especially in long term exposures (Buchwalter et al., 2007; Slaveykova and Wilkinson, 2005). Moreover, the uptake of metals also occurs from food (Hare, 1992) and this is not accounted for in BLM.

In the context of the BLM, pH, Ca^{2+} and Na^{+} are simply viewed as competing cations with respect to the binding of metals at the biotic ligand. However, in other contexts, (e.g. Sodium Balance Model, Paquin et al., 2002b), it is recognized that there are other more direct effects of these cations on the organism itself (McDonald, 1983; Milligan and Wood, 1982), effects that can be important even in the absence of exposure to a metal.

In this study, we evaluated pH and metal as limiting factors for macroinvertebrate community diversity. We used a bio-geochemical model to predict the accumulation of metals on the biological receptors given a specific solution composition. Instead of using a combined metal/proton toxicity approach (e.g., Balistrieri et al., 2015; Stockdale et al., 2010) we used a multivariate quantile regression model (Koenker and Bassett, 1978) to relate metal accumulations as toxic units and pH to the biological response.

The concept of "limiting factors" can enhance the interpretation of ecological data, wherever multiple stressors are simultaneously acting on the same community, yet not all of the limiting factors have been measured or included in the models (Barneche et al., 2016; Fornaroli et al., 2015, 2016; Iwasaki and Ormerod, 2012; Lancaster and Belyea, 2006; Schmidt et al., 2012a). Quantile regression, calculated at the extreme quantiles, allows the chosen independent variables to be considered as "constraints" to the distribution of biological communities, without compromising the model causal relationship (Cade et al., 1999). Thus quantile regression can be used to identify and evaluate ecological limiting factors (Cade and Noon, 2003) or the degree to which stressors limit the ecological potential at any given location (Schmidt et al., 2012a). This allows predictions of maximum potential values of a biological metric as a function of the studied stressor.

The first objective of this study was to compare the effects of different types of disturbances as mining and forest drainage, on the metal toxicity of stream water. The second objective was to compare the performance of two toxic unit indices developed on the basis of environmental quality standards and field data that describe chronic metal toxicity, as predictors of macroinvertebrate responses. The third objective was to address the relative importance of pH and chronic metal toxicity to stream macroinvertebrate communities and subsequently develop a quantitative model to predict macroinvertebrate diversity as a function of these stressors.

2. Material and methods

2.1. Study area, sampling procedure and biological metrics

We used two datasets from low-order streams, both of which included biological (benthic macroinvertebrate) and environmental (trace metal concentrations in water, water chemical characteristics, geological features, disturbance status) data.

The first dataset is from Finland (FIN) where 48 first- and second-order streams from two adjacent drainage basins with an overall spatial extent of 6648 km^2 were sampled. The bedrock geology of the two basins differ, thus 24 streams are circumneutral (NEU) whereas 24 are naturally acidic (ACI). From each drainage basin, 12 sites impacted by drainage (IMP) and 12 non-drained reference sites were chosen. Drainage ditching is practiced to channel surplus water to streams and thus enhance forest growth. This practice increases sediment load to the streams, which in turn increases metal and nutrient concentrations in the stream water (Åström et al., 2001); (Holden et al., 2004), becoming a potential disturbance for the biological community. The study sites in both regions were selected to control for differences in physical in-stream and riparian habitat. Impacted sites were selected based on the percentage of forest ditches in the near-stream catchment (a 1 km long, 100 m wide riparian buffer). Very little other land use activity occurred in the upstream catchment of the study sites (e.g., no agriculture within several kilometers of a site). All naturally acidic sites run over a black shale deposit, so that the impact of background geology on stream water chemistry could be clearly