



Unexpected Responses of Acid Mine Drainage Remediation: A Study of the North Fork of Clear Creek, Black Hawk, Colorado, USA

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The North Fork of Clear Creek (NFCC) is a high-gradient montane stream that flows through the City of Black Hawk on the east slope of the Rocky Mountains in Colorado, USA. For decades, it was negatively affected by acid mine drainage (AMD) from legacy mining activity in the vicinity of Black Hawk. In late March 2017, a high-density-sludge water treatment plant began to treat multiple point sources of AMD flowing into NFCC. We monitored the effectiveness of the remediation during 2017 and 2018 at seven instream sampling locations on NFCC: two upstream of the historical AMD inputs, and five downstream. Since beginning operation, the water treatment plant has decreased instream metal (Al, Cu, Fe, Mn, and Zn) concentrations to varying extents, depending on the metal; and annual patterns of cycling have differed among the metals. Total and dissolved Fe concentrations decreased immediately after the water treatment plant began operation, and Fe concentrations continued low even during low-flow periods (September-March). Total and dissolved Zn and Cu concentrations decreased initially but then partially rebounded during the low-flow periods in 2017 and 2018. This observation cannot be fully explained by the decrease in NFCC discharge during low flow. Instead, the elevated concentrations of Cu and Zn indicate separate, residual untreated sources of metals entering NFCC; and the locations of Cu and Zn entering the stream differ (possibly surface water, groundwater, or a combination of the two). An increase in the percentage of dissolved and thus potentially bioavailable Cu during AMD treatment may be the result of the considerably-decreased concentrations of particulate Fe. This release of Cu from Fe control is an unexpected consequence of AMD remediation. Geochemical speciation of Cu and Zn was predicted using the Windermere Humic Aqueous Model (WHAM7) at locations upstream and downstream of the water treatment plant. Additionally, WHAM7 was used to predict the amount of organism-bound metal or bioavailable Cu and Zn. Toxicity of the mixtures of those two metals to a metal-sensitive aquatic invertebrate (*Daphnia magna*) was predicted using two different forms of the metals: the measured dissolved metal concentration, and the predicted organism-bound metal concentration. During pre-treatment, the predicted toxicity for both metals was relatively high when using the dissolved metal concentrations (50-90%). Predicted toxicity during AMD treatment did not fully decrease to zero, due to effects from the untreated Cu and Zn sources entering NFCC. In contrast, based on WHAM7-predicted organism-bound metal concentrations, the predicted pre-treatment toxicity was generally lower than that predicted using dissolved metal concentrations. But surprisingly, the predicted toxicity during AMD treatment was similar and sometimes higher than during pre-treatment, due to the loss of protective effects from competing cations that were removed by the treatment process. The loss of this protective effect is another unexpected consequence of AMD remediation. Thus, predicting “safe” concentrations of metals in pre-remediation water chemistry can be misleading when trying to predict their toxicity in remediated water bodies, because water chemistry (and thus metal bioavailability and toxicity) can change when metal sources are diverted and/or remediated.