

COPPER TRANSPORT ALONG A SIERRA NEVADA STREAM

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ABSTRACT: Transport and cycling of micronutrients in streams are regulated by hydrologic, biologic and chemical processes. Simulation of these processes based on a copper and chloride injection experiment in an oligotrophic stream was conducted to determine the relative importance of these interdependent processes in the transport of copper, a micronutrient that can also be toxic to aquatic organisms at submicromolar concentrations. Results indicated that consideration of nonhydrologic processes (periphyton uptake and sediment sorption, for example) is essential in describing copper transport along the experimental reach.

INTRODUCTION

Identification and quantification of nonhydrologic processes may be essential in understanding micronutrient transport in certain aquatic environments. Chemical (e.g., coprecipitation, sorption) and biological (e.g., assimilation, biochemical reactions) processes are of particular importance in streams because they may retard downstream transport of a micronutrient. Concentrations of biologically reactive trace constituents [e.g., copper (Cu)] are also important inasmuch as they may act as micronutrients or as toxicants (at concentrations below 100 μL). These nonhydrologic processes are typically examined independently (i.e., employing an experimental design to suppress potentially interacting processes) and often in the laboratory in order to resolve complex details. Field experiments offer the opportunity to view the interactions of several processes under natural conditions. Analysis of field data with dynamic solute transport simulations further allows the basic hydrologic component of transport to be adequately considered. The purpose of this study was to apply, with a few modifications, an existing solute transport model (2) to identify significant processes controlling transport of a reactive micronutrient, Cu, during a dosing experiment conducted in Convict Creek, California. The model developed couples nonreactive, hydrologic transport with solute-periphyton, and solute-sediment interactions. The analysis indicates that omission of biological uptake or sediment sorptive processes results in markedly different modeled and observed solute Cu concentrations.

Convict Creek (lat. 37°37'N, long. 118°50'W), a perennial, snow-fed stream on the eastern slope of the Sierra Nevada in California, was chosen as the study site because background solute concentrations of copper (<1 μL total Cu) and chloride (0.2 mg/L Cl) are low, allowing the

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use of these constituents as tracers, and because the physiography of the stream is typical of many bordering the Great Basin of the United States. Soils of the lower part of Convict Creek Basin, including the area of study, are composed of alluvium and morainal materials. Mineralogic analyses of fine sand and silt (sediment fraction <74 μm) in the stream sediments indicate an abundance of feldspar, quartz and calcite (24). Rinehart and Ross (24) detailed the mineralogy of the basin.

Convict Creek is oligotrophic (<10 $\mu\text{g/L}$ NO_3^- -N, <1 $\mu\text{g/L}$ PO_4^{3-} -P, and 7.0 mg/L SiO_2 in stream waters). The waters are slightly alkaline (pH 7.9–8.5) and always at or near saturation with respect to dissolved oxygen. Major element total concentrations (in milligrams per liter) determined during the period of study were as follows: Ca, 23; Mg, 0.3; K, 0.7; Na, 1.4; SO_4^{2-} , 11.0; and Cl, 0.2. These concentrations may vary by as much as 60% with seasonal fluctuations in stream discharge. Cobbles (>8 mm in diam) that composed the uppermost layer of the stream sediment were typically coated with periphyton. Periphyton, dominated by diatoms and bluegreen algae, have been characterized and their sensitivity to copper defined in previous work (15,16).

EXPERIMENTAL PROCEDURE

The experimental injection of Cu and Cl into Convict Creek was done in late summer during a period of moderate flow (1.1 m^3/s) beginning at 1,330 hr. Cupric sulfate and sodium chloride were co-injected at a culvert 400 m upstream of the first sampling site (hereafter referred to as the "upstream" site). Turbulence in the first 100 m section of Convict Creek below the culvert insured complete mixing of tracer and stream water at the upstream site. The "downstream" site was located 700 m below the upstream site. Although this may appear to be a short distance over which to conduct a transport study, processes causing copper pulse attenuation were very evident (Fig. 1B–D). In Fig. 1, A depicts measurement of hydrologic parameters using Cl as a conservative tracer; B, fit of the physical transport submodel to observed solute Cu data; C, addition of periphyton uptake submodel as a nonconservative term; and D, fit of the final 3-component model with periphyton uptake and sediment-sorption submodels added to the physical transport submodel. [(Solute injection began at 1,330 hr).] Tracers were co-injected at a rate sufficient to yield at least an order of magnitude increase in both Cu and Cl concentrations relative to background levels. A square wave pulse of tracers was injected for 9 hr (Fig. 1). A longer injection period was not used because of the potential inhibitory effect of Cu on the periphyton. Co-injection of tracers was based on gravity flow. Variable solute concentrations of Cu and Cl at pulse height (Fig. 1 A–D) are due to adjustments made in volume in injection solution to compensate for changes in gravitational head of the Cu-Cl spiking solution. Average upstream pulse concentrations were used as input data in the modeling in order to smooth out these small time concentration fluctuations. Except for pulse height averaging, upstream station data were directly used to generate the input data curves for the models considered herein (Fig. 1). Methods for determining values for model parameters are summarized

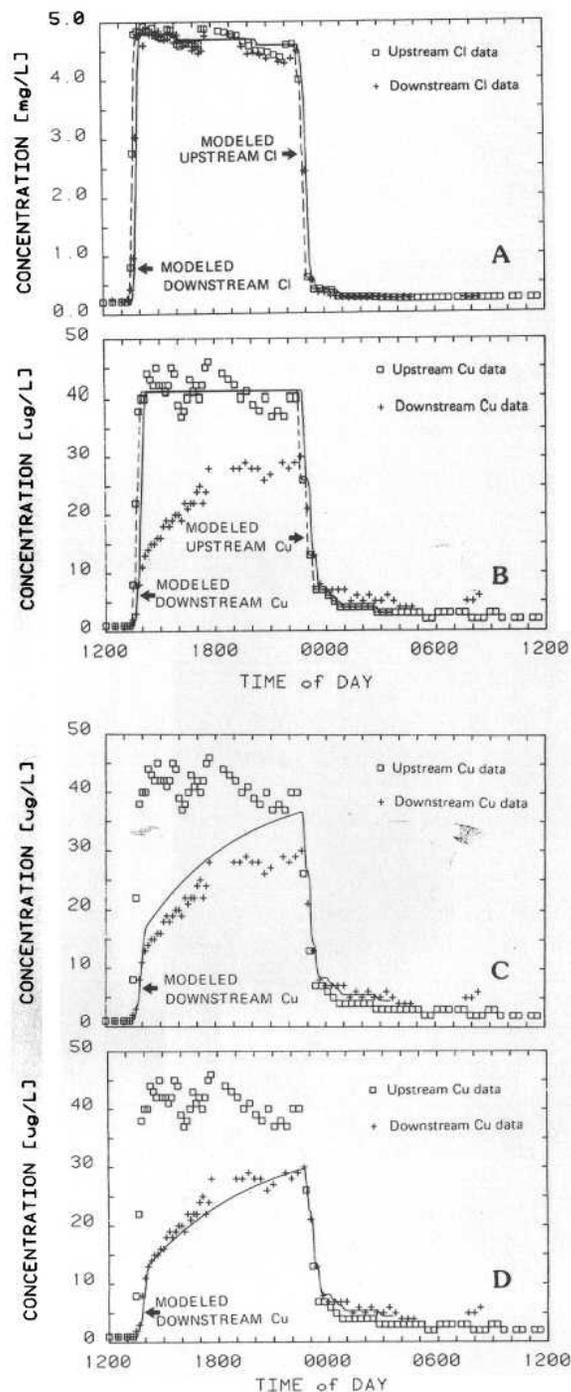


FIG. 1.—Development of Model to Describe Cu Transport in Convict Creek

TABLE 1.—Notation and Parameter Values Used in Cu Transport Model with Methods Outlined for Determining These Values

Parameter (1)	Description (2)	Parameter value(s) used (3)	95% CI (where available), n^a (4)	Method of determination (5)
A	Channel cross sectional area	1.3 m ²	0.1 m ² , 3	Channel cross-sectional depth profiles
C	Solute concentration	range = (1–40) µg/L	—	Flameless atomic absorption
C _B	Cu concentration in periphyton	range = (100–3,000) mg/L	—	Hot-HNO ₃ digestion of periphyton colonizing glass slides
C _S	Cu sorbed to sediment	range = (0.5–6) mg/L	—	1 N HCl partial fractionation of streambed sediment (22)
D	Dispersion coefficient	range = (8–15) m ² /s	—	Equation for open channel flow (5)
K _{dB}	Periphyton: solution partition coefficient	9 × 10 ⁴	6 × 10 ⁴ , 21	Calculated (C _B /C) at equilibrium
K _{dS}	Sediment: solution partition coefficient	500	200, 14	Calculated (C _S /C) at equilibrium
Q	Volume flow rate	1.1 m ³ /s	0.1 m ³ /s, 3	Pygmy current meter
R	Slope along reach	1.2%	0.1%, 11	Transit measurements
t	Time	9 hr pulse (36 sec time increment)		
x	Longitudinal distance	700 m reach (10 m node spacing)		
u	Average stream velocity	0.81 m/s	0.09 m/s, 3	Pygmy current meter
u*	Shear velocity	0.16 m/s	0.02 m/s, 3	Slope and depth measurements
w	Channel width	6.6 m	2.2 m, 3	Meter rule
λ _{Bf}	First-order rate coefficient for periphyton Cu uptake	10 ⁻⁴ s ⁻¹	—	Fitted parameter
λ _{Br}	First-order rate coefficient for periphyton Cu release	10 ⁻⁵ s ⁻¹	—	Fitted parameter

TABLE 1.—Continued

(1)	(2)	(3)	(4)	(5)
λ_{sf}	First-order rate coefficient for sediment sorption	10^{-4} s^{-1}	—	Copper sorption isotherms onto <74- μm sediment fraction at pH 7.6 (8)
λ_{sr}	First-order rate coefficient for sediment desorption	10^{-5} s^{-1}	—	Dialysis/AAS of copper release from sediment (9)
ρ_B	Mass of 'accessible' periphyton per volume stream water	60 mg/L	25 mg/L, 24	Biomass (chlorophyll- <i>a</i>) of periphyton on cobble (10)
ρ_S	Mass of 'accessible' sediment per volume stream water	$6 \times 10^4 \text{ mg/L}$	—	Fitted parameter

*CI = confidence interval; n = number of samples.

in Table 1. For ease in referencing, parameters are also defined in Table 1 in lieu of a notation appendix.

RESULTS AND ANALYSIS

A standard one-dimensional advection-dispersion model (7) was initially used (Fig. 2, Submodel 1) with CI as a conservative tracer (2,8,26) to determine fit of hydrologic parameters (Table 1). (In Fig. 2, the final 3-component model allows use of different λ values for both periphyton and sediment submodels during uptake, λ_{Bf} , λ_{Sf} , and release, λ_{Br} , λ_{Sr} .) Techniques for numerical solution of the model have been previously mentioned (2,3). Although there were pool and riffle areas along the study reach, the channel was assumed uniform. The dispersion coefficient, D , was calculated using an empirical equation for open channel flow: $D = (0.011u^2w^2)/u^*d$, in which u = the average stream velocity; w = the average channel width; u^* = the shear velocity; and d = the average channel depth (7). The conservative model using measured (e.g., discharge, Q , and cross-sectional area, A) and calculated (e.g., D) hydrologic parameters provided a good fit to observed CI concentrations (Fig. 1A). Both observed and model-generated CI concentrations show that pulse height was achieved at the downstream site approx 15 min after the upstream site.

In contrast to the CI data, the Cu data revealed a marked attenuation at the downstream site (Fig. 1B). Downstream Cu concentrations did not appear to achieve a plateau in peak height over the 9 hr injection period. The conservative model, although appropriate for CI, did not explain observed downstream Cu attenuation. A kinetic periphyton submodel (biological component) was then added to the transport model in the form of a first-order mass transfer equation (Fig. 2, Submodel 2). Parameter values for this biological submodel were based on measured Cu con-

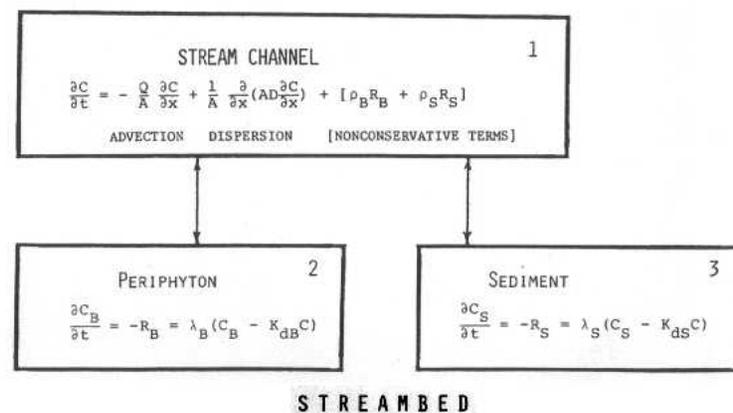


FIG. 2.—Schematic Diagram of Transport Model with Boxes Denoting: (1) Physical Transport Submodel with Nonconservative Terms in Brackets; (2) Kinetic Periphyton Submodel; and (3) Kinetic Sediment-Sorption Submodel

centrations in *in situ* periphyton. Algal biomass was measured by random sampling of periphyton on cobble. The rate coefficients, λ'_{Bs} , were the only fitted (i.e., not directly measured) parameters. Although a much improved fit to the leading and falling edge of the downstream Cu data was achieved, downstream data still showed considerably less Cu ($\sim 5 \mu\text{g/L}$) appearing downstream during the pulse than the model indicated (Fig. 1C).

Cu removal by sediment sorption was then considered in the model (Fig. 2, Submodel 3) with rate equations of the same general form as for the periphyton submodel, but with different parameter values (Table 1). The first-order mass transfer formulation is empirical. However, it has been used successfully in describing cation sorption by stream bed sediment (4,22). Onishi, et al. (22) also reviewed a model of similar form for radioisotope studies and examined potential application of this model for studying transport of organics including pesticides. The fitted parameters in this three-component model were the rate constants for periphyton (λ'_{Bs}) and the mass of accessible sediment per unit volume of overlying stream, ρ_S . Although a mass per unit bed area specification for ρ_S would have explicitly accounted for depth, the mass per unit volume specification was considered more appropriate here. Mountain streams are neither rectangular nor even well defined. An attempt was made to select a fairly uniform study reach. In general, however, channel depth and width may vary over relatively short distances and mass of accessible sediment will also vary. Adding depth explicitly as a model parameter adds one more value to be estimated. Additional parameters were not justified by the resolution of the field parameters or by the chemical data.

With three submodels, Cu transport along the reach was well defined (Fig. 1D). Fitted parameter values are consistent with previous work by others and are examined in the following. Final formulation of model equations is shown in Fig. 2, with model parameters defined and values

listed in Table 1. Deviations between observed and modeled stream concentrations may reflect analytical error and effects due to smoothing the upstream Cu data for model input data. "Dead" zone storage, groundwater discharge/recharge (3) and seston (suspended detritus) transport (18) were other processes examined but were of less importance in this experiment than processes included in the model. In contrast to the attenuation of the Cu pulse observed between upstream and downstream sites, the square wave Cu pulse, injected 400 m above the upstream station, was essentially preserved at the upstream site (Fig. 1B-D). This lack of Cu attenuation in the 400 m above the upstream site was expected because this mixing zone, characterized by high velocity and turbulence relative to other stream sections, provides low residence time for Cu to react with the streambed (approx 7 min in the mixing zone compared to 15 min in the experimental reach).

The 3-component model quantitatively describes the observed Cu injection data, but one might expect to achieve a reasonable fit of data with λ_B and ρ_S as fitted parameters, assuming the remaining measured parameters have values that are physically realistic. It is significant, however, that the λ_B and ρ_S values that produce this close fit to observed data for copper transport in Convict Creek are consistent with previously published values. The final rate coefficient values used in the periphyton submodel were 10^{-4} s^{-1} for sorption and 10^{-5} s^{-1} for release (Table 1). These values compare favorably with rate coefficients estimated for the diatom *Cyclotella* and the green alga *Chlamydomonas* from Cu uptake and release data [approx $3 \times 10^{-4} \text{ s}^{-1}$ or $\sim 1 \text{ hr}^{-1}$ for sorption, and $3 \times 10^{-5} \text{ s}^{-1}$ or $\sim 0.1 \text{ hr}^{-1}$ for Cu release (5)]. Mandelli (19) reported similar Cu sorption trends for marine phytoplankton. These previous Cu sorption studies on algae were conducted in the laboratory under continuous illumination, while periphyton in the field injection experiment were exposed to diurnal light conditions. Algal growth in response to elevated trace metal concentrations appears to be detrimentally affected by continuous light relative to diurnal light cycling (1,12). It is, therefore, possible that Cu uptake by algae may increase with light intensity. Agreement between observed and modeled Cu concentrations (Fig. 1D) indicates that if such a variation in sorption rates occurred during the injection experiment, it was beyond the resolution of this modeling effort. The accessible sediment value, ρ_S , $6 \times 10^4 \text{ mg/L}$ used in the kinetic sediment sorption submodel also compares well with the ρ_S value ($2 \times 10^4 \text{ mg/L}$) determined for Uvas Creek, a small pool-and-riffle mountain stream (2).

Published partition coefficients for algae, K_{dB} , show a wide variability (10^3 – 9×10^4) when K_{dB} is based on a ratio of total copper concentrations of algae to total copper concentration of bulk solution (5,13,21). If, however, K_{dB} is calculated as a ratio of total algal Cu to computed free ion activity, Cu^{2+} , in the bulk solution (27), then the K_{dB} range is narrowed considerably (1×10^7 – 4×10^7). Values of K_{dB} determined for Convict Creek periphyton were 9×10^4 and 2×10^7 , based on total and computed free Cu ion concentrations in stream water, respectively. This observation is consistent with previous results indicating that Cu uptake by algae correlates better with free ion activity than with total Cu con-

centration (14,20,23,25). It also points out the need for developing and applying transport models that couple with chemical speciation models (6) and a limitation of models, including the one used here, that do not consider chemical speciation in solute transport.

Rate coefficients for Cu-sediment sorption and desorption ($1 \times 10^{-4} \text{ s}^{-1}$ and $1 \times 10^{-5} \text{ s}^{-1}$, respectively) are of similar order of magnitude to determined values for strontium, Sr, interaction in Uvas Creek. A single value of $5 \times 10^{-4} \text{ s}^{-1}$ (includes Sr interactions with organic matter) was found suitable for both sorption and desorption (2) of Sr. Although one would not expect rate coefficients for Cu and Sr to be identical, it is noteworthy that rate coefficients determined in independent studies for two reactive trace elements are similar.

SUMMARY AND CONCLUSIONS

A 3-component model has been used to describe transport of a reactive solute, Cu, along a California mountain stream. The fact that measured, calculated and fitted parameter values for this model (Table 1) are well within the range of published values determined in the laboratory (2,3,7,13), and that a dispersion coefficient calculated using an empirical equation formulated from other studies (7) provides a good fit to the conservative model, suggests that this stream is not atypical and that this approach may be generally useful in studying solute transport in streams. This indicates that consideration of nonhydrologic mechanisms (both biological and chemical) in addition to conventionally examined physical transport processes (e.g., advection and dispersion) may be important in describing transport of reactive solutes in streams. The model is not meant to be predictive for all streams subjected to a reactive metal pollutant or even for this stream under very different environmental conditions (i.e., different temperatures, channel depths, etc.). Indeed, the degree of importance of nonconservative processes varies with time and location. Effects of physical parameters (e.g., temperature and light intensity) on Cu uptake rates are, e.g., not quantified in this model. It is believed, however, that this approach can be of value as a tool to identify the relative importance of interdependent hydrologic, chemical, and biological processes in solute transport of reactive constituents.

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