Available online at www.sciencedirect.com
SCIENCE DIRECT
Science of the Total Environment 367 (2006) 800 – 810
Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind
www.elsevier.com/locate/scitotenv

Simulation of future stream alkalinity under changing deposition and climate scenarios

Daniel L. Welsch [a,*], B. Jack Cosby [b], George M. Hornberger [b]

[a] Department of Geography, Frostburg State University, Frostburg, MD 21532 USA
[b] Department of Environmental Sciences, University of Virginia, PO Box 400123, Charlottesville, VA, 22904-4123, USA

Received 20 July 2005; received in revised form 27 January 2006; accepted 30 January 2006
Available online 4 April 2006

Abstract

Models of soil and stream water acidification have typically been applied under scenarios of changing acidic deposition, however, climate change is usually ignored. Soil air CO_2 concentrations have potential to increase as climate warms and becomes wetter, thus affecting soil and stream water chemistry by initially increasing stream alkalinity at the expense of reducing base saturation levels on soil exchange sites. We simulate this change by applying a series of physically based coupled models capable of predicting soil air CO_2 and stream water chemistry. We predict daily stream water alkalinity for a small catchment in the Virginia Blue Ridge for 60 years into the future given stochastically generated daily climate values. This is done for nine different combinations of climate and deposition. The scenarios for both climate and deposition include a static scenario, a scenario of gradual change, and a scenario of abrupt change. We find that stream water alkalinity continues to decline for all scenarios (average decrease of 14.4 μeq L^{-1}) except where climate is gradually warming and becoming more moist (average increase of 13 μeq L^{-1}). In all other scenarios, base cation removal from catchment soils is responsible for limited alkalinity increase resulting from climate change. This has implications given the extent that acidification models are used to establish policy and legislation concerning deposition and emissions.

Keywords: Alkalinity; Simulation; Climate change; Model; Stream

1. Introduction

The ability to predict future stream water chemistry is critical to understanding the impacts of current and proposed legislation aimed at reducing deposition of strong acid anions to catchment systems. A number of mathematical models of soil and surface water acidification in response to atmospheric deposition were developed in the early 1980's (e.g., Christophersen and Wright, 1981; Christophersen et al., 1982; Schnoor et al., 1984; Booty and Kramer, 1984; Goldstein et al., 1984; Cosby et al., 1985a,b,c). These models were based on process-level information about acidification and were built for a variety of purposes ranging from estimating transient water quality responses for individual storm events to estimating chronic acidification of soils and base flow surface water. One of these models (MAGIC — the *M*odel of *A*cidification of *G*roundwater *I*n *C*atchments; Cosby et al., 1985a,b,c) has been in use now for more than 15 years. MAGIC has been applied extensively in North America and Europe to both individual sites and regional networks of sites, and has also been used in Asia,

* Corresponding author. Tel.: +1 301 687 4891; fax: +1 301 687 4495.
E-mail address: dwelsch@frostburg.edu (D.L. Welsch).

0048-9697/$ - see front matter
doi:10.1016/j.scitotenv.2006.01.019

Africa and South America. The utility of MAGIC to simulate a variety of water and soil acidification responses at the laboratory, plot, hillslope and catchment scales has been tested using long-term monitoring data and experimental manipulation data (Beier et al., 1995; Cosby et al., 1990; Ferrier et al., 2001).

Most applications of MAGIC have been done without consideration of the impacts of climate change on stream chemistry. In particular, changing soil air CO_2 concentrations, capable of strongly influencing stream water chemistry in both the long and short term, have not been included in studies using catchment biogeochemical models. As climate changes, we expect that conditions for soil respiration will change, thus causing soil air CO_2 to increase or decrease. In general, warmer and wetter conditions enhance oxidation of soil organic C and result in greater subsurface CO_2 concentrations. Work by Norton et al. (2001) suggests that reasonable changes in soil air CO_2 can mask or enhance changes in stream alkalinity brought about by decreases in atmospheric deposition of strong acid anions, mainly SO_4^{2-}. In particular, they found that if a decline of 20 μeq L^{-1} SO_4^{2-} in deposition occurred together with a decline of 0.2% pCO_2, there would be no detectable change in stream alkalinity or pH. The ability to quantify these confounding factors is important when evaluating the past and proposed effects of air emissions legislation.

In this paper, we examine the possibility that long-term changes in drainage water alkalinity in response to changing soil CO_2 may obscure long-term changes in drainage alkalinity in response to changing acid deposition in a small headwater stream in the Blue Ridge of Virginia over 60 years, beginning in 1983.

Acidic deposition influences stream water chemistry through soil equilibrium processes that are well understood (Reuss and Johnson, 1985; Reuss et al., 1987). The influence of soil CO_2 is coupled with those of acidic deposition because both processes add acid anions to the soil (H^+ from climate change driven CO_2 increases, SO_4^{2-} from acidic deposition). The bicarbonate alkalinity (HCO_3^-) concentration of soil and stream water is tightly coupled to the amount of CO_2 in the soil air through the reactions:

$$CO_2(g) = CO_2(aq) \tag{1a}$$

$$CO_2(aq) + H_2O = H^+ + HCO_3^-. \tag{1b}$$

It has been established that the two dominant factors that influence the concentration of CO_2 in soil air are soil temperature and soil moisture (Edwards, 1975; Davidson et al., 1998; Lomander et al., 1998). If air temperature and precipitation increase in response to increased atmospheric CO_2, then the reaction in Eq. (1b) will shift to the right, resulting in an increase in stream water alkalinity from ionized carbonic acid. As excess protons (H^+) are generated in the soil through the reactions in Eqs. (1a) and (1b) above, base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) on soil exchange sites are removed and replaced by H^+. These base cations are then lost from the catchment in stream water, charge balanced by the bicarbonate (HCO_3^-) produced in Eq. (1b) above. This increase in stream HCO_3^- increases stream alkalinity in the short term, thus increasing the buffering capacity of the stream. However, eventually all base cations can be removed from the soil and replaced by H^+. Excess H^+ produced in Eq. (1b) above now is charge balanced by the HCO_3^-, and stream alkalinity plummets creating poor habitat for fishes and other aquatic organisms. Forest health begins to suffer due to the lack of base cations in the soil and lack of ability to buffer incoming acids.

In this paper, we examine the possibility that long-term changes in drainage water alkalinity in response to changing soil CO_2 may obscure long-term changes in drainage alkalinity in response to changing acid deposition in a small headwater stream in the Blue Ridge of Virginia over 60 years, beginning in 1983. We link a coupled series of mathematical models that are capable of predicting soil air CO_2 concentrations through space and time with MAGIC in order to understand the relative impacts that changes in climate and changes in acidic deposition have on a small stream. Nine scenarios generated from combinations of three climate scenarios and three deposition scenarios are analyzed.

This work builds on and tests the ideas presented by Norton et al. (2001) by using the series of models developed by Welsch and Hornberger (2004) to simulate soil air CO_2 in response to various climate and deposition scenarios. The results of this work are new because of our use of physically based rather than statistical or empirical models to represent soil respiration and CO_2 concentration, and because of our linking of climate change, a model of soil respiration and CO_2 concentration, and a model of catchment acid-base status to investigate the combined effects of these forcings on stream water chemistry into the future.

2. Study catchment

The field data used for calibration and the results of the simulations performed are for the South Fork of