



## Comparison among model estimates of critical loads of acidic deposition using different sources and scales of input data

T.C. McDonnell<sup>a</sup>, B.J. Cosby<sup>b</sup>, T.J. Sullivan<sup>a,\*</sup>, S.G. McNulty<sup>c</sup>, E.C. Cohen<sup>c</sup>

<sup>a</sup> E&S Environmental Chemistry, Inc., P.O. Box 609, Corvallis, OR 97339, USA

<sup>b</sup> Department of Environmental Science, University of Virginia, Charlottesville, VA 22903, USA

<sup>c</sup> USDA Forest Service, Eastern Forest Environmental Threats Assessment Center-Raleigh, 920 Main Campus Drive, Suite 300, Raleigh, NC 27606, USA

*The scale and source of model input data and the resulting estimates of weathering can have profound effects on steady-state critical loads modeling results.*

### ARTICLE INFO

#### Article history:

Received 12 February 2010

Received in revised form

3 June 2010

Accepted 4 June 2010

#### Keywords:

Acidification

Weathering

Sulfur

Critical load

Atmospheric deposition

### ABSTRACT

The critical load (CL) of acidic atmospheric deposition represents the load of acidity deposited from the atmosphere to the earth's surface at which harmful acidification effects on sensitive biological receptors are thought to occur. In this study, the CL for forest soils was estimated for 27 watersheds throughout the United States using a steady-state mass balance approach based on both national and site-specific data and using different approaches for estimating base cation weathering. Results suggested that the scale and source of input data can have large effects on the calculated CL and that the most important parameter in the steady-state model used to estimate CL is base cation weathering. These results suggest that the data and approach used to estimate weathering must be robust if the calculated CL is to be useful for its intended purpose.

© 2010 Elsevier Ltd. All rights reserved.

### 1. Introduction

Atmospheric deposition of sulfur (S) and nitrogen (N), derived from coal-fired electricity generation, industrial, and nonpoint air pollution sources, has caused acidification of soils, soil water, and drainage water across broad areas of the United States (U.S. EPA, 2008). Such acidification has been associated with enhanced leaching of sulfate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ) to drainage waters, depletion of calcium ( $\text{Ca}^{2+}$ ) and other nutrient base cations (Bc) from soil, reduced pH and acid neutralizing capacity (ANC) of surface waters, and increased mobilization of potentially toxic inorganic aluminum (Al; Sullivan, 2000). Resulting biological effects have included toxicity to fish and aquatic invertebrates and adverse impacts on forest vegetation, especially red spruce and sugar maple trees (U.S. EPA, 2009).

Resource managers are now confronted with the need for air pollution emissions reductions sufficient to allow damaged

resources to recover. In order to inform public policy regarding air pollutant emissions controls, it is important to determine 1) the levels of emissions and atmospheric deposition that are associated with varying degrees of chemical effects and 2) the linkages between water and soil chemistry and consequent biological impacts. One of the most important tools available to natural resource managers in this context involves constructing model estimates of critical loads. The critical load (CL) for acidification is the level of sustained atmospheric deposition of S, N, or acidity below which harmful effects to sensitive ecosystems are not expected to occur according to current scientific understanding (Nilsson and Grennfelt, 1988).

The CL is usually calculated as a long-term steady-state condition. However, under constant atmospheric deposition at the determined CL, it may take many decades or centuries for the sensitive chemical criterion (i.e., soil base cation  $[\text{BC}; \text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+]$  to Al ratio or water ANC) to reach the required level to protect ecosystem health. The steady-state CL for protection of either aquatic or terrestrial resources can be calculated using a mass balance, of which there are several alternative approaches.

The watershed supply of base cations due to weathering ( $\text{BC}_w$ ) is often the CL model parameter that has the most influence in the CL calculation, and it has substantial uncertainty (Li and McNulty,

\* Corresponding author.

E-mail addresses: [todd.mcdonnell@esenvironmental.com](mailto:todd.mcdonnell@esenvironmental.com) (T.C. McDonnell), [B.J.Cosby@virginia.edu](mailto:B.J.Cosby@virginia.edu) (B.J. Cosby), [tim.sullivan@esenvironmental.com](mailto:tim.sullivan@esenvironmental.com) (T.J. Sullivan), [steve\\_mcnulty@ncsu.edu](mailto:steve_mcnulty@ncsu.edu) (S.G. McNulty), [eccohen@fs.fed.us](mailto:eccohen@fs.fed.us) (E.C. Cohen).

2007, U.S. EPA, 2009). In essence, the maintenance of long-term ecosystem acid-base chemistry health depends on keeping the atmospheric acid load relatively low compared with the natural re-supply of BC through weathering. If the estimate of  $BC_w$  is inaccurate, the resulting CL calculation may be of little value for its intended purposes: communicating air pollution impacts to diverse audiences, assessing the effectiveness of emissions reductions programs, and supporting resource management decision-making.

The most common methods for estimating  $BC_w$  for inclusion in steady-state CL models involve either use of regional estimates of geologic substrate and clay content or simple empirical calculations designed to estimate what the level of historical weathering must have been in order to support the observed current concentrations of BC in drainage water. The former approach assumes that weathering varies with soil clay content and geologic substrate in ways that can be represented by available spatial soils and geologic data. Inputs to the soil clay/substrate approach for estimating  $BC_w$  include % clay and geologic acid sensitivity class based on mineralogy. The geologic types are acidic (e.g., granites, gneiss, sandstones, felsic rocks), intermediate (e.g., diorite, granodiorite, conglomerate, and most sedimentary rocks other than sandstone), and basic (e.g., mafic rocks, carbonates; Pardo and Duarte, 2007). It is assumed that the lowest weathering rates will occur with soils having low clay content, over acidic rock types (Sverdrup et al., 1990). The latter approach entails a number of assumptions about background pre-industrial water chemistry and the extent to which the base cation flux in drainage water has been changed in response to increased leaching of  $SO_4^{2-}$  and/or  $NO_3^-$  (the so-called F-factor approach; cf., Henriksen, 1984; Henriksen and Posch, 2001). Both approaches are uncertain, in that they are rooted in unsubstantiated assumptions and rely on data that may not be available at appropriate scales for the sensitive watersheds.

Terrestrial and aquatic ecosystems on federal lands receive atmospheric deposition of sulfur and nitrogen that currently, or in the future, may potentially exceed damage threshold levels. Various steady-state and dynamic model approaches have been developed to calculate the CL of atmospheric deposition (either S and/or N, alone or in combination) that would protect vulnerable receptors (e.g., fish, invertebrates, vegetation) and/or permit the recovery of impaired ecosystem receptors. Steady-state critical load calculations have been developed and applied across northern Europe and eastern Canada (Watmough and Dillon, 2002; Gregor et al., 2004; Ouimet et al., 2006), and have provided an important part of the basis for political and economic negotiations and national and international legislation. McNulty et al. (2007) calculated and mapped preliminary terrestrial CL values for forested ecosystems across the United States using relatively coarse national scale data (1 km<sup>2</sup>) to aggregate the inputs. The authors cautioned, however, that a more systematic analysis was needed before this approach could be used as a tool for identifying areas of potential forest health concern. Some recent efforts have focused on process-based dynamic model estimates of critical loads (cf., Sullivan et al., 2005, 2008).

The simple steady-state modeling approaches have important advantages in that model input data can be compiled and/or developed at broad scales and resulting model output can be mapped regionally or nationally. There are, however, several important disadvantages, perhaps the most important of which are the following:

1. In some watersheds and regions, the steady-state condition may not be reached for centuries. The steady-state approaches provide no information regarding the timing of expected adverse impacts, although some management decisions require such information.
2. Steady-state model projections have not been tested or confirmed, and in most cases *cannot* be tested or confirmed without waiting for decades or centuries for the establishment of conditions of watershed input–output balance.

3. Calculations based on input data derived from coarse regional or national scale databases and which are needed for regional or national scale CL assessment may contain large errors due to the scale and accuracy of the model input data.

In recognition of these, and other, limitations, and in order to facilitate development of regional and national critical loads estimates for federal lands, we compared terrestrial steady-state model estimates of critical loads derived using varying estimates of  $BC_w$  within different regions in the United States and for different types of watersheds. The steady-state model estimates were generated with the approach described by McNulty et al. (2007), using the Simple Mass Balance (SMB) CL model (Posch et al., 2001).

This paper compares steady-state model estimates developed using two scales of input data, one based on the national scale data used by McNulty et al. (2007), and another based on the highest resolution model input data that were available for each study watershed. The focus of the comparative analyses was to evaluate, for these 27 watershed locations, 1) differences in critical load estimates using the steady-state methodology, depending on the source and scale of the input data (coarse national scale versus a site-specific approach driven by local data availability), and 2) differences that result from applying an alternate approach for estimating  $BC_w$ .

## 2. Methods

### 2.1. Site selection and data compilation

Study watersheds were selected from among those previously modeled by Church et al. (1989), Sullivan and Cosby (2002, 2004), and Sullivan et al. (2005, 2007), using the Model of Acidification of Groundwater in Catchments (MAGIC; Cosby et al., 1985). Model watersheds were selected across a range of conditions with respect to current water chemistry, previously modeled CL values, and critical processes governing sulfur adsorption, base cation depletion, and extent of prior acidification. We selected two lake watersheds in the western United States, both at high elevation, one located in the Rocky Mountains and one in the Cascade Mountains. The balance of the study watersheds included 6 lakes in the northeastern U.S. and 19 streams in Virginia, West Virginia, North Carolina, Tennessee, and Georgia. Selected sites and their locations are listed in Table 1, along with data regarding major aspects of their drainage water chemistry.

For each of the watersheds, we retrieved MAGIC model calibrations associated with previously completed modeling projects conducted for the USDA Forest Service, National Park Service, or U.S. Environmental Protection Agency. These existing model calibrations provided the foundation for MAGIC estimates of  $BC_w$  applied to the steady-state CL modeling conducted in this project.

### 2.2. Critical loads modeling

#### 2.2.1. MAGIC model

MAGIC is an aggregated catchment model (Cosby et al., 1985). It was used in this study to estimate  $BC_w$  for each of the study watersheds. The base cation weathering terms in MAGIC are intended to represent the catchment-average weathering rates for the soil compartments. In this single soil-layer application of MAGIC the weathering rates in MAGIC reflect the catchment-average net supply of base cations to the surface waters draining the catchment. The sum of the MAGIC weathering rates for the individual base cations is similar in concept to the base cation weathering term,  $BC_w$ , in the SMB CL model. However, the former represents the BC weathering flux in drainage water, whereas the latter represents the flux within the plant rooting zone. Base cation weathering rates from MAGIC can provide an approximate surrogate for watershed averaged  $BC_w$  because the stream chemistry integrates soil conditions throughout the watershed.

Base cation weathering rates in MAGIC are calibrated parameters. The calibration procedure uses observed deposition of base cations, observed (or estimated) base cation uptake in soils, observed soil chemistry, observed stream water base cation concentrations, and estimated runoff. These data provide upper and lower limits for internal sources of base cations in the catchment soils. The two most important internal sources of base cations in catchment soils are modeled explicitly by MAGIC: 1) primary mineral weathering and 2) soil cation exchange. During the calibration process, observed soil base saturation for each base cation and observed soil chemical characteristics are combined with the observed input and output data to partition the inferred net internal sources of base cations between weathering and base cation exchange.

**Table 1**  
Location and selected chemical conditions of watersheds chosen for modeling. Units for ANC, NO<sub>3</sub>, and SO<sub>4</sub> are in µeq/L.

Site ID	Name	Lake/Stream	ANC	NO <sub>3</sub>	SO <sub>4</sub>	Latitude	Longitude	Elevation (m)
<i>Southeastern DDRP Streams</i>								
2A07811	False Gap Prong (TN)	S	16	39	44	35.674	83.363	549
2A07817	Forney Creek (NC)	S	31	21	24	35.538	83.526	732
2C041040	Thunderstruck Creek (WV)	S	48	43	184	39.25	79.61	658
2A07806	Roaring Fork (NC)	S	104	16	29	35.82	82.926	671
2A07821	Grassy Creek (NC)	S	126	8	18	35.468	82.261	552
2A08810	Bryant Creek (GA)	S	138	15	21	34.623	84.011	448
<i>Shenandoah National Park Streams, VA</i>								
DR01	Deep Run	S	-2	0	109	38.266	78.744	415
VT36	Meadow Run	S	-1	0	89	38.169	78.783	451
NFDR	North Fork of Dry Run	S	50	33	99	38.622	78.354	488
VT59	Staunton River	S	66	3	41	38.457	78.399	308
VT75	White Oak Canyon Run	S	122	33	53	38.567	78.364	354
VT66	Rose River	S	132	32	53	38.522	78.402	341
<i>Monongahela NF Streams, WV</i>								
DS04	Little Stonecoal Run	S	-59	7	117	38.996	79.395	932
FN1	Fernow - WS10	S	16	8	195	39.057	79.679	713
WV796S	Red Creek	S	34	0	85	39.063	79.331	1127
WV770S	Moss Run	S	95	12	208	38.706	79.942	621
WV771S	Left Fork Clover Run	S	152	18	171	39.138	79.767	469
<i>Joyce Kilmer/Shining Rock Streams, NC</i>								
SR1	Shining Rock Site 1	S	18	0	34	35.331	82.85	1717
JK1	Joyce Kilmer Site 1	S	26	15	53	35.352	83.936	670
<i>Western Lakes</i>								
EU-A	Eunice Lake (WA)	L	51	0	9	46.955	121.878	1633
LO-A	The Loch (CO)	L	53	16	31	40.282	105.668	3104
<i>Northeastern DDRP Lakes</i>								
1A1057	Hitchcock Lake (NY)	L	-18	0	118	43.848	75.042	567
1E2049	Gross Pond (ME)	L	-4	0	82	44.057	69.391	29
1A1046	Partlow Lake (NY)	L	56	5	111	44.002	74.826	534
1C2035	Smith Pond (NH/VT)	L	65	0	118	43.161	72.033	328
1E2054	Brettuns Pond (ME)	L	229	0	113	44.403	70.258	122
1C3063	Martin Meadow Pond (NH/VT)	L	326	0	108	44.446	71.596	326

Weathering is assumed constant in MAGIC, although base cation exchange varies through time as anion fluxes change and as the soil base saturation increases or decreases. Therefore, the calibration simulations are performed over an historical period of approximately 150 years. Weathering and cation exchange selectivity coefficients are selected during calibration such that the model begins with reasonable soil and stream conditions; these conditions respond to the 150-year period of deposition changes at the site. The final simulated values of stream and soil base cations are consistent with the current observed stream export and soil base saturation in the watershed. The partitioning of observed base cation export into weathering and cation exchange by MAGIC is thus heavily constrained by observed deposition, soil, and stream water data. Weathering estimates are expected to become more robust and reliable with increasing data quality and abundance. The catchment-average estimates of weathering rates derived from MAGIC calibrations provide data-constrained, site-specific, and conceptually appropriate values for inclusion in the SMB model for that site.

## 2.2.2. SMB model

The SMB model represents major biogeochemical processes affecting soil acidification using a steady-state input/output budget approach. The SMB model was applied to each of the study watersheds in the manner described by McNulty et al. (2007) for national scale mapping. A second SMB application was based on available site-specific data.

Steady-state critical load estimates using the SMB model can be used to classify the landscape according to the risk of soil acidification over large areas. The SMB model can calculate the CL for S deposition alone, or for S and N deposition combined. For the analyses reported here, we based the comparison on CLs calculated for S deposition only.

**2.2.2.1. National scale SMB application.** The critical load for S (in units of eq/ha/yr) can be estimated by the SMB model as:

$$CL(S) = BC_{dep} - Cl_{dep} + BC_w - BC_u - ANC_{le(crit)} \quad (1)$$

where (all parameters expressed as fluxes, for example in units of eq/ha/yr):

BC<sub>dep</sub> = total atmospheric deposition of base cations (Ca + K + Mg + Na)  
Cl<sub>dep</sub> = total atmospheric deposition of chloride

BC<sub>w</sub> = total weathering rate for base cations (Ca + K + Mg + Na)

BC<sub>u</sub> = total vegetative uptake of the nutrient base cations (Ca + Mg + K) by trees removed from the watershed by harvesting

ANC<sub>le(crit)</sub> = critical acid neutralizing capacity (ANC) leaching limit

The base cation weathering rate (BC<sub>w</sub>) was estimated separately for different bedrock types as:

$$\text{Acidic bedrock: } BC_w = (56.7\% \text{ clay}) - (0.32\% \text{ clay}^2) \quad (2)$$

$$\text{Intermediate bedrock: } BC_w = 500 + (53.6\% \text{ clay}) - (0.18\% \text{ clay}^2)$$

$$\text{Basic bedrock: } BC_w = 500 + (59.2\% \text{ clay})$$

where:

% clay = average % clay in soil profile

Table 2 provides a description of the bedrock classes.

Base cation uptake (BC<sub>u</sub>) from the soil by vegetation, with subsequent removal from the watershed, was estimated for 21 forest types by:

$$BC_u = AVI * NC * SG * \%bark * 0.65 \quad (3)$$

where:

AVI = average forest volume increment (m<sup>3</sup>/ha/yr)

NC = percent base cation nutrient concentration in bark and bole

SG = specific gravity of bark and bole wood (g cm<sup>-3</sup>)

% bark = percent of volume growth allocated to bark

0.65 = fraction of tree volume removed from the site

Uptake values for each forest type are given by McNulty et al. (2007).

The ANC critical leaching limit (ANC<sub>le(crit)</sub>) can be specified according to a critical ratio of BC:Al or Ca:Al in soil solution that is thought to be associated with damage to trees from Al toxicity (Cronan and Grigal, 1995). Alternatively, the ANC leaching limit can be specified on the basis of base cation limitation for tree growth and health. For this study the critical leaching limit was specified as:

**Table 2**

Parent material class descriptions used for estimating weathering (modified from McNulty et al., 2007).

Parent Material Class	Parent Material Category	Silica (SiO <sub>2</sub> ) Content	Calcium–ferromagnesium Content (Ca, Mg, and Fe Oxides)	Examples
Acidic	Extremely siliceous	> 90%	Extremely low (generally <3%)	Quartz sands (beach, alluvial or Aeolian), chert, quartzite, quartz reefs and silicified rocks
	Highly siliceous	72–90%	Low (generally 3–7%)	Granite, rhyolite, adamellite, dellenite, quartz sandstone and siliceous tuff
Intermediate	Transitional Siliceous/ Intermediate	62–72%	Moderately low (generally 7–14%)	Granodiorite, dacite, trachyte, syenite, most greywacke, most lithic sandstone, most argillaceous rocks (mudstone, claystone, shale, slate, phyllite, schist) and siliceous/intermediate tuff
	Intermediate	52–62%	Moderate (generally 14–20%)	Monzonite, trachy-andesite, diorite, andesite, intermediate tuff and some greywacke, lithic sandstone and argillaceous rock
Basic	Mafic	45–52%	High (generally 20–30%)	Gabbro, dolerite, basalt and mafic tuff (uncommon)
	Ultramafic	< 45%	Very high (generally >30%)	Serpentinite, dunite, peridotite, amphibolite, and tremolite–chlorite–talc schists
	Calcareous	Low <sup>a</sup>	CaCO <sub>3</sub> dominate other bases variable	Limestone, dolomite, calcareous shale and calcareous sands
Organic	Organic	Low <sup>a</sup>	Organic matter dominate bases variable	Peat, coal and humified vegetative matter
Other	Alluvial Sesquioxide	Variable <sup>a</sup> Variable <sup>a</sup>	Variable Variable, dominated by sesquioxides such as iron and aluminum oxides	Variable Laterite, bauxite, ferruginous sandstone and ironstone

<sup>a</sup> Category not defined by silica content.

$$ANC_{le(crit)} = -Q^{2/3} * \left( 1.5 * \frac{BC_{dep} + BC_w - BC_u}{K_{gibb} * \left( \frac{BC}{Al} \right)_{crit}} \right)^{1/3} - 1.5 * \frac{BC_{dep} + BC_w - BC_u}{\left( \frac{BC}{Al} \right)_{crit}} \quad (4)$$

where:

BC<sub>w</sub> = total weathering rate for nutrient base cations (Ca, Mg, K)BC<sub>dep</sub> = total atmospheric deposition of nutrient base cations (Ca, Mg, K)Q = annual runoff in m<sup>3</sup>/ha/yrK<sub>gibb</sub> = the gibbsite equilibrium constant (value was variable; see McNulty et al., 2007)(BC/Al)<sub>crit</sub> = 1 for conifer forests and 10 for deciduous forests

The factor 1.5 arises from the conversion from molar to equivalent units.

2.2.2.2. *Site-specific SMB application.* The highest resolution data available for soil texture and bedrock type were compiled for each study watershed for calculation of site-specific steady-state SMB model CL estimates. This necessitated determination of watershed boundaries for each of the study watersheds. Watershed boundaries had been delineated in previous studies for some of the watersheds selected for modeling in this project. For other watersheds, the boundaries were delineated from a digital elevation model (DEM) using ArcGIS.

Spatial soil data for the site-specific SMB application were derived predominantly from SSURGO databases (<http://soils.usda.gov/survey/geography/ssurgo/>). Soil data were obtained from local Soil and Water Conservation Districts or Forest Service personnel for watersheds where SSURGO data were not available. Digital bedrock geology data were obtained from the USGS ([http://pubs.usgs.gov/of/2005/1351/index\\_map.htm](http://pubs.usgs.gov/of/2005/1351/index_map.htm)) for all watersheds. We used SMB inputs for BC<sub>u</sub> from McNulty et al. (2007). Site-specific SMB input data for runoff, BC<sub>dep</sub>, BC<sub>dep</sub>, and Cl<sub>dep</sub> matched those used for the MAGIC model runs. Model calculations performed for the site-specific SMB model CL estimates generally followed those described by McNulty et al. (2007). The 1 km<sup>2</sup> McNulty et al. (2007) data were transferred to the study watersheds by taking an average of a 3 × 3 cell window of data located in the center of each watershed. If a watershed was smaller than a 3 × 3 cell window, only the cell centers which fell within the watershed boundary were averaged. Required input parameter descriptions for the SMB model are shown in Table 3.

Significant differences in both the source and scale of bedrock and soils data existed between the national and site-specific SMB model applications. Input data for both bedrock and soils were obtained from 1:250K STATSGO data in the national scale SMB model application. The site-specific SMB application used bedrock data from USGS Statewide Geology datasets (1:250K or 1:500K) and soils variables obtained from 1:24K SSURGO data.

Data inputs for atmospheric deposition and runoff were estimated using the best available data and site-specific knowledge on a watershed-by-watershed basis in the site-specific SMB application. The national scale SMB modeling effort used nationally derived datasets for deposition and runoff data (at resolutions of 1 km for runoff; from 330 m to 2.5 km for deposition). There were no

differences between the two SMB applications in either data source or scale for forest type.

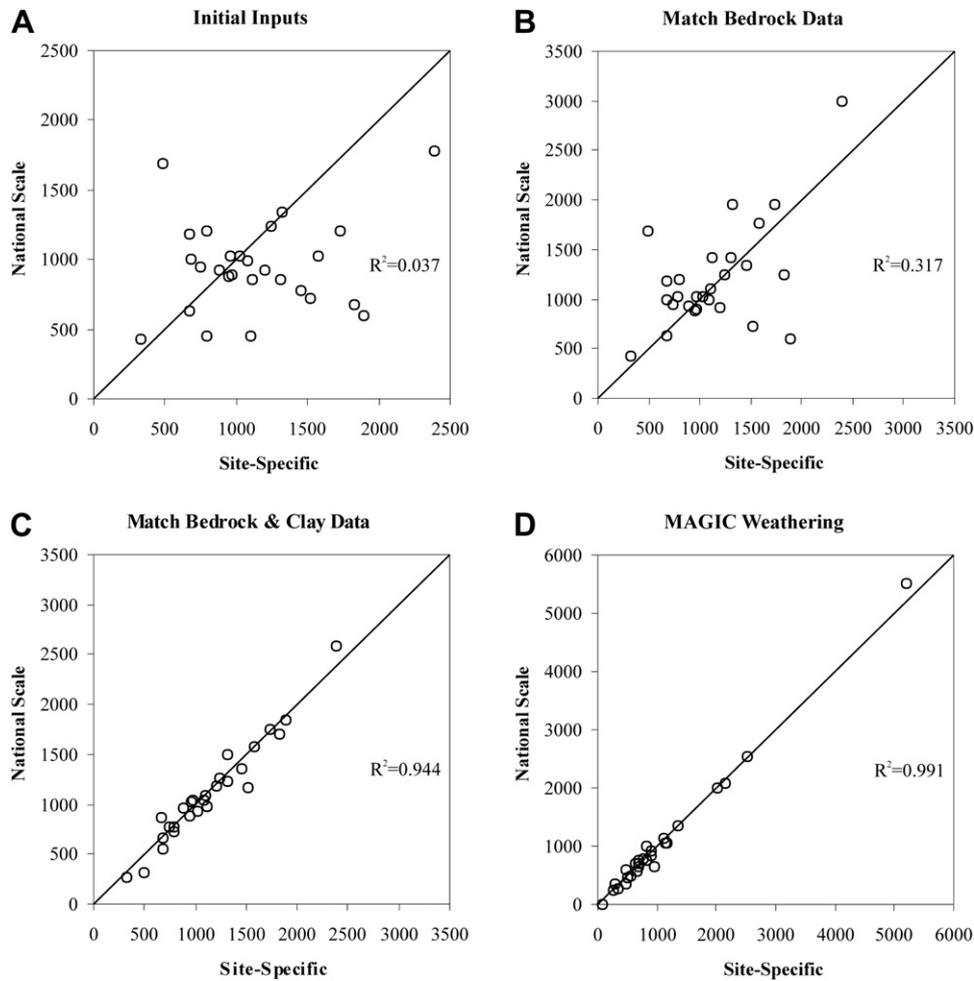
### 3. Results and discussion

Comparisons among the national and site-specific SMB steady-state model estimates of CL are shown in Fig. 1 in 4 panels. Panel A depicts the differences and similarities between the national and site-specific SMB applications, using the available input data (without adjustment) at those two scales of application. There was not good agreement in CL estimates between the two approaches. Even though the same steady-state model equation was used, differences in the input data derived at the national versus local scale had substantial influence on model results. In some cases, the observed discrepancy could be partially attributed to differences in specified bedrock type (which was assumed to partially regulate base cation supply, cf., Table 4). For the national application, the bedrock of all of the study watersheds was classified into the most sensitive (acidic) bedrock class. In contrast, available geologic data used in the site-specific application revealed greater diversity in bedrock class, with three watersheds classified as basic and seven

**Table 3**

Description of parameters represented in the Simple Mass Balance (SMB) model.

Parameter	Unit	Description
Bedrock Type	NA	A = Acidic, I = Intermediate, B = Basic
% Clay	%	Average % clay in soil profile
BC <sub>u</sub>	eq/ha/yr	Vegetative uptake of Ca + Mg + K
Q	m <sup>3</sup> /ha/yr	Annual runoff
K <sub>gibb</sub>	m <sup>6</sup> /eq <sup>2</sup>	Gibbsite equilibrium constant
BC <sub>dep</sub>	eq/ha/yr	Total deposition of Ca + Mg + K + Na
BC <sub>dep</sub>	eq/ha/yr	Total deposition of Ca + Mg + K
Cl <sub>dep</sub>	eq/ha/yr	Total deposition of Cl
BC/Al	NA	Critical base cation to Al ratio in soil solution
BC <sub>w</sub>	eq/ha/yr	Weathering of Ca + Mg + K + Na
BC <sub>w</sub>	eq/ha/yr	Weathering of Ca + Mg + K
ANC <sub>le(crit)</sub>	eq/ha/yr	Critical ANC leaching



**Fig. 1.** National scale versus site-specific Simple Mass Balance (SMB) model comparisons. Panel A depicts the initial comparisons. For the analysis shown in Panel B, bedrock inputs to the national scale SMB reported by McNulty et al. (2007) were adjusted to match the values that were used for the site-specific SMB model runs. For the analyses shown in Panel C, both bedrock and soil percent clay inputs to the national scale SMB were adjusted to match values that were used for the site-specific SMB model runs. For Panel D, MAGIC model estimates of weathering were inserted into both the national and site-specific SMB calculations. Reference 1:1 lines are added.

as intermediate. For the analyses shown in panel B, we substituted site-specific bedrock data into the national scale analyses for watersheds in which the two approaches had given different geologic sensitivity types. In response, the model comparison was improved (Fig. 1B). For the analysis shown in Fig. 1C, we also substituted the higher resolution SSURGO soils data regarding percent clay into the national scale analyses for watersheds in which the two approaches had given different values. The analyses based on common input data for bedrock geology and soil percent clay (Fig. 1C) showed considerably better agreement between national and site-specific SMB model applications. As an alternative to using the SMB clay/substrate calculations for  $BC_w$ , one could substitute an entirely different approach for estimating weathering. For example, there exist a variety of modeling approaches that might be used to estimate  $BC_w$ , which could then be substituted into the SMB model. To test this approach, we extracted weathering estimates from MAGIC for each of the study watersheds and inserted them into both the national and site-specific SMB approaches. Results of that comparison (Fig. 1D) showed good agreement.

Results of the comparisons shown in Fig. 1 indicate that methods used to quantify weathering and the associated input data strongly influence differences in model results when the scale of

analysis is changed. Bedrock geology and average % clay in soil are the two variables used to estimate the weathering contribution of base cations to the soil solution and drainage water of the modeled watersheds in the SMB model. In many cases, available national and site-specific data suggested different values for these two variables (Table 4). These differences accounted for most of the scatter observed in the SMB model output comparison (Fig. 1A) that examined the results of differences in the source and scale of input data.

The SMB model equations used to represent  $BC_w$  (Equation (2)) are designed such that an intermediate bedrock type will weather approximately 500 eq/ha/yr more base cations than an acidic bedrock for a given clay fraction. Basic bedrock types are assumed to result in higher base cation production than intermediate types. However, this difference is not as large as the difference between acidic and intermediate types. This makes the distinction between acidic and intermediate bedrock types more crucial than distinguishing between intermediate and basic bedrock. After determining the general range of  $BC_w$  by defining the bedrock type, the magnitude of  $BC_w$  is estimated using a value that reflects the average % clay in the soil. Differences in % clay inputs can also have significant effects on the final CL value (Fig. 1, Table 4).

**Table 4**  
National and site-specific Simple Mass Balance (SMB) model inputs for bedrock type and percent clay in soils.

Stream or Lake Name	Bedrock Type <sup>a</sup>		Percent Clay	
	National	Site-Specific	National	Site-Specific
Brettuns Pond	A	B	8.37	8.10
Bryant Creek	A	A	21.83	13.89
Deep Run	A	A	14.19	15.29
Eunice Lake <sup>b</sup>	A	I	8.11	4.96
False Gap Prong	A	A	18.00	18.00
Fernow - WS10	A	A	22.44	22.80
Forney Creek	A	A	15.63	15.93
Grassy Creek	A	A	19.88	13.75
Gross Pond	A	I	11.75	20.00
Hitchcock Lake	A	A	9.95	35.00
Joyce Kilmer Site 1	A	A	16.76	11.50
Left Fork Clover Run	A	A	16.07	16.80
Little Stonecoal Run	A	A	12.90	17.70
Martin Meadow Pond	A	I	8.70	3.83
Meadow Run	A	A	15.11	13.81
Moss Run	A	A	17.42	14.20
North Fork of Dry Run	A	I	17.88	10.05
Partlow Lake	A	A	10.95	9.71
Red Creek	A	A	12.75	20.80
Roaring Fork	A	I	15.93	16.20
Rose River	A	B	17.90	14.99
Shining Rock Site 1	A	I	18.87	11.19
Smith Pond	A	A	8.62	5.99
Staunton River	A	I	17.88	14.24
The Loch	A	A	12.50	2.88
Thunderstruck Creek	A	A	15.75	18.35
White Oak Canyon Run	A	B	17.88	14.91

<sup>a</sup> Bedrock types are indicated as follows: A, acidic; B, basic; I, intermediate.

<sup>b</sup> Percent clay was not available for Eunice Lake watershed at the fine scale; data were taken from another subalpine watershed (The Loch).

#### 4. Summary and conclusions

Comparison of steady-state (at both national and site-specific scale) model estimates of terrestrial CLs at sites throughout the United States illustrate that:

1. The source and scale of the model input data have a large influence on the resulting CL estimates, and
2. Differences in steady-state CL values obtained at varying input data scales are mainly attributable to differences in model estimates of base cation weathering.

Therefore, it is important to match the scale of the CL model application, and associated input data, with the intended use of the model results. In addition, particular focus is needed on the validity of the data used to estimate weathering. It appears that, unless weathering estimates are reasonable, steady-state model estimates of CL may be inadequate as a basis for resource management decision-making.

#### Acknowledgments

The research described in this paper was supported through funding provided by the Eastern Forest Environmental Threat Assessment Center, Southern Research Station, U.S. Forest Service, Asheville, NC. This manuscript has not been subjected to agency review and no official endorsement is implied.

#### References

- Church, M.R., Thornton, K.W., Shaffer, P.W., Stevens, D.L., Rochelle, B.P., Holdren, G. R., Johnson, M.G., Lee, J.L., Turner, R.S., Cassell, D.L., Lammers, D.A., Campbell, W.G., Liff, C.L., Brandt, C.C., Liegel, L.H., Bishop, G.D., Mortenson, D.C., Pierson, S.M., Schomoyer, D.D., 1989. Direct/Delayed Response Project: Future Effects of Long-Term Sulfur Deposition on Surface Water Chemistry in the Northeast and Southern Blue Ridge Province. In: Level III Analyses and Summary of Results, vol. III. U.S. Environmental Protection Agency, Washington, D.C.
- Cosby, B.J., Hornberger, G.M., Galloway, J.N., Wright, R.F., 1985. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Water Resour. Res.* 21 (1), 51–63.
- Cronan, C.S., Grigal, D.F., 1995. Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. *J. Environ. Qual.* 24, 209–226.
- ICP modeling and mapping. In: Gregor, H.D., Werner, B., Spranger, T. (Eds.), *Manual on Methodologies and Criteria for Mapping Critical Levels/Loads and Geographical Areas Where they are Exceeded*. Umweltbundesamt, Berlin, Germany, 212 pp.
- Henriksen, A., Posch, M., 2001. Steady-state models for calculating critical loads of acidity for surface waters. *Water Air Soil Pollut. Focus* 1 (1–2), 375–398.
- Henriksen, A., 1984. Changes in base cation concentrations due to freshwater acidification. *Verh. Internat. Verein. Limnol.* 22, 692–698.
- Li, H., McNulty, S.G., 2007. Uncertainty analysis on simple mass balance model to calculate critical loads for soil acidity. *Environ. Pollut.* 149, 315–326.
- McNulty, S.G., Cohen, E.C., Moore Meyers, J.A., Sullivan, T.J., Li, H., 2007. Estimates of critical acid loads and exceedances for forest soils across the conterminous United States. *Environ. Pollut.* 149 (3), 281–292.
- Nilsson, J., Grennfelt, P. (Eds.), 1988. *Critical Loads for Sulphur and N*, Report from a Workshop Held at Skokloster, Sweden, 19–24 March 1988, *NORD Miljörapport 1988*, vol. 15. Nordic Council of Ministers, Copenhagen, pp. 225–268.
- Quimet, R., Arp, P.A., Watmough, S.A., Aherne, J., Demerchant, I., 2006. Determination and mapping critical loads of acidity and exceedances for upland forest soils in Eastern Canada. *Water Air Soil Pollut.* 172, 57–66.
- Pardo, L.H., Duarte, N., 2007. Assessment of Effects of Acidic Deposition on Forested Ecosystems in Great Smoky Mountains National Park Using Critical Loads for Sulfur and Nitrogen. USDA Forest Service, Burlington, VT.
- Posch, M., DeSmet, P.A.M., Hettelingh, J.P., Downing, R.J., 2001. Calculation and Mapping of Critical Thresholds in Europe. Status Report 2001. Coordination Center for Effects. National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands, iv + 188 pp.
- Sullivan, T.J., Cosby, B.J., 2002. Critical Loads of Sulfur Deposition to Protect Streams within Joyce Kilmer And Shining Rock Wilderness Areas from Future Acidification. Report prepared for USDA Forest Service, Asheville, NC. E&S Environmental Chemistry, Inc., Corvallis, OR.
- Sullivan, T.J., Cosby, B.J., 2004. Aquatic Critical Load Development for the Monongahela National Forest, West Virginia. Report Prepared for USDA Forest Service, Monongahela National Forest, Elkins, WV. E&S Environmental Chemistry, Inc., Corvallis, OR.
- Sullivan, T.J., Cosby, B.J., Tonnessen, K.A., Clow, D.W., 2005. Surface water acidification responses and critical loads of sulfur and nitrogen deposition in Loch Vale Watershed, Colorado. *Water Resour. Res.* 41, W01021. doi:10.1029/2004WR003414.
- Sullivan, T.J., Cosby, B.J., Snyder, K.U., Herlihy, A.T., Jackson, B., 2007. Model-based Assessment of the Effects of Acidic Deposition on Sensitive Watershed Resources in the National Forests of North Carolina, Tennessee, and South Carolina. Final report prepared for USDA Forest Service, Asheville, NC. E&S Environmental Chemistry, Inc., Corvallis, OR.
- Sullivan, T.J., Cosby, B.J., Webb, J.R., Dennis, R.L., Bulger, A.J., Deviney Jr., F.A., 2008. Streamwater acid-base chemistry and critical loads of atmospheric sulfur deposition in Shenandoah National Park, Virginia. *Environ. Monit. Assess.* 137, 85–99. doi:10.1007/s10661-007-9731-1.
- Sullivan, T.J., 2000. Aquatic effects of acidic deposition. Lewis Publ., Boca Raton, FL, 373 pp.
- Sverdrup, H., De Vries, W., Henriksen, A., 1990. Mapping Critical Loads. Environmental Report 1990:14 (NORD 1990:98). Nordic Council of Ministers, Copenhagen, 124 pp.
- U.S. Environmental Protection Agency, 2008. Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur Ecological Criteria (Final Report). U.S. Environmental Protection Agency, Washington, DC. EPA/600/R-08/082F.
- U.S. Environmental Protection Agency, 2009. Risk and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur. U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- Watmough, S.A., Dillon, P.J., 2002. The impact of acid deposition and forest harvesting on lakes and their forested catchments in south central Ontario: a critical loads approach. *Hydrol. Earth Syst. Sci.* 6, 833–848.