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Steady-state sulfur critical loads and exceedances for protection of aquatic ecosystems in the U.S. southern Appalachian Mountains

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ABSTRACT

Atmospherically deposited sulfur (S) causes stream water acidification throughout the eastern U.S. Southern Appalachian Mountain (SAM) region. Acidification has been linked with reduced fitness and richness of aquatic species and changes to benthic communities. Maintaining acid-base chemistry that supports native biota depends largely on balancing acidic deposition with the natural resupply of base cations. Stream water acid neutralizing capacity (ANC) is maintained by base cations that mostly originate from weathering of surrounding lithologies. When ambient atmospheric S deposition exceeds the critical load (CL) an ecosystem can tolerate, stream water chemistry may become lethal to biota. This work links statistical predictions of ANC and base cation weathering for streams and watersheds of the SAM region with a steady-state model to estimate CLs and exceedances. Results showed that 20.1% of the total length of study region streams displayed ANC <100 $\mu eq \cdot L^{-1}$, a level at which effects to biota may be anticipated; most were 4th or lower order streams. Nearly one-third of the stream length within the study region exhibited CLs of S deposition <50 $meq \cdot m^{-2} \cdot yr^{-1}$, which is less than the regional average S deposition of 60 $meq \cdot m^{-2} \cdot yr^{-1}$. Owing to their geologic substrates, relatively high elevation, and cool and moist forested conditions, the percentage of stream length in exceedance was highest for mountain wilderness areas and in national parks, and lowest for privately owned valley bottom land. Exceedance results were summarized by 12-digit hydrologic unit code (subwatershed) for use in developing management goals and policy objectives, and for long-term monitoring.

1. Introduction

Atmospheric sulfur (S) deposition, originating largely from coal-fired electrical power generation and other industrial sources, causes soil, groundwater, and stream water acidification across broad areas of the southeastern United States (U.S. Environmental Protection Agency [USEPA], 2008). Such acidification has been associated with enhanced leaching of sulfate (SO_4^{2-}), depletion of calcium (Ca^{2+}) and other nutrient base cations from soils, reduced pH and acid neutralizing capacity (ANC) of surface waters, and increased mobilization of potentially toxic inorganic aluminum (Al_i) from soil to streams (Sullivan, 2000). Biological effects include toxicity to fish and aquatic invertebrates (Cosby et al., 2006; USEPA, 2009).

Sulfur is the primary determinant of precipitation acidity and SO_4^{2-} is the dominant anion in streams throughout most of the Southern Appalachian Mountain (SAM) region (Sullivan et al., 2004). Nitrate (NO_3^-) is important at some locations, especially at streams that flow from high-elevation old-growth forests in North Carolina and Tennessee (Cook et al., 1994). Streams are generally dilute and clear-water with limited contributions of naturally occurring organic acidity. Although a substantial proportion of atmospherically deposited S can be retained in watershed soils,

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SO_4^{2-} concentrations in many mountain streams have increased due to atmospheric S deposition and low S retention in soils (Elliott et al., 2008), causing increases in base cation concentrations and decreased stream water ANC.

Acidic soils and streams have developed in this region over a period of many decades in response to high levels of atmospheric S deposition. Many streams in Great Smoky Mountains (GRSM) and Shenandoah (SHEN) national parks and surrounding national forests show signs of acidification, including streams in wilderness areas. Both of these parks and several wildernesses are federally mandated Class I areas, and receive special protection against air pollution impacts under the Clean Air Act. As a result of emissions controls regulation (USEPA, 2009), atmospheric S deposition has decreased throughout the eastern United States since the early 1980s, and further decreases are expected.

Ecosystem sensitivity to acidification is fairly well documented for this region, particularly within the National Acid Precipitation Assessment Program (NAPAP, 1991), the Fish in Sensitive Habitats (FISH) project (Bulger et al., 1999), and the Southern Appalachian Mountains Initiative (SAMI) assessment (Sullivan et al., 2004, 2007).

Stream water ANC is one measure that reflects the ability of a watershed to neutralize acidic inputs. As the rate of acidic deposition increases, ANC often decreases in proportion to the natural resupply of base cations from the soil. At certain levels of acidification, increases in the hydrogen ion (H^+) and Al_i concentration are directly toxic to fish, including brook trout (*Salvelinus fontinalis*; Baldigo et al., 2007; Bulger et al., 1999), a favored native game fish of cold, high-elevation streams. Various ANC thresholds are associated with different levels of biological effects. In the SAM region and in mountainous areas of the northeastern United States, moderate effects on macroinvertebrate and fish species richness are associated with ANC concentrations between ~50 and 100 $\mu eq \cdot L^{-1}$ (Cosby et al., 2006; Sullivan et al., 2006). More substantial effects have been observed at ANC concentrations <50 $\mu eq \cdot L^{-1}$. Most aquatic species, including the relatively acid-tolerant brook trout, can be extirpated at ANC concentrations <0 $\mu eq \cdot L^{-1}$ (Bulger et al., 1999; Cosby et al., 2006; Sullivan et al., 2006; USEPA, 2009).

Soils in this region have developed from the slow weathering of parent rock material, some of which is inherently low in base cations. Adequate amounts of available Ca, magnesium (Mg), and potassium (K) are all essential to maintain an acid-base chemistry that will support persistence of native fish and aquatic invertebrate species. Land managers and regulators have a legally mandated concern for the current and future health of native aquatic species within the SAM. Where the existing stream water acidity is too high to support the native biota, and where ambient stream water ANC is insufficient for buffering, policy-makers may need to call for added air pollution emissions reductions to enable recovery of impacted species, and to prevent further impacts. Thus, to inform public policy regarding air pollutant emissions reductions, it is important to determine 1) the emission and atmospheric deposition levels that are associated with varying degrees of chemical effects and 2) the linkages between water and soil chemistry and subsequent biological impacts.

One approach to addressing these issues is to construct model estimates of regional surface water acid-base chemistry and critical loads (CLs). The CL for S acidification is the level of sustained atmospheric S deposition below/above which harmful effects to sensitive ecosystems are unlikely/likely, based on current understanding (Nilsson and Grennfelt, 1988). The CL is typically calculated as a steady-state value, using models such as the Steady State Water Chemistry (SSWC) model (Henriksen and Posch, 2001). However, data used to inform the steady-state CL calculation may also be derived dynamically using mass balance equations in a process model such as the Model of Acidification of Groundwater in Catchments (MAGIC; Cosby et al., 1985).

The long-term maintenance of well-buffered aquatic ecosystems depends primarily on maintaining atmospheric S levels that are lower than the natural re-supply rate of base cations through weathering (BC_W). Thus, base cations derived from weathered substrates are generally most influential in determining CLs (McDonnell et al., 2010). However, because BC_w predictions can contribute substantial uncertainty to CL estimation (Li and McNulty, 2007; USEPA, 2009), it is essential to continue to improve the certainty of weathering estimates.

Steady-state CL calculations have been developed and applied across northern Europe (Gregor et al., 2004) and eastern Canada (Ouimet et al., 2006; Watmough and Dillon, 2002), providing a basis for political and economic negotiations and national and international air pollution legislation. Some recent efforts in the United States have focused on process-based dynamic model estimates of critical or associated target loads (cf., Sullivan et al., 2005, 2008). Land managers and regulators are also interested in regional predictions at watershed locations where current stream water ANC is affecting the health of aquatic biological communities (USEPA, 2009).

This work incorporates results from recent regional statistical modeling to predict stream water ANC and soil BC_w throughout the SAM region. The BC_w modeling results are used here together with other model input parameters to estimate steady-state S CLs and CL exceedances. Stream ANC estimates are used to assess potential biological effects associated with modeled S deposition.

Previous regional efforts to characterize stream water sensitivity to acidic deposition have been based on stratified random sampling of a subset of streams (cf., Whittier et al., 2002). Results were used to make general statements about ecosystem sensitivity throughout the full population of surface waters; however, methods were insufficient for determining the location of sensitive reaches. This study resolves that problem by generating spatially explicit CL and exceedance estimates for all streams within the SAM region.

As a result of emissions regulation and advances in hydraulic fracturing technology for natural gas production, reduced S emissions at coal-fired power plants and shifts to natural gas-powered electric generation have primarily been responsible for significant reductions in acidic deposition throughout the United States (NAPAP, 2011). Results reported here also consider how changes in exposure to S deposition over time relate to the inherent acid sensitivity of the landscape and expected future stream conditions with respect to acidification.

The SAM region comprises an irregular patchwork of land ownerships, protection status, resource management goals, and sensitivity to degradation from S deposition. National parks and wildernesses are home to terrestrial and aquatic ecosystems that are afforded more legal protections than those that exist on other lands (Organic Act 16 U.S.C. §1 (1997); Organic Act 16 U.S.C. §1601(a) (1997); Wilderness Act 16 U.S.C. §1131 (1997)). It is therefore highly desirable to determine the extent to which acid-sensitive streams occur within these protected areas. Furthermore, present-day land managers need to determine acid-sensitive locations to make informed resource management decisions and recommendations to air quality regulators and policy-makers.

2. Methodology

The study area covers the SAM region and surrounding terrain, from northern Georgia to southern Pennsylvania, and from eastern

Kentucky and Tennessee to central Virginia and western North Carolina. The region is primarily comprised of the Blue Ridge, Ridge and Valley, and Central Appalachian ecoregions, but also includes small portions of the Piedmont, Northern Piedmont, and Western Allegheny Plateau (Fig. 1; Omernik, 1987). The Blue Ridge ecoregion is dominated by metamorphic and igneous parent materials, whereas the Ridge and Valley and Central Appalachian ecoregions are dominated by sedimentary parent materials characterized by northeast to southwest trending sandstone ridges and limestone valleys. Elevations range from about 300 to 2000 m. Uplands of oak, hickory, pine, and other mesic forests and woodlands are interspersed with crop and pasture lands, which occur primarily in the lowlands. Spruce-fir and northern hardwood forests predominate at the highest elevation sites.

To develop CLs and CL exceedance results reported here, we conducted the following workflow:

1.Aggregated available measured ANC data and developed a statistical hurdle model to predict a threshold ANC response (above/below 300 $\mu eq \cdot L^{-1}$) for all streams and a continuous ANC value for only those streams with a high probability of having low ANC.
2.Calibrated BC_w using a process-model (MAGIC) for a subset of the ANC sample sites that also contained measured soil chemistry data. Calibrated weathering rates were used as the response variable to develop statistical relationships with landscape characteristics for generating regional estimates of BC_w for all catchments in the study region.
3.Used the ANC threshold model to identify streams within the study region that were most likely to be associated with low-ANC (<300 $\mu eq \cdot L^{-1}$) conditions.
4.Combined regional estimates of BC_w with gridded surfaces of the remaining SSWC input terms to generate aquatic CLs, based

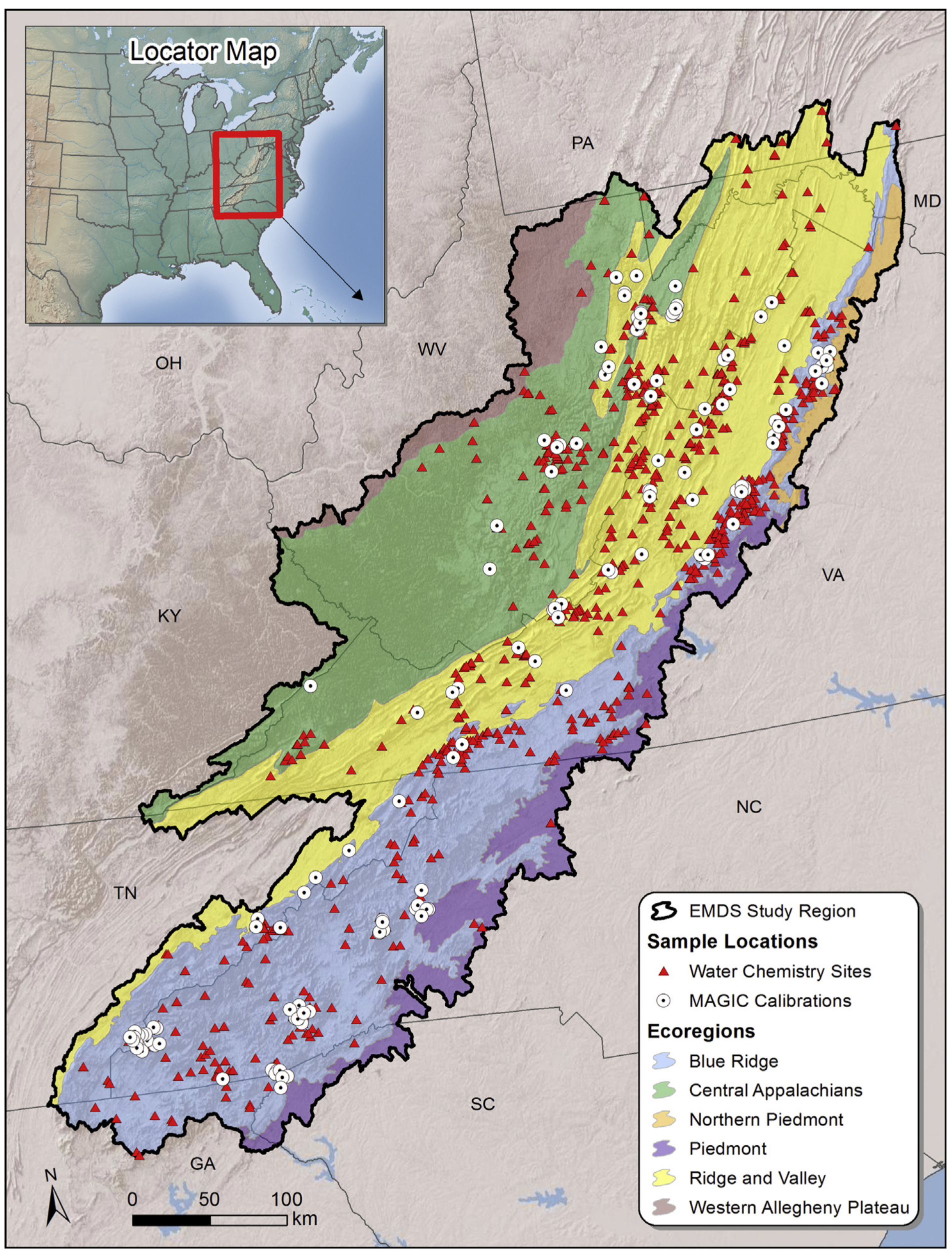

Fig. 1. Spatial distribution of sampled water chemistry sites, MAGIC calibration sites, and location of Omernik (1987) ecoregions within the study region.

on a selected ANC target for recovery, for expected low-ANC streams.

5. Used spatially continuous estimates of total S deposition to determine the exceedance of the calculated CL using the SSWC model.

The regional CL and CL exceedance results presented here are based on statistical predictions of ANC for all streams and BC_w predictions for all catchments located within the study region (Povak et al., 2013, 2014).

2.1. ANC and BC_w response data

2.1.1. Measured ANC

Stream water chemistry data were obtained from several national and regional databases, including the National Stream Survey (NSS), Environmental Monitoring and Assessment Program (EMAP) stream surveys, Virginia Trout Stream Sensitivity Study (VTSSS), and others. Stream chemistry data sources were described by Sullivan et al. (2004, 2011). A total of 933 sampling locations were included. Those that had soil acid-base chemistry data within the watershed (Fig. 1) were selected for MAGIC modeling ($n = 140$).

Water chemistry data were collected between 1986 and 2009, with the largest proportion of the data (43%) collected during the VTSSS survey in 2000. Stream ANC was calculated as the equivalent sum of the base cation concentrations (Ca^{2+}, Mg^{2+}, K^+, Na^+, ammonium [NH_4^+]) minus the sum of the mineral acid anion concentrations (chloride [Cl^-], NO_3^-, SO_4^{2-}). The most recent spring sample was used to characterize ANC status for each site. The distribution of ANC was negatively skewed, with 75% of the sites showing values <163 $\mu eq \cdot L^{-1}$. Values for ANC had a mean of 188 $\mu eq \cdot L^{-1}$, a median of 72 $\mu eq \cdot L^{-1}$, and the inter-quartile range (IQR) was 33–163 $\mu eq \cdot L^{-1}$ (range: −109–3890 $\mu eq \cdot L^{-1}$). A 30-m digital elevation model (DEM) was used to create a synthetic stream network (described below) to which all ANC sample points were georeferenced within a geographical information system (GIS).

2.1.2. MAGIC calibrated BC_w

BC_w was estimated using the MAGIC model for 140 of the 933 sampled water chemistry sites. MAGIC is a lumped-parameter model developed to predict the long-term effects of acidic deposition on surface water chemistry (Cosby et al., 1985). The model simulates soil solution and surface water chemistry to predict the monthly or annual average concentrations of the major ions. Central to MAGIC calculations is the size of the pool of exchangeable base cations in the soil. As the fluxes to/from the pool change in response to atmospheric deposition and biomass export (i.e., tree harvesting), the chemical equilibria between soil and soil solution shift to cause changes in surface water chemistry. MAGIC has been used to reconstruct the history of acidification and to simulate future trends in a large number of catchments in both North America and Europe (e.g., Cosby et al., 1990; Hornberger et al., 1989; Jenkins et al., 1990a,b,c; Lepistö et al., 1988; Norton et al., 1992; Whitehead et al., 1988; Wright et al., 1990, 1994). For a more complete description of the model, see Cosby et al. (1985, 2001).

Because it is a lumped-parameter model, MAGIC must be calibrated with observed stream, soil, and atmospheric deposition data before it can be used to examine potential system responses. The BC_w rate was extracted from MAGIC model calibrations conducted here for each stream watershed and used as the response variable for predictive modeling. Most sites modeled with MAGIC had relatively low measured ANC (<50 $\mu eq \cdot L^{-1}$). The distribution of BC_w among the MAGIC model sites was also skewed towards relatively low values, with 75% of the sites below 91 $meq \cdot m^{-2} \cdot yr^{-1}$. Simulated values for BC_w at the modeled sites had a median of 66 $meq \cdot m^{-2} \cdot yr^{-1}$ and an IQR of 42–91 $meq \cdot m^{-2} \cdot yr^{-1}$ (range: 3–257 $meq \cdot m^{-2} \cdot yr^{-1}$), with a mean of 73 $meq \cdot m^{-2} \cdot yr^{-1}$.

2.2. ANC and BC_w predictions

Objectives for ANC and BC_w predictive modeling were to develop and validate statistical models that best explained observed ANC and MAGIC model-simulated BC_w values across the study region. Exploratory studies evaluated statistical performance of ordinary least-squares (OLS), logistic regression (logR), geographically weighted regression (GWR), multivariate adaptive regression splines (MARS), classification and regression tree (CART), boosted classification-regression tree (BCT/BRT), and random forest (RF) methods. Considering up to six statistical performance metrics, RF models generally outperformed all other models. Therefore, RF modeling techniques were used to generate continuous ANC and BC_w estimates for the region (Povak et al., 2013, 2014). The RF model is an adaptation of CART analysis that uses an ensemble of regression or classification trees to produce robust model predictions. Each individual tree within the ensemble is developed using random subsamples of the data and predictor variables (Breiman, 2001).

A suite of initial candidate predictor variables was chosen to represent potential broad- to fine-scale climatic, lithologic, topo-edaphic, vegetative, and S deposition variables with the potential to influence ANC and BC_w. In order to incorporate average upslope conditions that potentially influenced stream chemistry at specific locations along a stream, it was necessary to express all candidate landscape predictor variables on a grid basis with a cell size of 30 m. This resolution was sufficient to conduct flowpath analyses that were subsequently used to develop topographically determined streams and to prepare the predictor variable datasets for ANC and BC_w regionalization. Values of predictors from the area contributing to each 30-m grid cell were upslope averaged within the study region, based on methodology described in McDonnell et al. (2012).

For predicting ANC, a two-stage hurdle modeling approach was applied. It used an ANC threshold to preselect locations that were well buffered (high ANC), and a continuous model that generated ANC values for the remaining low-ANC sites. The selected final model was the one that displayed the lowest misclassification and root mean squared error (RMSE) rates. For each 30-m grid cell in the study region, the predictor variables were entered into the hurdle modeling framework. The threshold model predicted the probability that the grid cell had a low ANC value (<300 $\mu eq \cdot L^{-1}$). If the resultant probability value was less than a specified threshold (0.7), then the grid cell was considered well-buffered and assigned an arbitrarily large ANC value. If the probability of encountering low ANC for a particular grid cell was greater than or equal to the specified threshold, the environmental data for that grid cell were entered into the continuous model for prediction.

Predictions of BC_w were generated with a single continuous RF model for each 30-m grid cell within the study region. It was not possible to generate a robust hurdle model for predicting BC_w due to the low number of MAGIC-calibrated BC_w rates ($n = 140$). However, results from the ANC threshold model were used to constrain BC_w estimates and resultant CLs to locations that were predicted to exhibit low ANC, as described further in the next section. Streams that had high ANC were assumed to also have high BC_w and CL. Predicted BC_w rates were also generated using water chemistry data at locations where such data existed ($n = 933$).

These watersheds comprised only 9% of the study region and therefore could not be used for regional analyses. Two statistical methods (with and without water chemistry) and one process-based method (MAGIC) were then used, where available, to generate a continuous BC_w surface for the study region.

2.3. Estimating sulfur critical loads and exceedances

Watersheds were delineated based on hydrologically conditioned DEM derivatives from the National Hydrography Dataset (NHDPlus; USEPA and U. S. Geological Survey [USGS], 2005). This process delineated a total of 140,504 watersheds within the study region, with an average size of approximately 1 km^2 (median = 0.8; IQR = 0.5–1.3; range = <0.001–17.0). Sulfur CLs for each topographically determined catchment were then calculated using the SSWC model (Henriksen and Posch, 2001), as described below.

The CL estimation process involves selection of one or more sensitive receptor(s), one or more chemical indicator(s) of biological response for the sensitive receptor(s) of concern, and one or more critical chemical indicator criteria values that have been shown to be associated with adverse biological impacts. For the sensitive receptor stream water, the most commonly selected chemical indicator is ANC. A number of critical values of ANC have been used as the basis for CL calculations, the most common of which have been 0, 20, 50, and 100 $\mu eq \cdot L^{-1}$ (cf., Posch et al., 2001; USEPA, 2009). The first two levels approximately correspond to chronic and episodic effects on brook trout, respectively (Bulger et al., 1999). An ANC threshold of 50–100 $\mu eq \cdot L^{-1}$ is considered to be generally protective of ecological health (cf., Cosby et al., 2006; USEPA, 2009).

2.3.1. SSWC model for estimating CL

The SSWC model (Henriksen and Posch, 2001) is calculated essentially as a balancing of watershed base cation (e.g., Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) inputs and outputs. The base cation inputs to the subject watershed are BC_w and atmospheric deposition (BC_{dep}). The base cation outputs include nutrient (i.e., Ca^{2+}, Mg^{2+}, K^{+}; Bc) uptake by tree boles that are subsequently removed from the watershed through timber harvest (Bc_{up}). Also included in the model with the base cation output terms is an allowance (or buffer) for the base cations needed to support ecosystem health. In the SSWC and other aquatic CL approaches, this buffer is expressed as an ANC leaching flux (ANC_{limit}), which is calculated as the product of the selected threshold ANC value and water runoff. In this study the ANC threshold value was set at 50 $\mu eq \cdot L^{-1}$.

The watershed supply of base cations due to weathering is the model parameter that is typically most influential to CL calculations and contributes most to uncertainty (Li and McNulty, 2007; McDonnell et al., 2010; USEPA, 2009). In essence, the maintenance of long-term aquatic ecosystem acid-base chemical health depends on keeping the atmospheric acid load relatively low compared with the natural re-supply of base cations through weathering and atmospheric deposition. Thus, the CL is controlled largely by BC_w and the desired steady-state ANC (ANC_{limit}). Estimates of BC_w for SSWC model application are often based on the generalized "F-factor" approach (Henriksen and Posch, 2001), which has been shown to be unreliable (Rapp and Bishop, 2009). The use of BC_w estimates obtained through statistical relationships between MAGIC-calibrated BC_w and landscape characterisitcs in this study represents a divergence from standard SSWC application methods.

The CL for S acidity [CL(A)] was calculated for this study (as described by Henriksen and Posch, 2001) as:

$$CL(A) = BC_{dep} + BC_w - Bc_{up} - ANC_{limit} \quad \text{(Eq. 1)}$$

in which all units are in $meq \cdot m^{-2} \cdot yr^{-1}$.

Because each term in Eq. (1) can be estimated at a broad spatial scale, it is possible to use the SSWC model to develop regional estimates of the CL of S deposition and associated S deposition exceedances across the landscape. The S deposition exceedance represents the extent to which ambient S deposition exceeds the calculated CL needed for ecosystem protection or recovery. It is calculated as the ambient S deposition minus the CL to protect stream resources against damage caused by excess S deposition. This model function allows assessment of regional patterns in acidification sensitivity (CL) and effects (extent to which ambient acidic deposition exceeds the CL). It also allows for mapping and calculation of total and percent of stream length within a region or subregion of interest that falls within certain CL or exceedance classes. Details on derivation of Eq. (1) terms are described in the Supplementary Material.

2.3.2. SSWC CL exceedance

The CL exceedance was determined by calculating the extent to which ambient estimates of S deposition were above or below the CL. For the purposes of this study, the CL is considered to be *in exceedance* if the level of S deposition is *more than 15% above* the CL. If S deposition is *more than 15% below* the CL then the catchment is considered to be *not in exceedance*. Catchments where S deposition is within 15% of the CL are considered to be uncertain with respect to exceedance of the CL. Total S deposition was derived from the total deposition (TDEP) project developed by the USEPA (2013). Estimates of S deposition were calculated for two time periods as three-year averages centered on 2001 and 2011. These deposition rates were used to evaluate changes in CL exceedance over the period 2001 to 2011.

3. Results

3.1. ANC

Results from the continuous ANC model showed very good agreement with observed values of ANC ($R^2 = 0.92$, RMSE = 24.9). Low-ANC conditions occurred in areas characterized by siliceous bedrock, relatively wet and cool growing season, low soil pH and clay levels, large amounts of forested land cover, and a small watershed contributing area (Povak et al., 2013).

Regional predictions of stream ANC are shown in Fig. 2. Portions of both SHEN and GRSM show values <100 $\mu eq \cdot L^{-1}$, as do many designated wilderness areas. From a public land manager's perspective, it is important to recognize that 50% of the streams within the study region were predicted to have high ANC and associated high CL. Nevertheless, of the high-ANC area, only 5% occurs on public land.

Approximately 6% (13,310 km) of the streams within the study region could be characterized using measured ANC based on available stream survey data. Previously, the stream water ANC status of the remaining 210,867 km of stream was largely unknown. However, regional statistical modeling results showed that 20.1% of the stream length in the study region was predicted to have ANC <100 $\mu eq \cdot L^{-1}$ (Table 1). This is nearly nine times the total length of stream that had previously been characterized to be in this range using measured ANC data.

The length of streams having predicted ANC sufficiently low as to be associated with probable biological effects varied with stream order. The length of streams with predicted ANC <50 $\mu eq \cdot L^{-1}$ was highest for 1st and 2nd order streams (Fig. 3). Streams having ANC between 50 and 100 $\mu eq \cdot L^{-1}$ were also skewed towards low stream orders (≤4th order).

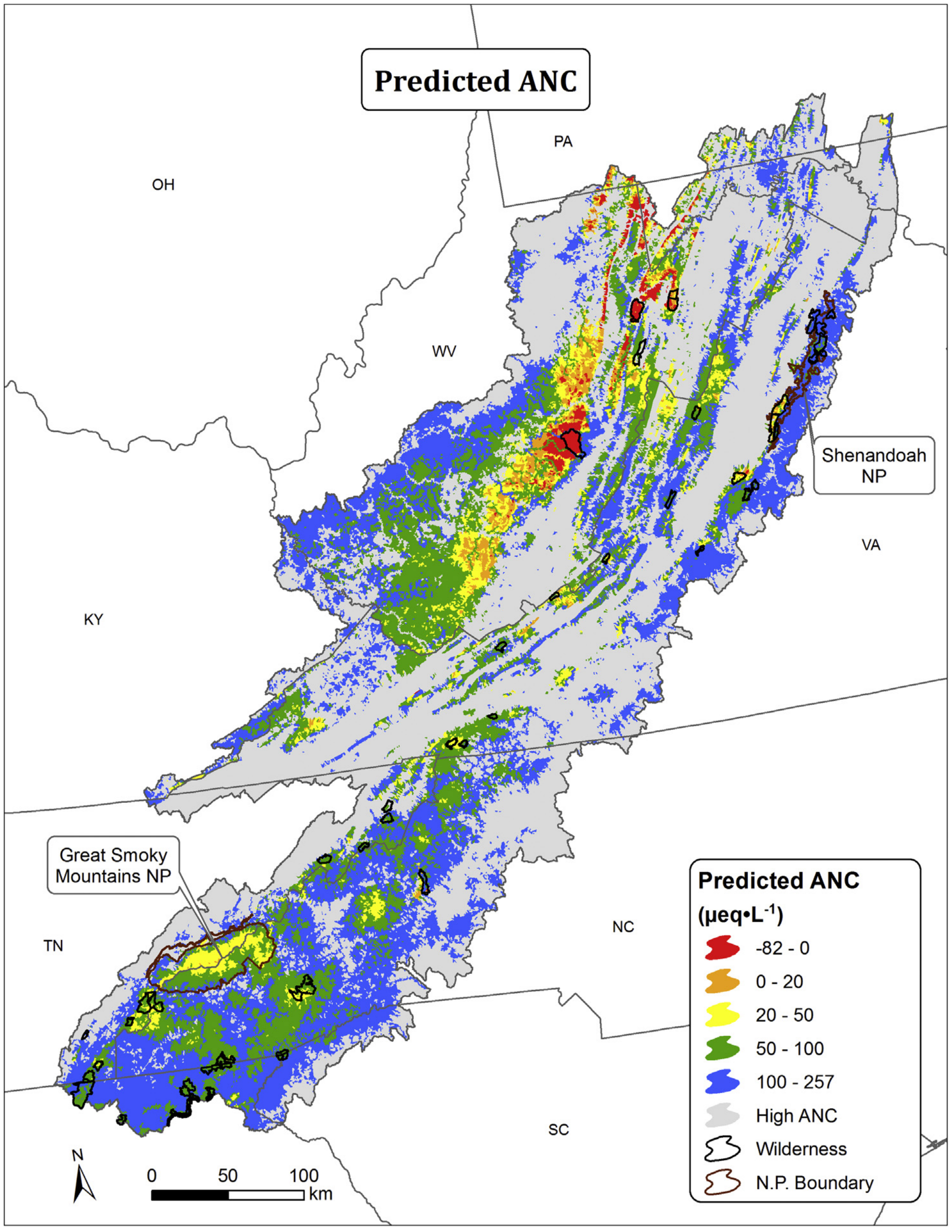

Fig. 2. Predicted response classes for stream ANC.

3.2. BC_w

Results from the BC_w predictive modeling showed good agreement with MAGIC-calibrated BC_w, particularly for observed BC_w values below 150 $meq \cdot m^{-2} \cdot yr^{-1}$ (Fig. 4). Above this value, there were few data points to inform the model, which led to poor performance at BC_w values above about 150 $meq \cdot m^{-2} \cdot yr^{-1}$. The uncertainty associated with each of these three methods for estimating BC_w is shown in Table 2. Overall, uncertainty among the methods was generally low, but uncertainty was highest for the statistical estimates based on landscape characteristics alone and lower for statistical estimates using both water chemistry and landscape data. BC_w derived from MAGIC showed the lowest uncertainty; however, these latter estimates only apply directly to 1% of the stream length within the study region. Low BC_w sites (<150 $meq \cdot m^{-2} \cdot yr^{-1}$) were generally associated with drier areas having siliceous lithology; low S deposition; high conifer cover; and low clay, organic matter, and nitrogen content in soil.

Table 1
Stream length by ANC class for streams that are located outside of water chemistry watersheds (Predicted) and streams associated with water chemistry sampling (Measured).

ANC Class ($\mu eq \cdot L^{-1}$)	Stream length in km (%)			
	Predicted		Measured	
<50	10,430	(4.9)	1844	(13.9)
50–100	31,961	(15.2)	2946	(22.1)
100–150	38,578	(18.3)	1502	(11.3)
150–200	20,941	(9.9)	1073	(8.1)
>200	108,957	(51.7)	5945	(44.7)
Total	210,867	(100)	13,310	(100)

3.3. Critical load

Nearly 30% of the stream length within the study region was determined to have CL of S deposition <50 $meq \cdot m^{-2} \cdot yr^{-1}$ (Table 3,

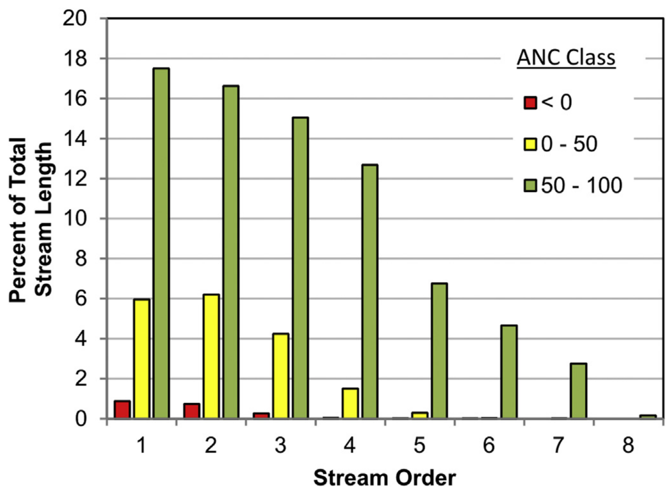

Fig. 3. Percent of stream length by stream order within the ANC ($\mu eq \cdot L^{-1}$) classes that are expected to be associated with biological effects.

Fig. 5). Many of the wildernesses and national parks occupy portions of the study region having S critical load values classified in the 0–25 $meq \cdot m^{-2} \cdot yr^{-1}$ or 25–50 $meq \cdot m^{-2} \cdot yr^{-1}$ classes. There were numerous other areas classified in the 0–25 $meq \cdot m^{-2} \cdot yr^{-1}$ CL category (Fig. 5), and most of these areas are under U.S. Forest Service or state management.

3.4. Exceedance

Average 2011 S deposition across all topographically determined catchments was 60 $meq \cdot m^{-2} \cdot yr^{-1}$. Streams throughout the study region were shown to be in exceedance of the CL of S for an ANC threshold of 50 $\mu eq \cdot L^{-1}$ and were commonly located in wilderness areas and national parks (Fig. 6). The percent of stream length in exceedance was highest for wilderness areas

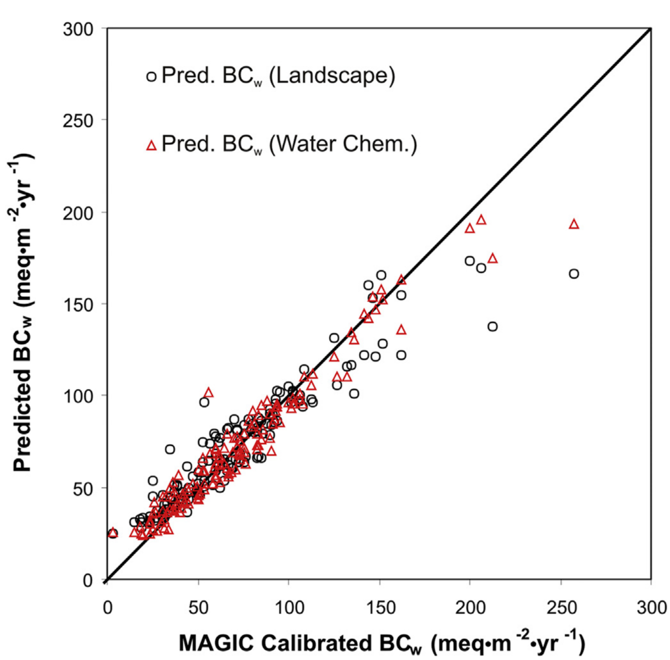

Fig. 4. Relationship between predicted and MAGIC calibrated BC_w. The black line shows the 1:1 relationship.

Table 2
Uncertainty and percent of the study region associated with each of the three methods for estimating BC_w.

Type	Method	Percent of Study Region	Uncertainty[a] ($meq \cdot m^{-2} \cdot yr^{-1}$)
Statistical	Landscape data	100%	11.2
Statistical	Water chemistry	9%	8.9
Process	MAGIC	1%	4

[a] For the statistical models, uncertainty is represented by the prediction RMSE. Uncertainty in MAGIC is represented by the standard deviation among 10 successful calibrations.

under all federal jurisdictions and non-wilderness in national parks (Fig. 7). Estimates of S deposition in 2001 exceeded the CL for nearly 4900 km of stream located in wilderness areas and national parks (Fig. 7a). According to 2011 S deposition estimates, stream length in exceedance within wilderness and national parks was reduced to approximately 3000 km, which accounts for more than half of the stream length in these areas (Fig. 7b). Other federal land, managed primarily by the U.S. Forest Service, showed a similar exceedance response to declines in S deposition between 2001 and 2011 as did wilderness and national parks. However, the length of stream exceedance in 2011 on other federal land was more than three times higher (9160 km) than in wilderness and national parks. The majority (57%) of stream length on private land was not in exceedance according to 2001 S deposition, and this percentage increased to 70% non-exceedance based on 2011 S deposition. However, because of the large amount of private land within the study area (85%), there was more than three times as much stream length in exceedance on private land (40,046 km) in 2011 as compared with federally managed lands (12,137 km).

A generalized spatial representation of CL exceedance is shown in Fig. 8. The exceedance results for the topographically determined catchments ($n = 140{,}504$) are expressed on the basis of 12-digit hydrologic unit code (HUC) boundaries ($n = 1561$) according to estimates of S deposition for years 2001 (Fig. 8a) and 2011 (Fig. 8b). These HUC delineations partition the landscape according to watershed drainage area and are frequently used by the U.S. Forest Service and others for land management. The median values of the exceedance results for all watersheds contained within each 12-digit HUC are shown on the upper panels of Fig. 8 and the 90th percentile exceedance values are shown on the lower panels. These percentile values were used to reflect the central tendency (median) and the extent of relatively sensitive (90th percentile) streams within each 12-digit HUC. Decreases in the extent of exceedance from 2001 to 2011 are clearly evident. However, portions of all national forests and parks remain in exceedance in 2011 according to these HUC-based percentile metrics.

Table 3
Steam length (km) associated with various CL classes. The class labeled as "High CL" represents locations predicted by the hurdle model to have ANC >300 $\mu eq \cdot L^{-1}$. Note that units of $meq \cdot m^{-2} \cdot yr^{-1}$ of S can be converted to $kg \cdot ha^{-1} \cdot yr^{-1}$ of S by dividing by 6.25.

CL class ($meq \cdot m^{-2} \cdot yr^{-1}$)	Stream length in km (%)
0–25	13,840 (6.1)
25–50	53,623 (23.8)
50–75	35,098 (15.6)
75–100	6878 (3.1)
100–206	3187 (1.4)
High CL	112,197 (50)
Total	224,823 (100)

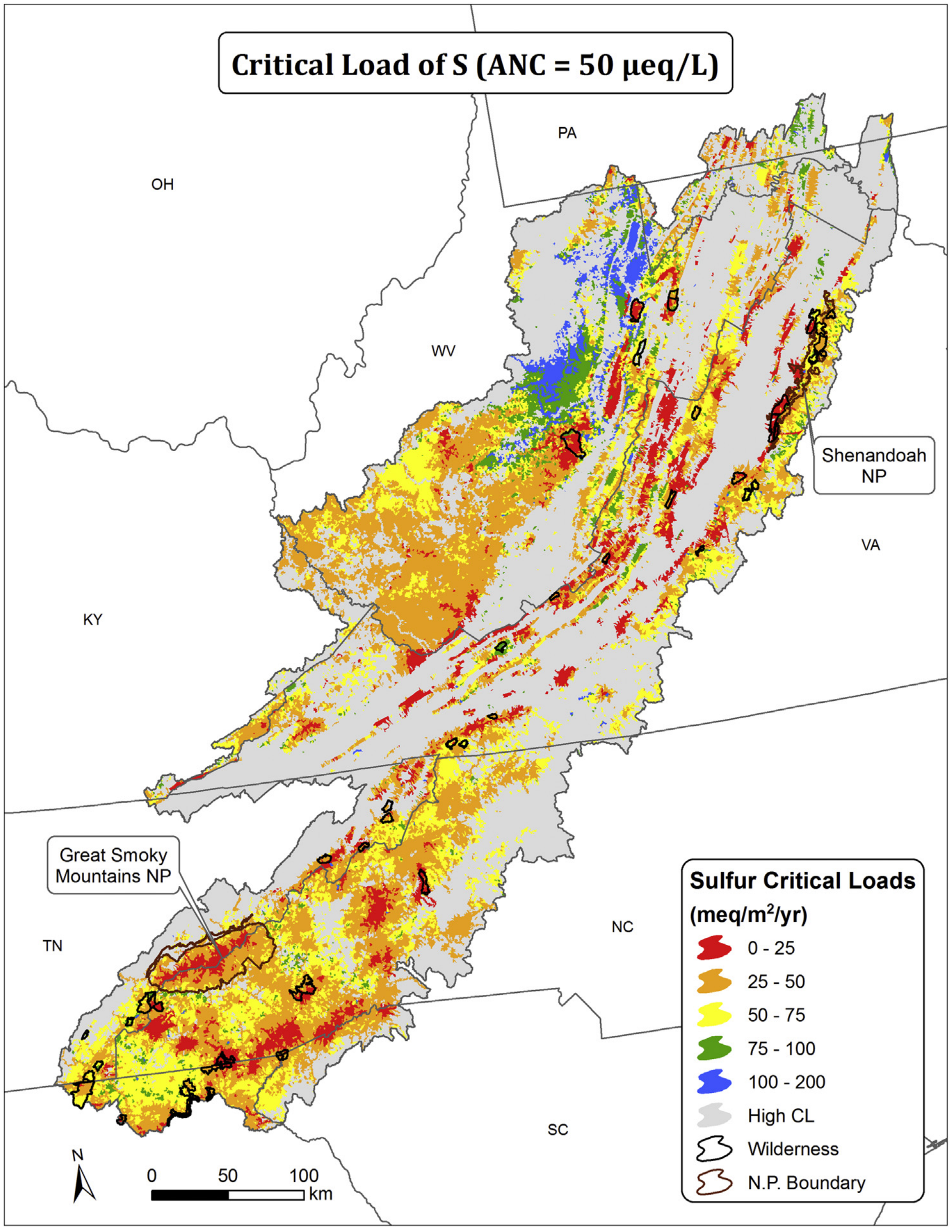

Fig. 5. Predicted response classes for critical load of atmospheric S deposition to achieve stream ANC = 50 $\mu eq \cdot L^{-1}$ under steady-state conditions.

4. Discussion

Knowledge of both regional acid sensitivity and spatial patterns in ambient acidic deposition across the landscape allows for spatially targeted land, aquatic, and air resource management. Regional stream ANC and CL results presented here can be used by land managers, policy-makers, and other stakeholder groups. The statistical approaches incorporated in this study estimated ANC for every stream (Fig. 2) and CL for every catchment (Fig. 5) in the SAM region. This was accomplished in part because the ANC hurdle modeling approach was able to distinguish between watersheds with low ($\leq$300 $\mu eq \cdot L^{-1}$) vs. high (>300 $\mu eq \cdot L^{-1}$) ANC streams. The assumption that streams with high ANC are drained by watershed soils characterized by high BC_w was useful for focusing SSWC CL modeling on locations that were most sensitive to acidic inputs.

Stream ANC <100 $\mu eq \cdot L^{-1}$ is considered to have the potential to cause moderate or substantial impacts on aquatic biota (Bulger et al., 1999; Cosby et al., 2006; USEPA, 2009). The stream surveys included here identified about 4800 km of stream length in this category. Statistical techniques employed in this study further identified the locations of an additional ~38,000 km of stream length predicted to have ANC <100 $\mu eq \cdot L^{-1}$ (Table 1). The measured and predicted locations of low ANC streams are of interest to federal, state, tribal, and private land managers concerned with and responsible for aquatic ecosystem health.

The S CL (Fig. 5) and exceedance results (Fig. 6) were developed for an ANC critical limit of 50 $\mu eq \cdot L^{-1}$. Managers are cautioned when applying these regional results in certain instances. For example, model simulations reported by Sullivan et al. (2011) suggested that not all streams in the study region exhibited preindustrial ANC levels as high as 50 $\mu eq \cdot L^{-1}$. In these instances, evaluating CL exceedance based on an ANC endpoint that is not achievable, even in the absence of anthropogenic S deposition, may not be appropriate. Land managers will need to select appropriate

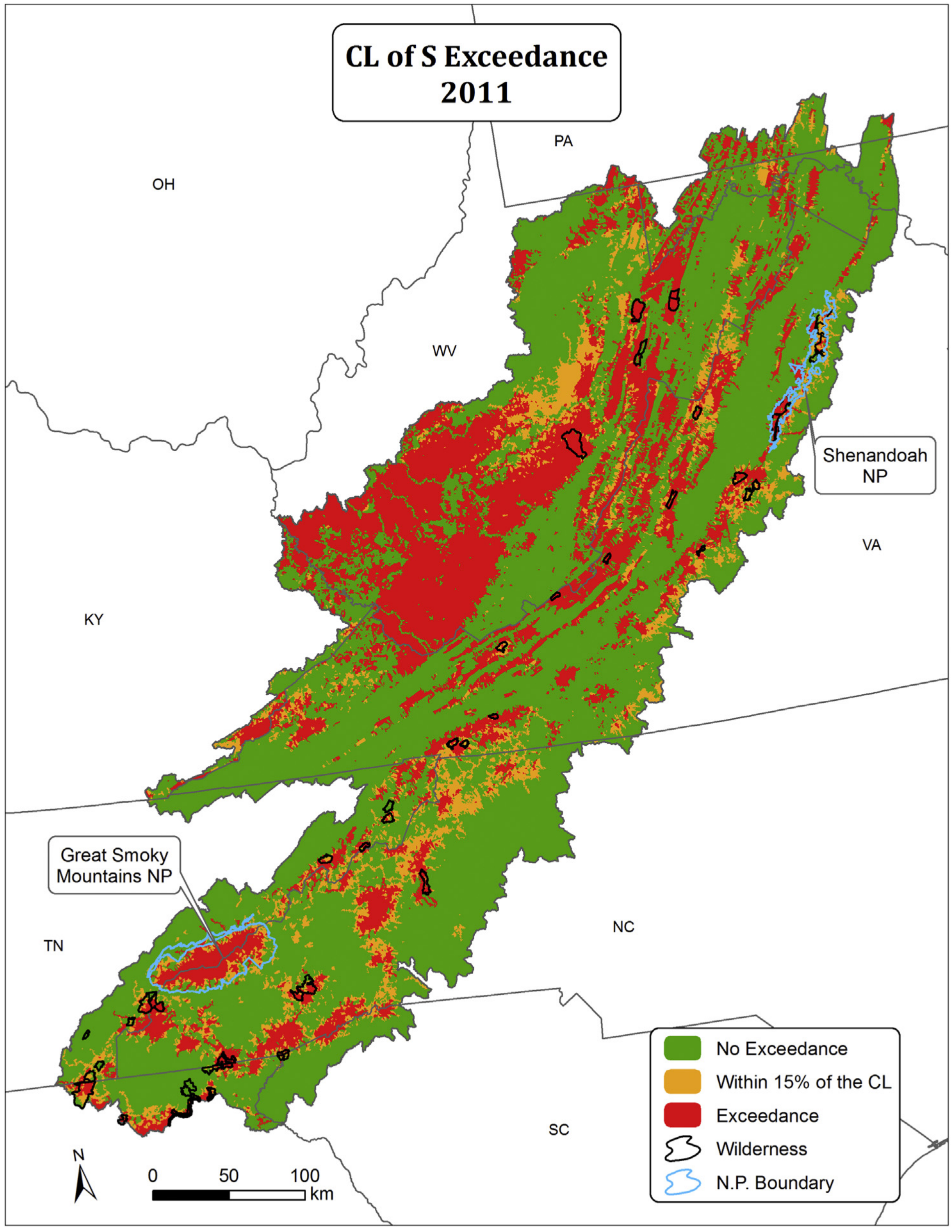

Fig. 6. CL exceedance across the study region for the ANC critical criterion equal to 50 $\mu eq \cdot L^{-1}$ according to annual S deposition derived as a three-year average centered on 2011.

critical ANC limits for protecting acid-sensitive aquatic biota on the lands that they manage.

4.1. Uncertainty

Evaluation of CL exceedance requires consideration of the uncertainties associated with the calculated CL and the estimates of S deposition used to evaluate CL exceedance. The steady-state CLs presented here were based on dynamic and statistical modeling, each of which included uncertainties as described here and in Povak et al. (2013, 2014). Uncertainty in the CLs estimated in this study was lowest for watersheds characterized with MAGIC calibrations and water chemistry, and results were more uncertain for other streams. The spatial variation in uncertainty associated with landscape-scale estimates of BC_W, an approximation of the uncertainty in the CL, is shown in Povak et al. (2014) and summarized in Table 2. Research led by the USEPA is ongoing to evaluate uncertainty associated with steady-state CL model parameters and S deposition (Blett et al., 2014; USEPA, 2013).

The TDEP estimates of S deposition used to determine CL exceedance in this study were expressed at a resolution of 4 km and only partially capture the relatively fine-scale variability in total deposition that occurs with differences in land use and forest type (Weathers et al., 2006). Furthermore, TDEP does not capture S deposition derived from cloud water and may underestimate the extent of CL exceedance in high-elevation areas where cloud water is an important contributor to total S deposition. It will be important to continue efforts to downscale regional models of total deposition to develop more accurate estimates of exceedance (Jung et al., 2013).

The disparity between the modeled CL and estimated S deposition was used in this study to apply an uncertainty window to the exceedance results. For the results shown here, the

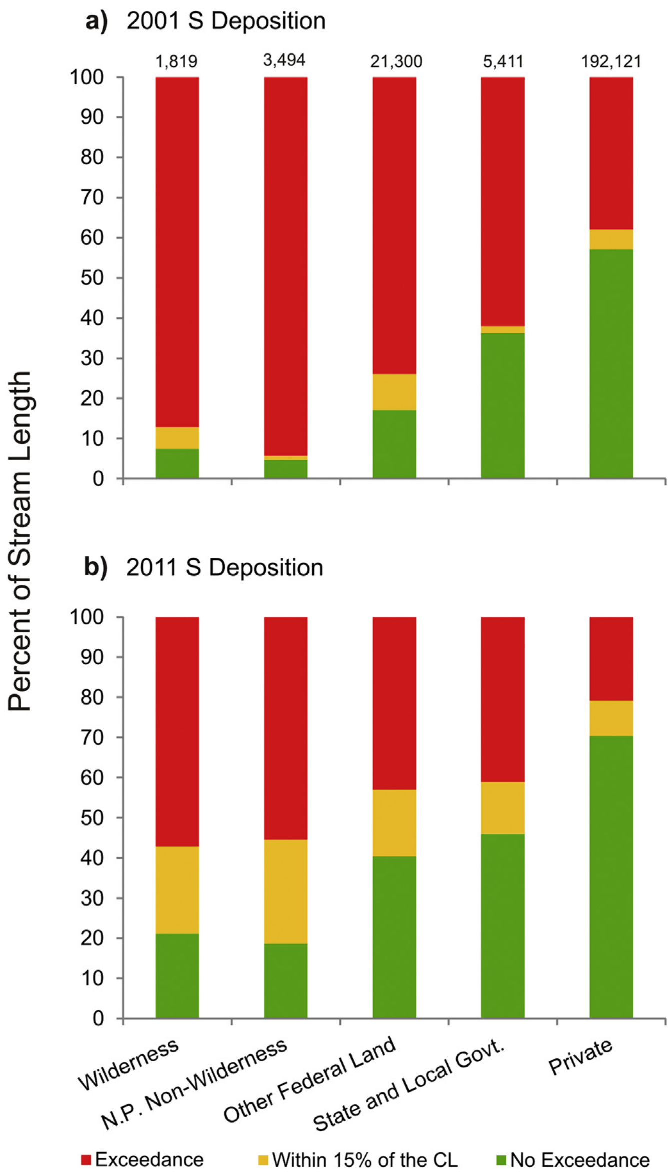

Fig. 7. Percent of stream length within various CL exceedance classes for the primary land management types found within the study region. The CL exceedance was determined from annual S deposition calculated as a three-year average centered on years a) 2001 and b) 2011. An ANC threshold of 50 $\mu eq \cdot L^{-1}$ was used to derive the CL. Numbers above the bars indicate the total length of stream (km) within each land allocation.

uncertainty window associated with CL exceedance was set to ±15% to represent an arbitrary level of uncertainty with respect to both CL and S deposition. Streams exposed to S deposition greater than 15% of the CL were considered to be in exceedance. If exposure to S deposition was less than 15% of the CL, the stream was considered to not exceed the CL. Exceedance was considered uncertain for streams with differences between the CL and S deposition that fell within the uncertainty window. For each land allocation, uncertainty in CL exceedance was higher based on 2011 deposition as compared with 2001 (Fig. 7). Streams located in wilderness and national parks showed more uncertainty than other public and private land. Resource managers and policy makers using these CL results for decision making can adjust the uncertainty window associated with CL exceedance as desired.

4.2. Natural resource management and policy implications

The results from this study can help land managers identify areas at risk or areas where S deposition is a concern. For example, some managers in the region have active programs to reintroduce the southern strain of brook trout in streams where they have been extirpated. The ANC (Fig. 2) and exceedance (Fig. 6) results provide fisheries managers with information regarding the likelihood that stream acidification may hinder the reintroduction of brook trout or other species in both the short and long term.

Currently, U.S. Forest Service land managers utilize HUC boundaries to classify watershed condition (Potyondy and Geier, 2011) and identify watersheds that may benefit from restoration efforts to improve ecosystem heath. Exceedance results were calculated here at the resolution of the topographically determined catchments (Fig. 6), and then summarized by larger management units (12-digit HUCs; Fig. 8). The results presented in Fig. 8 will aid U.S. Forest Service managers in the classification of watershed condition (Potyondy and Geier, 2011) and can be used for regional forest planning. Currently, the nitrogen (N) plus S CL results from McNulty et al. (2007) are used by the U.S. Forest Service for protection of terrestrial resources against impacts caused by soil acidification. The results from this study offer an improvement in the CL predictions for the HUCs by incorporating CLs and exceedances for protection of aquatic resources. Land managers can also use the ANC results in Fig. 2 to aid in classifying the water quality condition for streams where samples have not been collected. Only about 9% of the watersheds in the region have been sampled and analyzed such that water chemistry data are appropriate to calculate stream ANC (Table 2).

Results from this study and previous efforts (Povak et al., 2013, 2014) have been integrated into a GIS-based ecosystem management decision support (EMDS) system (Reynolds et al., 2012). The EMDS system can be used by land managers and policy makers to explore results presented here and generate new results by making adjustments to input parameters in a user-friendly environment. The system can support development of policy recommendations during review of the U.S. National Ambient Air Quality Standards (NAAQS) and aid resource managers who are responsible for the protection and restoration of aquatic ecosystems.

It will be important to field-verify the ANC stream predictions (Fig. 2) with additional stream water sampling before adjustments to current land management practices are made. The ANC results shown here can be used to aid in identifying appropriate sampling locations. Since soil acidification typically precedes surface water acidification, the regional ANC results also provide additional perspective on terrestrial acid-base status. Lands containing streams having low ANC will likely have soils with low concentrations of nutrient base cations. Therefore, in addition to stream sampling, it may be necessary to collect additional soil chemistry data before restoration projects are proposed.

The regional CL and exceedance results can be used to develop public policy related to air emissions reduction strategies. Previously, state and regional air quality agencies and organizations have worked cooperatively with federal agencies and other stakeholder groups to evaluate what effect S and N emissions reductions would have on stream ANC (Sullivan et al., 2004). Additional sulfur dioxide emissions reductions are anticipated in the southeastern United States (ARS, 2007) in order to meet the NAAQS for fine particulates and to reach the natural background visibility goal in federally mandated Class I areas by the year 2064. Results from this study provide a scientifically rigorous foundation for air quality agencies to evaluate the regional effectiveness of both current and proposed emissions reductions programs with regard to aquatic ecosystem health. Although decreases in S deposition between 2001 and 2011

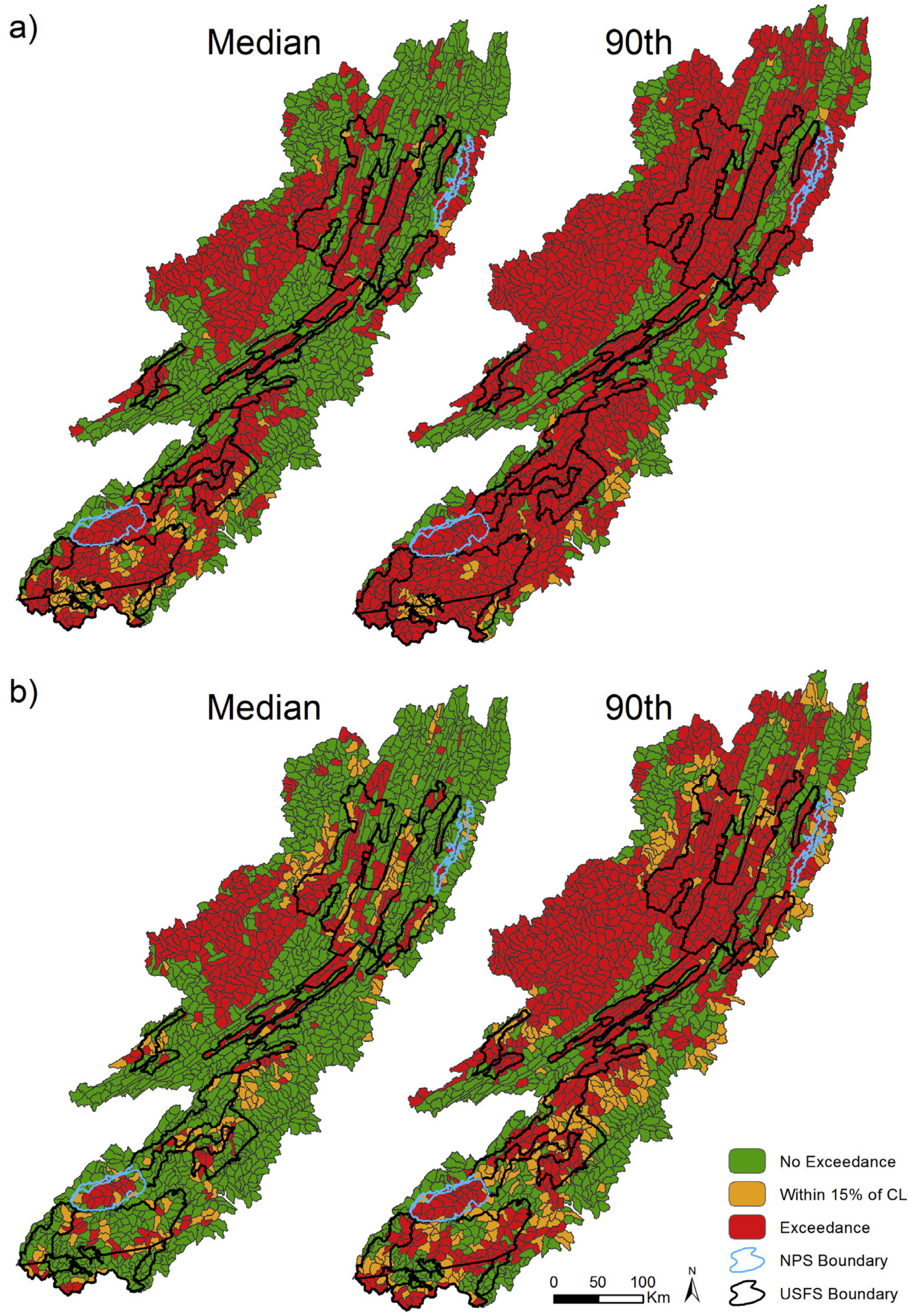

Fig. 8. Exceedance results aggregated by 12-digit hydrologic unit code (HUC). The median and 90th percentile from the range of exceedance results for the individual study catchments contained within each 12-digit HUC are shown. Exceedance results were based on annual S deposition calculated as a three-year average centered on years a) 2001 and b) 2011. An ANC threshold of 50 was used to derive the CL. The U.S. Forest Service land ownership boundaries are shown with black outlines and two national parks are shown with blue outlines.

have reduced the extent of CL exceedance (Figs. 7 and 8), further reductions in S deposition will likely be necessary to protect sensitive ecosystems. The CL exceedance results show that federal lands, particularly national park and wilderness areas (some of which are Class I areas), are disproportionately in exceedance relative to the remaining study region (Figs. 6 and 7). In some of these areas, there is a reasonable likelihood that current regulatory programs may be insufficient to reduce S deposition to a level that will allow stream ANC to reach desired targets. The results from this study provide land managers with spatially explicit information on where S deposition may be exceeding the CL (Figs. 6 and 8), providing the basis for evaluating alternative management options to improve aquatic ecosystem health.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2014.07.019.

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