Comparison of Methods for Estimating Critical Loads of Acidic Deposition in the Western Adirondack Region of New York

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Final Report

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Abstract

Acidic deposition via wet, dry, and cloud deposition continues to impair hundreds of surface waters in the Adirondack region of New York. Methods for quantifying effects and recovery potential can be developed from the concept of the critical load (CL), which, in this report, refers to the rate of acidic deposition, in the form of sulfur and/or nitrogen, that, when exceeded, causes harm to an ecosystem. The objective of this study was to compare and evaluate three approaches referred to as 1) the *empirical CL*, 2) the *dynamic CL* and 3) *scenario modeling* for estimating future acid-base chemistry conditions and the CL of sulfur and/or nitrogen needed to avoid future stream acidification in the Adirondack region of New York. The empirical CL of acidic deposition was calculated with the aim of protecting against mobilization of inorganic aluminum from soil to stream waters in the Adirondack Mountains. When this empirical CL is exceeded, biological harm to the stream ecosystem is expected to occur. Empirical CLs were calculated for 10 study streams and extrapolated to a wider regional population of Adirondack streams. Empirical results were compared with results of dynamic model simulations using the Model of Acidification of Groundwater in Catchments (MAGIC) based on aluminum mobilization and surface water acid neutralizing capacity.

Key Words: acidification, critical load, sulfur, base cation, aluminum

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Summary

Acidic deposition via wet, dry, and cloud deposition continues to impair many surface waters in the Adirondack region of New York despite decreases in deposition rates over the past 30 years. Methods for quantifying effects and recovery potential can be developed from the concept of the critical load (CL). In this report, a CL refers to the rate of acidic deposition that, when exceeded, causes harm to an ecosystem. The CL provides a straightforward framework for the translation of research results into information that can be useful to legislators and policymakers. A variety of modeling approaches designed around the CL concept are currently being applied to ecosystem acidification in the Adirondack region of New York, mostly confined to lake acidification. Nevertheless, the various approaches provide different types of information about current and future ecosystem condition, and there exist limitations and significant uncertainties in virtually all of the current approaches. Therefore, the objective of this study was to compare and evaluate three approaches for estimating the CL of sulfur (S) and/or nitrogen (N) needed to avoid current and future stream acidification in the Adirondacks. A large database of stream and soil chemistry was available for this work through the New York State Energy Research and Development Authority (NYSERDA)-supported projects with the following abbreviated titles: "Western Adirondack Stream Survey" (the WASS Project; 200 sites sampled in 2003-2005); "The Buck Creek Monitoring Watershed Study" (continuously monitored for chemistry and flow since 2001); and "The Adirondack Sugar Maple Assessment" (50 plots in 20 of the WASS watersheds sampled in 2009).

In the first approach, referred to as the *empirical CL*, the deposition rate of S+N, above which mobilization of inorganic aluminum (Al_i) occurs, was determined from an empirical formulation that relates the deposition rate to the ability of soil to neutralize acidity, expressed as the calcium (Ca) concentration in soils. The empirical approach only provides the CL under current soil conditions without information on future responses to deposition. Therefore, in the second approach, hereafter referred to as the *dynamic CL*, we used the Model of Acidification of Groundwater in Catchments (MAGIC; Cosby et al., 1985a, b) to estimate the CL of S needed to achieve various target values of water chemistry to protect biota by the years 2050 and 2100. Such a dynamic CL is called a target load (TL) in Europe. In the third approach, referred to hereafter as *scenario modeling*, the MAGIC model was used to evaluate responses of stream chemistry to various S deposition scenarios over defined timeframes. Scenario modeling does not determine a CL, but can be used in a way similar to CLs by comparing results to values of key measurements or indices of ecosystem condition.

Empirical CL modeling demonstrated that acidic deposition effects could be quantified as a simple function of deposition rate and exchangeable Ca in the Oa horizon of the soil when measurements of base cation surplus (BCS) in stream water were incorporated. The BCS provides a measure of acid neutralization that relates directly to mobilization of Al_i, the form toxic to aquatic biota; Al_i mobilization occurs when the

BCS is < 0. Based on this relationship, high-flow data indicated that 126 of 172 WASS streams (73%) were estimated to be receiving atmospheric deposition rates above their CL. Dynamic CL modeling indicated that for five of ten streams where sufficient data were available for this modeling (50%), CL values were often estimated to be zero (threshold not attainable by the endpoint year even with zero acidic deposition) and were consistently less than 60 meq m^{-2} yr^{-1} for various combinations of chemical criterion, critical threshold value, and end year (year defined to reach the chemical criterion). The calculated CL to prevent mobilization of Al$_i$ by the year 2050, ranged from zero for four study streams, to over 175 meq m^{-2} yr^{-1} for three study streams. The remaining three study streams had CLs between 54 and 94 meq m^{-2} yr^{-1} to maintain BCS > 0 in the year 2050. Scenario modeling indicated that five of the modeled streams had simulated pre-industrial acid neutralizing capacity (ANC) below 50 µeq L^{-1}, whereas the other five had ANC above 50 µeq L^{-1}. Under aggressive emissions controls, all modeled streams were projected to have positive ANC by the year 2050, but ANC for six of these streams was approximately 50 µeq L^{-1} or less in 2050 and four of these streams were projected to be unable to attain ANC above 50 µeq L^{-1} over the next 300 years.

The empirical CL results were consistent with the MAGIC dynamic CL results in that the six most acidified streams were receiving deposition above their CL for Al$_i$ mobilization in 2000-2004, and that would likely not change by 2050. Still, dynamic CL estimates for the three most strongly buffered watersheds indicated that current deposition could be increased by approximately two-to-five times through the year 2050 without causing Al$_i$ mobilization. In contrast, the empirical approach indicated that two of these sites were receiving deposition that was only 1-to-3 meq m^{-2} yr^{-1} below the CL for Al$_i$ mobilization, and one site was already in excess of the empirical CL. This discrepancy was likely related to differences in the CL, depending on whether base-flow or high-flow chemistry was being modeled. In watersheds where till was deposited during past glaciations, base flow is controlled by subsoil neutralization as water passes through the till en route to surface waters, whereas during high flow, acidic upper soil horizons exert an important control over stream chemistry. These results emphasize the importance of using high-flow stream chemistry for assessing processes of acidification and recovery in the ecologically significant upper soil horizons. The overall comparison between the MAGIC dynamic CL estimates and the empirical CL estimates indicates a consistency for watersheds that are acidic most, if not all, of the year (chronically or near chronically acidic). These watersheds are likely to have little or no till to provide neutralization during base flow.

1 *Introduction*

Acidic deposition via wet, dry, and cloud deposition continues to impair many surface waters in the Adirondack region of New York. In the New York State Energy Research and Development Authority (NYSERDA)-funded Western Adirondack Stream Survey (WASS) Project, during 2003-2005, 67 of 172 streams were determined to be chronically acidic and another 57 streams were identified as prone to episodic acidification and aluminum (Al) levels harmful to biota (Lawrence et al., 2008a). With approximately two-thirds of these streams still experiencing acidification, it is not clear how much further recovery should be expected. Some degree of chemical recovery has been measured, but in many cases has not been sufficient to promote biological recovery (e.g., Driscoll et al., 2001). Further information is needed to establish 1) the levels of acidic deposition at which these stream ecosystems become harmed, and 2) the recovery potential of ecosystems under various levels of acidic deposition.

Methods for quantifying effects and recovery potential can be developed from the concept of the critical load (CL), which, in this report, refers to the rate of acidic deposition, in the form of sulfur (S) and/or nitrogen (N), that, when exceeded, causes harm to an ecosystem (McNulty et al., 2007). A variety of modeling approaches designed around this concept are currently being applied to ecosystem acidification (Pardo, 2010; Lovett et al., 2009) and substantial progress has been made in acidification modeling over the past two decades (cf., Sullivan et al., in review a, b). Still, the various approaches provide different types of information about current and future ecosystem condition, and there remain limitations and significant uncertainties in virtually all of the current approaches. Acidification modeling continues to be a developing field in which no single approach fully addresses all aspects of the problem.

The objective of this study was to apply three approaches for estimating the CL of S or S+N to evaluate current and future stream acidification in the Adirondack region. A large database of stream and soil chemistry was available for this work through the NYSERDA-supported projects with the following abbreviated titles: "The Western Adirondack Stream Survey" (the WASS Project), "The Buck Creek Monitoring Watershed Study," and "The Adirondack Sugar Maple Assessment," plus recently improved deposition estimates. In the first approach, referred to hereafter as the *empirical CL*, the deposition rate above which mobilization of inorganic aluminum (Al_i) occurs, was determined from an empirical formulation that relates the deposition rate to the ability of soil to neutralize acidity, expressed as the calcium (Ca) concentration in soil. This approach is unique in that it focuses on the form of Al_i toxic to many species of aquatic biota rather than on acid neutralizing capacity (ANC) or pH as a chemical indicator of biological harm. The empirical formulation was applied to 172 WASS watersheds to evaluate their acidification status. Nevertheless, the empirical approach only provided the CL under current soil conditions without providing information on future soil responses to deposition. Therefore, in the second

approach, hereafter referred to as the *dynamic CL*, we used the Model of Acidification of Groundwater in Catchments (MAGIC; Cosby et al., 1985a, b) to estimate, for a subset of 10 watersheds, the CL needed to achieve various ANC and base cation surplus (BCS; described below) target values by the years 2050 and 2100. Note that this dynamic CL is specific to various endpoint years. We refer to this calculation as a dynamic CL in keeping with previous CL research in the United States (cf., Sullivan et al., 2004, 2008; U.S. EPA, 2008). Terminology in Europe is different and would describe such a time variant CL analysis as a target load (TL; Posch et al., 2001; Henriksen and Posch, 2001). In the third approach, referred to hereafter as *scenario modeling*, the MAGIC model was used to evaluate responses of stream chemistry to various deposition scenarios over defined time frames in the same subset of 10 watersheds. Scenario modeling does not determine a CL, but can be used in a way similar to CLs by comparing results to values of key measurements or indices of ecosystem condition, such as ANC. By evaluating several deposition scenarios, results can be used to determine the deposition level that is necessary to avoid exceeding the target value of a chemical indicator linked to ecosystem damage. Because scenario modeling includes a defined time frame, it provides a time-dependent estimate of deposition effects that predicts the results of various emission reduction strategies. The three approaches are summarized in Figure 1.
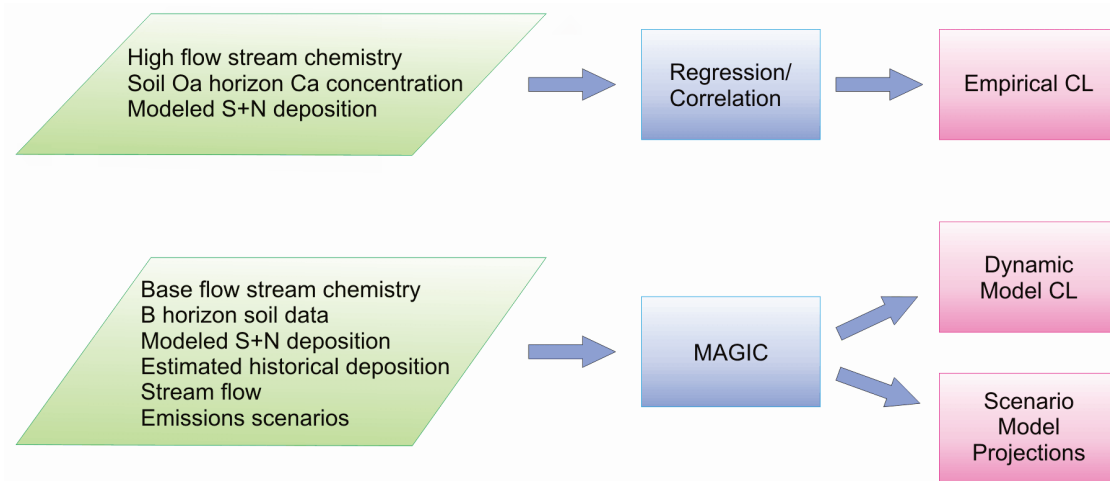
Figure 1. Modeling approach flow diagram.

2 *Methods*

2.1   Chemical Indices of Acidification

The chemical effects of acidic deposition are often viewed in terms of pH, which provides a direct measure of acid concentration. Atmospheric deposition of acidifying compounds to the landscape will lower the pH of surface waters if the added acidity is not fully neutralized within the watershed. The ability of the watershed to neutralize inputs of acidity is directly dependent on the availability of Ca^{2+}, and the other generally less abundant "base cations" including magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+), primarily from watershed soils and subsoil geologic material such as till. The acidification status of a water body can therefore be viewed in simple terms as a function of 1) the amount of acid deposited, and 2) the acid neutralization ability of the watershed.

The primary chemical index for quantifying acidification status is the surface water ANC, which can be estimated (ANC_e) with the following equation (Wright et al., 2005):

$$ANC_e = SBC - SAA \tag{1}$$

where SBC is the sum of the four base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and SAA is the sum of inorganic strong acid anions including sulfate (SO_4^{2-}), nitrate (NO_3^-), and chloride (Cl^-). All concentrations are reported in $\mu eq\ L^{-1}$. Whereas pH is a direct measure of acidity, surface water ANC reflects the capacity of watershed processes to neutralize inputs of acidity. Several decades of acidic deposition studies have relied on these measurements to quantify the acidification status of, and trends in, lake chemistry (Driscoll et al., 2007). Measurements of ANC (measured by titration and sometimes referred to as ANC_{Gran}), pH, and Al_i have also been related to the tolerances of various aquatic biota. Values below an ANC_{Gran} of 50 $\mu eq\ L^{-1}$, pH of 6.0 (Driscoll et al., 2001), and an Al_i concentration above 2.0 (Baldigo et al., 2007) have been identified as levels that define risk to aquatic biota.

Target values for chemical indices are essential in assessing acidification and recovery from acidic deposition, but the use of ANC and pH target values can be complicated by natural acidity associated with dissolved organic carbon (DOC) derived from decomposition of plant material. Concentrations of DOC have been shown to vary by more than a factor of 10 in Adirondack lakes (Munson and Gherini, 1993), and as a result of natural organic acidity, some lakes and streams were likely to have had values of ANC less than 50 $\mu eq\ L^{-1}$ before the onset of acidic deposition. An example of organic acid effects on ANC measurements can clearly be seen in a comparison of two neighboring tributary streams of Buck Creek, (referred to hereafter as the North and South tributaries) located in the western Adirondack region. The

chemistry of these two streams responds very differently to changes in flow (Figure 2) despite being co-located and receiving similar levels of acidic deposition. The North Tributary is chronically acidic, whereas the South Tributary becomes more acidic as flow increases. This contrast is due in large part to concentrations of DOC in the North Tributary that are typically about four times higher than in the South Tributary (Lawrence et al., 2008b). The relatively high DOC concentrations in the North Tributary are caused by a small headwater wetland and the presence of organic rich soils throughout the watershed. Both of these landscape features are common in the western Adirondack region (e.g., Canham et al., 2004).

Figure 2. Variations in ANC as a function of flow in the North and South tributaries of Buck Creek Inlet, N.Y.

Naturally acidic environments with indigenous species of plants and animals, such as the North Tributary watershed of Buck Creek, are also affected by acidic deposition (Lawrence et al., 2007). Organic soil horizons that develop from plant litter often have soilwater pH values that are less than 3.5 (Sullivan et al., 2006), well below the average pH of precipitation for this region (Lawrence et al., 2004). Soils and wetlands with accumulated organic matter export acidic water enriched in DOC to streams and lakes (Canham et al., 2004).

Measurements of pH and ANC are influenced by natural organic acidity that makes it difficult to distinguish between the effects of anthropogenic acidic deposition and natural acidity based solely on these measurements. Trends of increasing DOC concentrations over time have been recently identified in Adirondack lakes and streams, adding further importance to the role of natural acidity (Driscoll et al., 2007; Lawrence et al., in press).

To address the effects of natural acidity, a chemical index referred to as the base cation surplus (BCS) was recently developed (Lawrence et al., 2007). This index provides an alternative approach for assessing the acidification status of a catchment that is based on the threshold of Al_i mobilization in soil rather than ANC and pH measurements in surface waters. Mobilization of Al_i occurs at a BCS value that closely approximates zero, regardless of organic acid or DOC concentrations. The generality of the threshold relationship, its consistency with the theoretical basis for Al_i mobilization, and a lack of other known mechanisms to explain regional mobilization of Al_i, provide strong evidence that the measurable concentrations of Al_i in surface waters of the Adirondack region is an unambiguous indication of anthropogenic acidic deposition effects (Lawrence et al., 2007).
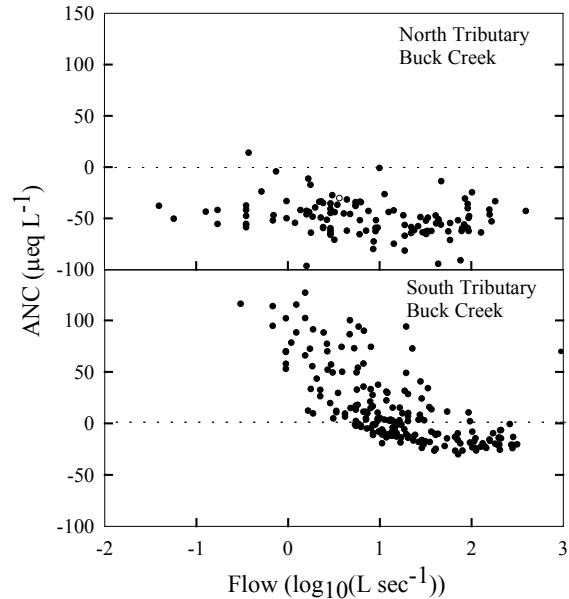
The empirical CL approach presented in this report is based on Al_i mobilization and therefore requires the use of the BCS as the index instead of ANC because the ANC value for the threshold of Al_i mobilization varies among streams in response to varying DOC concentration (Lawrence et al., 2007). For the dynamic CL and scenario modeling reported here, both the ANC and BCS chemical indicators are used.

2.2 Study Region

Data on stream chemistry and soil chemistry used in this analysis were collected in a 4,585 km^2 area of the Black and Oswegatchie River basins of New York that lie within the boundary of the Adirondack Ecological Subregion (McNab and Avers, 1994), which roughly corresponds to the boundaries of the Adirondack Ecoregion and the Adirondack Park. The study region is characterized by rugged, irregular terrain formed by repeated glaciations that last receded approximately 10,000 years ago. Bedrock geology is a complex mixture of granitic and gneissic rocks with a variety of less common metasedimentary formations scattered throughout the region (Ito et al., 2005). Surficial deposits reflect this complexity and include highly weatherable calcareous minerals in some areas (Ito et al., 2005). The study region is almost entirely forested with varying mixtures of northern hardwood and conifer species. Surface elevations average 504-m and range from 197 to 1,159-m.

Mean annual precipitation ranged from approximately 800 to over 1600-mm across the region during the period 1988 to 1999 (Ito et al., 2002). Extended periods of below-freezing winter temperatures usually result in an accumulation of snow that melts over a few weeks in spring and causes the highest sustained stream flows of the year. Atmospheric wet deposition rates of both N and S in the study region remain high relative to other northeastern states, averaging approximately 7 kg N or S ha^{-1} yr^{-1} in the center of the study region from 2004-2008 (http://nadp.sws.uiuc.edu/NTN/ntnData.aspx, accessed January, 2010).

2.3 Stream Flow and Chemistry Data

Continuous stream flow data (1942-2008) were available in the study region from the U.S. Geological Survey (USGS) gage on the Independence River at Donnattsburg, NY (Station 04256000), approximately 50-km west of Buck Creek. Stream flow data were also compiled from the North and South tributaries of Buck Creek from 1998 to 2008.

This study includes evaluation of snowmelt stream chemistry to more accurately reflect the full extent of acidification, as well as the standard approach of using baseflow chemistry, which reflects conditions that are least acidic. Inclusion of high-flow stream chemistry is also advantageous because it provides a useful indicator of soil processes, including mobilization of toxic Al, which primarily occurs in the more acidic, upper soil horizons (Lawrence et al., 2008b).

The snowmelt stream samples used in this analysis were collected in the WASS Project (Figure 3), March 29 to April 1, 2004, from 189 streams within the drainages of the Black and Oswegatchie rivers (Lawrence
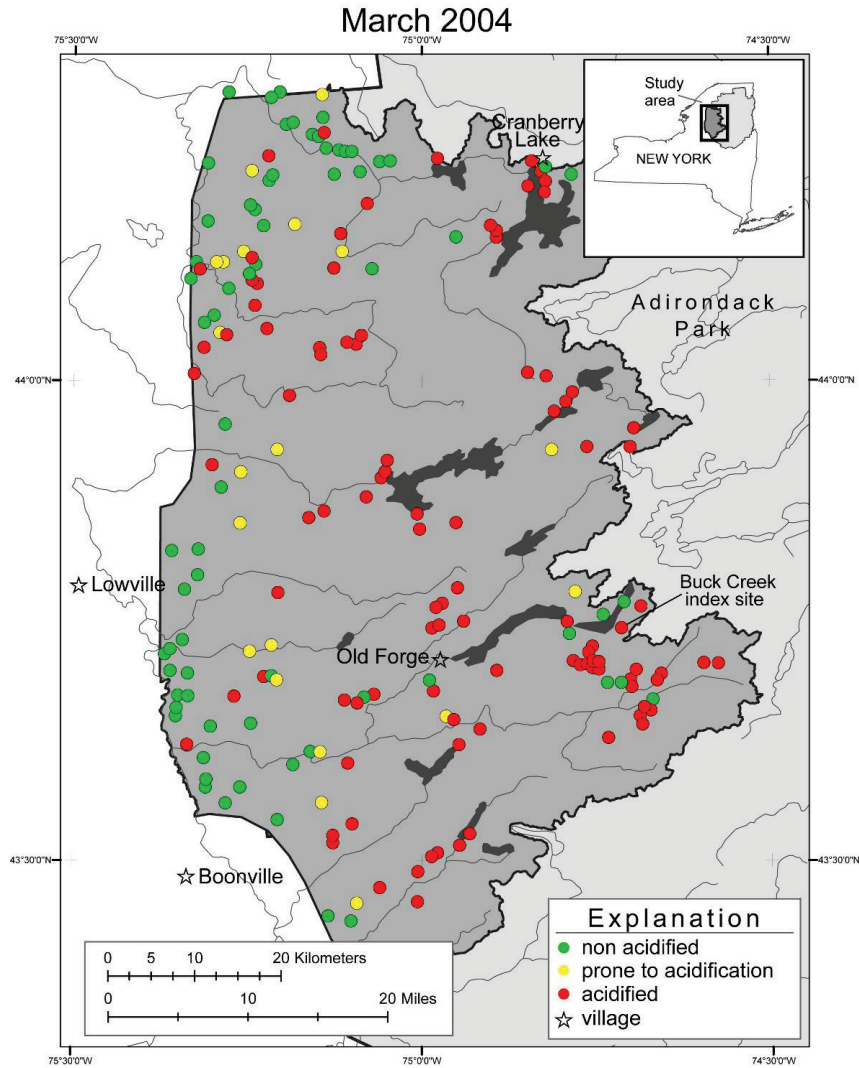
Figure 3. Acidification categories of streams sampled in the March-April 2004 WASS survey. Non-acidified streams had base cation surplus (BCS) values > 25 µeq L^{-1}; streams prone to acidification had BCS values > 0 µeq L^{-1} but < 25 µeq L^{-1}; acidified streams had BCS values < 0 µeq L^{-1}.

et al., 2008b). The streams were chosen randomly from a population of 565 streams in the study region that fit the following criteria: 1) the stream appeared on a USGS 1:24,000-scale quadrangle map, 2) the stream was accessible by hiking to and from the sampling location within one hour, and 3) the stream's watershed did not contain upstream lakes or ponds that drained more than 25% of the total drainage area defined by the sampling point. Study streams varied in their acidification status, as reflected in the BCS (Lawrence et al., 2007). Stream order of the selected streams ranged from one-to-three, but most were first order. The four-day sampling period was specifically chosen to minimize variations in flow during the collection period. Flow-driven variations in chemistry can be problematic for regional surveys of high-flow conditions such as this because sampling conditions can change during the time needed to reach all the

sites. During the four days of sample collection, flow measured at Buck Creek, an index gage located within the study area, was relatively stable, but remained high, varying from 216 to 346 L s^{-1} (Lawrence et al., 2008a). Stream water samples from the March-April 2004 survey were analyzed in the Adirondack Lakes Survey Corporation (ALSC) laboratory for pH, ANC$_{GRAN}$, and concentrations of Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$, total fluorine (F), DOC, ammonium (NH$_4^+$), total monomeric Al, and organic monomeric Al$_i$ according to U.S. EPA-approved methods; Al$_i$ was determined by difference.

Spring, high-flow water samples from four additional streams were included in the analyses. These samples were collected on April 6, 2004 from the North and South tributary streams of Buck Creek and from two additional streams (N1 on May 14, 2008 and S14 on March 22, 2003) located east of the Oswegatchie-Black drainage. Samples from Buck Creek and N1 were analyzed in the USGS laboratory in Troy, NY, following the same USEPA approved methods used by the ALSC laboratory, and detailed in Lawrence et al. (1995). The data used for watershed S14 were reported by Christopher et al. (2008).

The empirical CL analysis used only high-flow stream chemistry data collected in March-April 2004. The dynamic CL and scenario modeling of the 10 watersheds required data on base-flow stream chemistry for MAGIC calibration. Most of the streams in these watersheds were chronically acidic so the chemical concentrations of most constituents did not vary greatly between high- and low-flow sampling. Therefore, to provide input data for calibration, stream data collected during WASS surveys conducted in August 2003, October 2003, March-April 2004, August 2004, and March 2005 were averaged for eight of the ten watersheds where CL and scenario modeling were done. For the two most well-buffered streams (24001, 28030), Ca^{2+} concentrations varied approximately 50 to 100 µmol L^{-1} between low and high flow. Therefore, only low-flow data (August 2003 and August 2004) were averaged for MAGIC calibration.

2.4   Soil Chemistry Data

Acidification modeling studies often use data from the B horizon to represent soil processes, but results from the WASS project (Lawrence et al., 2008b), and earlier results from elsewhere in the Northeast (Lawrence et al., 1997), indicated that 1) during high-flow conditions, acid neutralization in streams was significantly correlated to base cation availability in the upper soil horizons, and 2) in watersheds with Ca-depleted soils, the Oa horizon played a greater role in neutralization of stream water than the upper B horizon. Therefore, data from 21 watersheds where both Oa horizon soil chemistry and spring high-flow stream chemistry were used in calculating the empirical CL. Soil data from eight of these watersheds were available through the WASS project. Samples were collected from the faces of hand-excavated soil pits in summer 2004, at three locations within each of five plots chosen to represent landscape variability within the watershed (15 total soil sampling locations per watershed). Soil from each plot was combined before analysis, yielding five measurements per watershed. Although the areal extent of the various types of landscapes were not quantified, the soil data obtained from this sampling approach were statistically correlated with stream chemistry (Lawrence et al., 2008b).

Soil data from the North and South Tributary watersheds of Buck Creek (sampled in 1997-1998) were also included; samples were collected at 30 locations in each watershed along seven, evenly-spaced transects perpendicular to the stream. Samples from the Oa-horizon were collected using the same method as the WASS soil sampling, and data were averaged to yield one value per watershed.

Additional soil data were also available through the NYSERDA-funded project entitled "Acid Deposition Effects on Adirondack Ecosystems: Linkages among Streams, Soils, and Sugar Maple Health" (short title: "Adirondack Sugar Maple Assessment Project"). In summer 2009, samples were collected in two to three plots in each of 11 watersheds where spring high-flow stream chemistry data were available through the WASS or other sources (for watersheds N1 and S14, as described above). Within each plot, Oa horizon samples were collected from five locations along a 50 m transect with a 10 cm x 10 cm pin block that enabled a 100 cm^2 block of the forest floor (Oi, Oe, Oa and/or A horizons) to be collected (Federer et al., 1984). The Oa horizon was then separated from the block of soil. Measurements were averaged by plot and watershed to obtain a single watershed value. Soil samples collected through the Adirondack Sugar Maple Assessment Project were analyzed in the USGS laboratory in Troy, NY, using methods given in Lawrence et al. (2008b).

Soil data used in the dynamic CL and scenario modeling were obtained from the samples collected from the upper 10 cm of the B horizon in the eight watersheds sampled in the WASS project plus the North and South Tributary watersheds of Buck Creek, as described above. All soil samples used in the empirical CL, dynamic CL and scenario modeling were analyzed for exchangeable Ca^{2+}, Mg^{2+}, Na^+, K^+, loss-on-ignition, total carbon (C), total N , pH (water extraction and $CaCl_2$ extraction), total acidity, and exchangeable Al_i in the USGS laboratory in Troy, NY, using methods given by Lawrence et al. (2008b).

2.5   Atmospheric Deposition to Complex Terrain

Current estimates of total atmospheric deposition of S and N were needed for each of the study watersheds. To obtain these estimates, we created an empirically based, spatially explicit model based on the work of Weathers et al. (2006). This type of deposition modeling was necessary because the complex terrain of the study area was expected to result in considerable variability in deposition loading among the 189 study watersheds (e.g., Weathers et al., 2000, 2006). Total (wet + dry) deposition of S (SO_4-S, SO_2-S) and N (NO_3-N, NH_4-N, HNO_3-N) across the Adirondack region were estimated for the period 2000-2004 using a modification of the Weathers et al. (2006) approach. Wet deposition for areas below 675-m elevation was calculated from interpolated mean annual National Acid Deposition Program (NADP) precipitation chemistry from the seven stations that lie within or near the region and Parameter-elevation Regressions on Independent Slopes Model (PRISM) precipitation data. Dry deposition for areas below 675-m elevation was calculated from interpolated mean seasonal Clean Air Status and Trends Network (CASTNET) air chemistry available from six stations within or outside the study region, and mean deposition velocities assigned to landcover data obtained from the North America Land Cover Characteristics data base . Total

deposition to areas above 675-m was calculated from a model of elevation and empirical throughfall data collected in previous studies (Weathers et al., 2006). Spatial data were estimated at a 30x30-m resolution and used to calculate mean deposition and total loading to the study watersheds.

2.6 Rationale for the Empirical Critical Load Based on Al_i Mobilization

The empirical approach developed in this study for estimating the CL employs the threshold of Al_i mobilization (a BCS of zero) as the target value. This approach is based on the premise that Al_i mobilization should be completely avoided because it 1) harms a wide range of aquatic biota (Gensemer and Playle, 1999), and 2) did not occur before the onset of acid deposition (Lawrence et al., 2007). Using Al_i mobilization to estimate the CL provides two advantages over ANC for assessing impacts on biota. First, Al_i can be directly toxic to even relatively acid-tolerant fish species such as brook trout (*Salvelinus fontinalis*) at concentrations so low that they approach analytical limits of measurement (Baldigo et al., 2007), whereas ANC is an integrated measure of acid buffering that is indirectly related to biota but does not provide specific information on chemical tolerances. Second, mobilization of Al_i occurs at a true geochemical threshold that is highly relevant to the welfare of aquatic ecosystems (Baldigo et al., 2007, 2009; Passy, 2006). Thus, BCS yields a concrete target value, whereas ANC relates to acid deposition over a gradient without a breakpoint, making target values more ambiguous and variable. For example, although a target value of ANC equal to 50 μeq L^{-1} has been demonstrated as a level below which a large number of species are likely to be harmed by acidification (Driscoll et al., 2001), some surface waters likely had an ANC below 50 μeq L^{-1} before the onset of acidic deposition (Sullivan et al., In Review a).

Despite the biological relevance of Al_i, ANC is more often used as an acidification index, because monitoring programs do not always measure Al_i and modeling Al_i dynamics in natural systems is complex. In the empirical approach that we present, this complexity is avoided by using the BCS mobilization threshold of 0 as the target value, thereby negating the need to model Al_i concentration. The limitation of this approach is that it determines the empirical CL based only on current soil conditions. Future changes in the availability of soil Ca^{2+}, either soil recovery or further acidification, would change this empirical CL.

2.7 Computation of Empirical Critical Loads

The CL for Al_i mobilization can be considered in simplest terms as a function of 1) the acidic deposition level and 2) the ability of the watershed to neutralize inputs of acidity. Surface water chemistry can be used to indicate if a watershed is receiving acidic deposition at a level that exceeds that watershed's ability to prevent Al_i mobilization through release of base cations. In this report we test the premise that this information can be combined in a simple graphical exercise to approximate the extent to which ambient deposition may or may not exceed the CL for mobilization of Al_i.

For each of the 21 watersheds for which soil data were available, S + N deposition was plotted against base saturation (BS) of the Oa horizon. Values of BCS < 0 in the streams of these watersheds during the 2004 snowmelt were used to identify watersheds that had soils in which Al_i was being mobilized and transported into the streams. The streams with BCS < 0 would be expected to cluster in the upper left of the graph (high deposition, low BS), whereas watersheds with BCS > 0 would be expected to cluster in the lower right (low deposition, high BS). If data separated in this manner, a diagonal line could be drawn to divide the two groups. This dividing line could then be used to represent the CL as a function of BCS. The vertical distance above or below the CL estimate, termed the neutralization status, would represent either the reduction in deposition required to prevent Al_i mobilization or the increase in deposition that could occur without mobilizing Al. The neutralization status would be positive for watersheds where Al_i is mobilized, negative for watersheds where Al_i is not mobilized, and 0 for watersheds where deposition equals the CL.

Critical load estimated from the empirical approach provides a new method for estimating the CL under current conditions, but does not address the temporal component of recovery that will be required to reverse acidification effects. For example, it is possible that deposition will have to remain below the empirically determined CL for many years before Al_i mobilization ceases. The dynamic modeling using the MAGIC model augments, for a small subset of watersheds, our empirical method of estimating CL with a dynamic estimate that is time variant.

2.8   Description of the MAGIC Model for Prediction of Surface Water Chemistry

Predictions of surface water chemistry needed for scenario and dynamic CL modeling were provided by MAGIC, a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry (Cosby et al., 1985a,b). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters and therefore requires base-flow or annual average chemistry data for surface waters as input for model calibration. MAGIC consists of 1) a submodel in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO_4^{2-} adsorption, cation exchange, dissolution-precipitation-speciation of Al_i and dissolution-speciation of inorganic C; and 2) a mass balance submodel in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass and loss to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. Specifically, MAGIC uses the B horizon soil chemistry to characterize the soil pool of exchangeable base cations. As the fluxes to and from this pool change over time due to weathering, atmospheric deposition, ion exchange, and leaching, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The

degree and rate of change of surface water acidity thus depend both on flux factors associated with precipitation, deposition, and hydrology, and the inherent characteristics of the affected soils.

Cation exchange is modeled using Gaines-Thomas equilibrium equations with selectivity coefficients for each base cation and Al. Sulfate adsorption is represented by a Langmuir isotherm (Cosby et al., 2001). Aluminum dissolution and precipitation are assumed to be controlled by equilibrium with a solid phase of $Al(OH)_3$. Aluminum speciation is calculated by considering hydrolysis reactions as well as complexation with SO_4^{2-} and fluoride (F^-). Effects of carbon dioxide (CO_2) on pH and on the speciation of inorganic C are computed from equilibrium equations. Organic acids are represented in the model as tri-protic analogues. Weathering of base cations and the uptake rate of N are assumed to be constant, as estimated from the calibration. A set of mass balance equations for base cations and strong acid anions is included.

Given estimates of the trajectory of likely historical deposition at a site, the model equations are solved numerically to give long-term reconstructions of surface water chemistry. For complete details of the model, see Cosby et al. (1985 a,b; 2001). MAGIC has been used to reconstruct the history of acidification and to simulate future trends in response to changes in deposition on a regional basis and in a large number of individual catchments in both North America and Europe (e.g., Lepisto et al., 1988; Whitehead et al., 1988; Cosby et al., 1989, 1990, 1996; Hornberger et al., 1989; Jenkins et al., 1990a-c; Wright et al., 1990, 1994; Norton et al., 1992; Sullivan and Cosby, 1998; Sullivan et al., 2004, 2008), but this is the first time MAGIC has been used for CL modeling in this region.

The nature of the model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters within the model that can be directly measured or observed in the system of interest (called fixed parameters). The model is then run (using observed and/or assumed atmospheric and hydrologic inputs) and the outputs (stream water and soil chemical variables, called criterion variables) are compared to observed values of these variables. If the observed and simulated values differ by more than the amount designated for the calibration window, the values of another set of parameters in the model (called optimized parameters) are adjusted to improve the fit. After a number of iterations, the simulated-minus-observed values of the criterion variables usually converge to zero (within some specified tolerance). The model is then considered calibrated. The estimates of the fixed parameters and deposition inputs are subject to uncertainties so a "fuzzy" optimization procedure is implemented for calibrating the model. The optimization procedure consists of multiple calibrations using random values of the fixed parameters drawn from the observed possible range of values, and random values of deposition drawn from a range including uncertainty about the estimated values. Each of the multiple calibrations begins with 1) a random selection of values of fixed parameters and deposition, and 2) a random selection of the starting values of the optimized parameters. The optimized parameters are then adjusted using the Rosenbrock (1960) algorithm to achieve a minimum error fit to the target variables. This procedure is undertaken 10 times. The final

calibrated model is represented by the ensemble of parameter values and variable values of the 10 calibrations.

2.9 Computation of Critical Loads and Scenario Modeling with MAGIC

The acid-base chemistry modeling for this project was conducted using 2004 as the Base Year. The effects model was calibrated to the available atmospheric deposition and water chemistry data (see below) and then interpolated or extrapolated to yield Base Year estimates of stream chemistry, which served as the starting point for specifying future emissions control scenarios, and for modeling future water chemistry.

Empirical relationships between regional emissions from EPA's National Emissions Inventory (NEI) and ionic concentrations in precipitation from NADP, coupled with historical regional emissions inventories, were used to estimate the time series of historical wet S and N deposition (cf., Driscoll et al., 2001, Sullivan et al., 2007). It was assumed that NH_4^+ deposition in the past, prior to the availability of monitoring data, varied with NO_3^- deposition because agricultural and industrial development generally occurred in parallel in the United States. Dry deposition was calculated using dry to wet ratios from the Community Multiscale Air Quality (CMAQ) Modeling System. The spatial coverage of deposition created for this project, as described in Section 2.5, was used to calculate Base Year, area-weighted average total deposition for each study watershed.

The MAGIC model was calibrated to each of the 10 WASS watersheds for which adequate model input data were available. Plots of simulated versus observed stream chemistry (Figure 4) indicated that the calibration was successful for the study watersheds. After calibration at each of the study watersheds, MAGIC was used to simulate 1) the critical S deposition load required to allow chemical recovery in order to reverse adverse effects on stream biota, and 2) the length of time required to achieve cessation of Al_i mobilization at various deposition scenarios.

Four scenarios of future acidic deposition were simulated. They were based on the following assumptions:

1. Continued acidic deposition at Reference Year levels (No Change scenario)
2. Acidic deposition at levels expected to occur under existing and anticipated emissions controls (Existing Regulations scenario)
3. Future emissions controls that are somewhat more restrictive than existing and anticipated regulations (Moderate Emissions Controls scenario)
4. Aggressive future emissions controls (Aggressive Emissions Controls scenario)

The CL of S deposition was calculated in an iterative fashion to achieve each of the specified benchmark concentrations of ANC (20 and 50 µeq L^{-1}) and BCS (0 and 25 µeq L^{-1}). For all these S CL simulations, N deposition was assumed to follow expectations based on the Existing Regulations scenario. Although N was used in the model, only CLs for S were determined since they are generally lower than those for N and
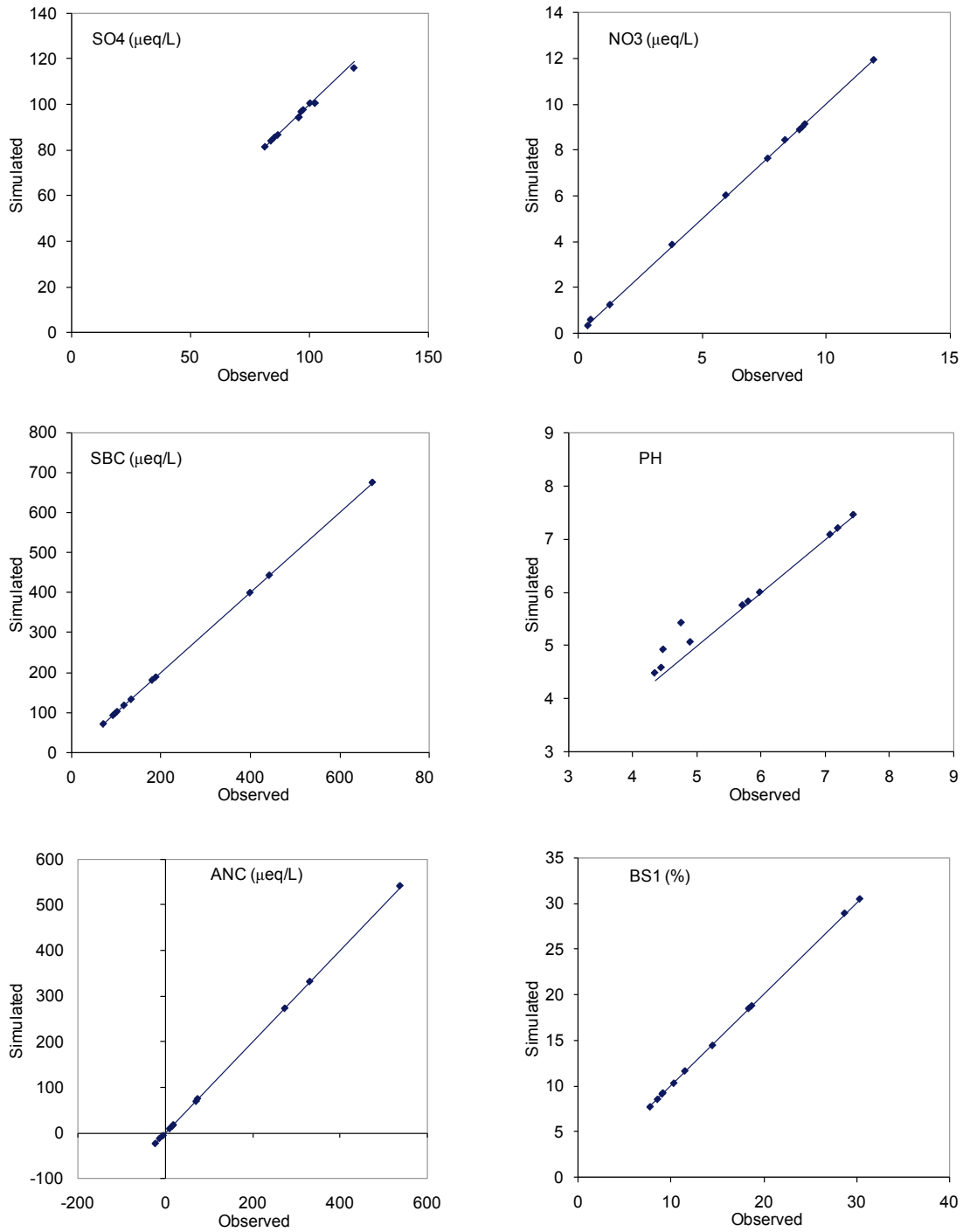
Figure 4. Simulated (MAGIC model) versus observed stream concentrations of SO$_4^{2-}$, NO$_3^-$, sum of base cations (SBC), pH, calculated ANC, and soil percent base saturation for the 10 study streams, Adirondack Mts., NY.

are, therefore, more conservative. Sulfur also has a greater influence on acidification than N because much of the N deposited on the landscape is taken up by vegetation, and therefore may not directly acidify, whereas most of the S is directly acidifying within the terrestrial and aquatic ecosystems in the Adirondacks.

The CLs to achieve BCS targets of 0 and 25 μeq L^{-1} were calculated as described below. The BCS is defined as:

$$BCS = ANC_e - RCOO(s) \tag{2}$$

where ANC_e is the SBC (Ca^{2+}, Mg^{2+}, Na^+ and K^+) minus the SSA (SO_4^{2-}, NO_3^-, Cl^-), and RCOO(s) is the strong organic acid anion concentration. The target ANC_e for a CL simulation to achieve a target BCS is then given by:

$$Target\ ANC_e = Target\ BCS + RCOO(s) \tag{3}$$

These target ANC values were used as inputs to the MAGIC simulations used to estimate the CL to achieve the various BCS targets in the future.

Current wet deposition of base cations and Cl$^-$ was taken from the NADP/NTN monitoring station at Huntington Forest. For each of these ions, background pre-industrial deposition was assumed to be 10% of current deposition. Deposition inputs after 1850 were assumed to increase linearly to estimated values obtained for 1950. Deposition estimates during 1950 to 1978 for Na^+, K^+, Mg^{2+}, Ca^{2+}, and Cl$^-$ were derived from empirical relationships between wet deposition and emissions of particulate matter (PM-10; Nizich et al., 1996). The model calculations assumed an initial fixed dry to wet deposition ratio for each base cation and for Cl$^-$. These values were assumed initially to be 0.5 for each of the base cations and 0.25 for Cl$^-$, with minor adjustments made during calibration.

Past, current, and future total (wet + dry) deposition amounts of major ions were expressed as the area-weighted average for each study watershed. Although the absolute values of total deposition were variable from watershed to watershed, the patterns of change over time were considered to be constant.

3 *Results and Discussion*

3.1 Empirical Critical Loads

Atmospheric deposition of S and N in the study region was highest in the South and lowest in the Northeast (Figure 5) and increased with elevation. For the time period 2000-2004, total deposition estimates for S + N ranged from approximately 90 to 125 meq m^{-2} yr^{-1} (see Table 1 for unit conversions). The total area of the study region is 4,585 km^2. Numerous studies over the past several decades have identified the western region of the Adirondacks as one of the most impacted by acidic deposition in the U.S. Nevertheless, the WASS data showed that the acidification status of streams in the region, measured by the BCS, was not statistically correlated to modeled mean acidic deposition rates (Figure 6) for the studied watersheds. This was partly due to

Table 1. Unit conversions for atmospheric deposition data.

Chemical Species	kg ha^{-1} yr^{-1}	eq ha^{-1} yr^{-1}	meq m^{-2} yr^{-1}
SO_4^{2-}	1.00	20.8	2.08
S	1.00	62.4	6.24
NO_3^-	1.00	16.1	1.61
NH_4^+	1.00	55.4	5.54
N	1.00	71.4	7.14

the limited variation in estimated total deposition within the region, and partly due to the large variation in acid sensitivity that occurs within the region. Values of the BCS in the study streams varied from about -150 µeq L^{-1} to nearly 900 µeq L^{-1}, although most streams fell in the range of -100 µeq L^{-1} to 100 µeq L^{-1} (Figure 6). This variation in acid sensitivity is the result of the spatially complex mineralogy of till and bedrock in the region, which can be seen in streamwater Ca^{2+} concentrations that ranged from 18 to 600 µeq L^{-1} (Figure 7). As the most abundant base cation, Ca^{2+} availability is the primary determinant of a watershed's ability to prevent mobilization of Al_i from acidic deposition. The strong relationship observed between concentrations of exchangeable Ca^{2+} in the Oa horizon soil and concentrations of Ca^{2+} in stream water during high flow (Figure 7) reflects the importance of the Oa horizon in controlling neutralization of high-flow stream chemistry in these small watersheds.

The concentration of exchangeable Ca^{2+} in the Oa horizon among the 21 watersheds where soil data were available varied from 1.8 to 51 cmol$_c$ kg^{-1} (Figure 7), but only three watersheds had values above 20 cmol$_c$ kg^{-1}. Despite the limited number of watersheds with relatively high exchangeable Ca^{2+} in the soil, plotting Oa-horizon Ca^{2+} versus atmospheric deposition of S and N revealed a separation between the watersheds in which mobilization of Al_i did occur (above the line) and those in which it did not (below the line; Figure 8). With this data set, a line of separation could be drawn that was consistent with our premise that deposition effects can be quantified in simplest terms as a function of deposition rate and neutralization capacity expressed as exchangeable Ca^{2+} in the Oa horizon of the soil. The line was drawn to be vertically equidistant from the single red point and two green points closest to the line of separation. The equation of

Figure 5. Total estimated wet plus dry deposition of sulfur (top) and nitrogen (bottom) across the study region using the Weathers et al. (2006) method (see text).
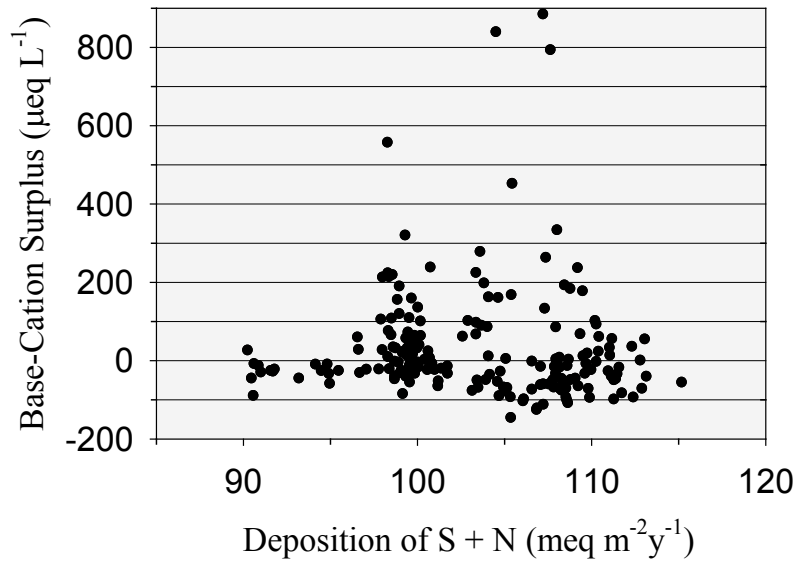
Figure 6. Values of the base cation surplus as a function of sulfur plus nitrogen deposition for the Adirondack region.

$$y = 9.45*\ln(x) - 24.4$$
$$R^2 = 0.69$$
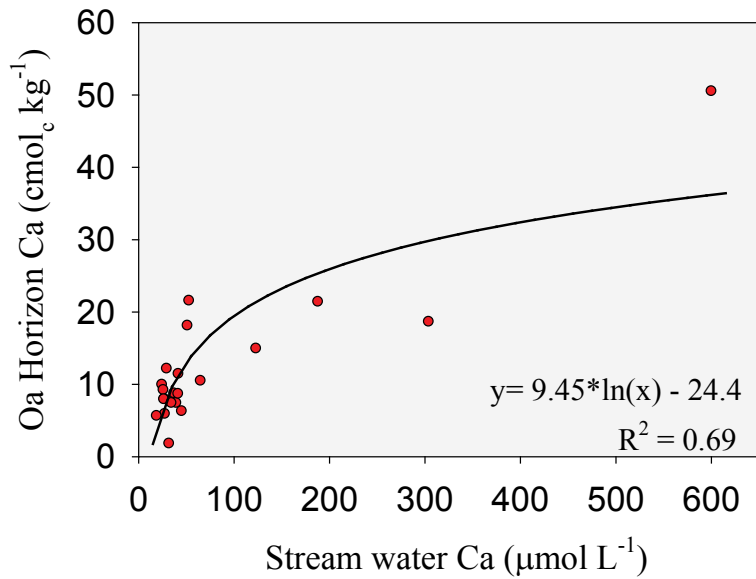
Figure 7. Concentrations of exchangeable Ca in the Oa soil horizon as a function of Ca concentrations in stream water during high flow for 21 western Adirondack watersheds. The equation for the best-fit line is shown.
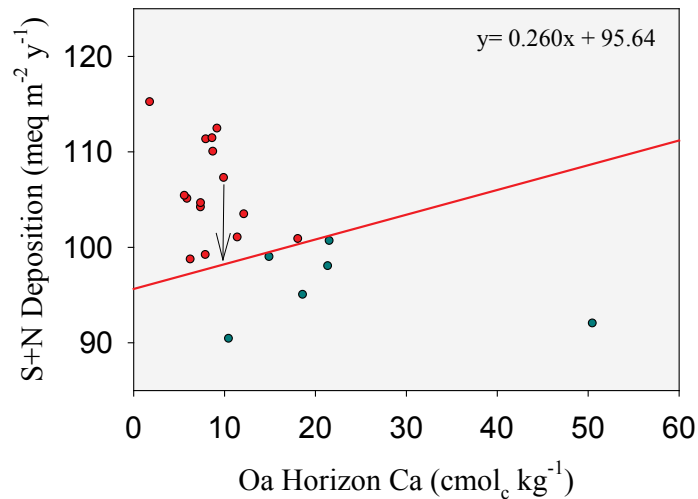
Figure 8. Relationship between total (wet + dry) S plus N deposition versus exchangeable Ca concentration in the soil Oa horizon for the 21 study watersheds. Red symbols indicate watersheds in which the BCS in stream water was less than zero, green symbols indicate watersheds in which the BCS in stream water was greater than zero. The red line separates watersheds with BCS values less than and greater than zero, and represents the critical load as a function of exchangeable Ca concentration. The equation of the red line is given in the upper right corner.

this line gives the CL for mobilization of Al_i as a function of the exchangeable Ca concentration in the Oa horizon. On this basis, six of the study watersheds were receiving deposition rates below the CL and 15 were receiving deposition rates that were above the CL.

Additional data from watersheds with both lower and higher Ca^{2+} availability that are receiving deposition rates near the CL would be useful in reducing the uncertainty regarding exactly where to place the line in Figure 8. Within the range of exchangeable soil Ca^{2+} of 5 to 25 $cmol_c$ kg^{-1}, however, the CL is reasonably constrained by the field measurements. In this regard, the data presented in Figure 8 are consistent with the theory that the critical load increases as Oa neutralization capacity (expressed as exchangeable Ca^{2+} concentration) increases.

The applicability of this CL formulation for the study region can be tested with data from the additional 172 WASS streams sampled in March-April 2004, which were not used to determine the CL equation given in Figure 8. Soil data were not available for these watersheds, but the relationship between exchangeable Ca^{2+} in the Oa horizon and Ca^{2+} concentrations measured in stream water for the 21 watersheds with soil data (Figure 7) enabled Oa horizon exchangeable Ca^{2+} to be estimated from stream water Ca^{2+} concentrations. With data on estimated deposition and estimated soil Ca^{2+}, the neutralization status was then calculated for each of the 172 WASS watersheds. With this approach, 73% of these watersheds were determined to be receiving deposition levels that exceeded their CL (Figure 9). On the basis of BCS
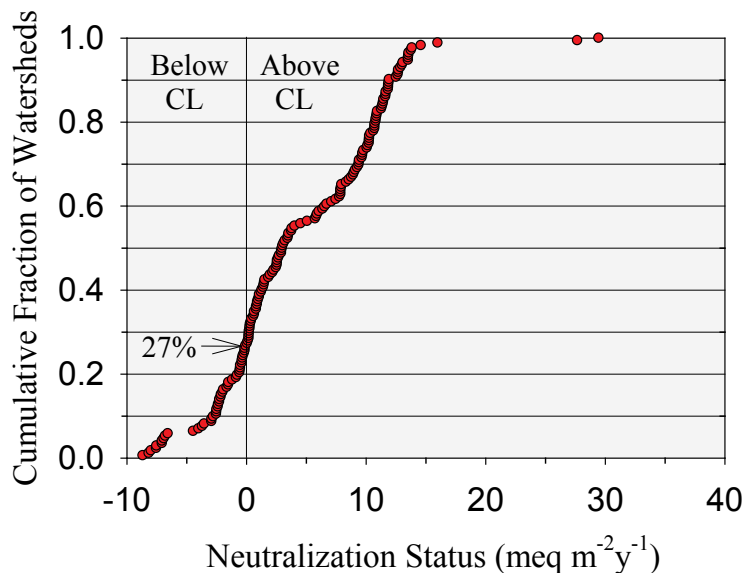
Figure 9. Neutralization status of 172 watersheds plotted as a cumulative fraction. The vertical line divides the distribution into values that are above and below the critical load (CL).

measurements of stream water taken in the March-April 2004 stream survey, 66% of these watersheds were determined to be at risk of mobilizing Al_i (Lawrence et al., 2008a). The similarity of these two percentages (73% and 66%) provides support for the veracity of the empirical CL estimates developed here. Results also indicate that, based on the approach used here for estimating atmospheric deposition, 26% of the watersheds were receiving S + N deposition in 2000 to 2004 that was 10 to 30 meq m^{-2} yr^{-1} higher than their critical load (Figure 9), which would be equivalent to 1.6 to 4.8 kg S ha^{-1} yr^{-1} or 4.8 to 14.4 kg SO_4^{2-} ha^{-1} yr^{-1} if all acidic deposition occurred as S.

3.2 Dynamic Critical Loads Modeling

Results of dynamic CL modeling with MAGIC are summarized in Table 2 for two endpoint years: 2050 and 2100. The CL results varied with selection of chemical criterion (ANC or BCS), threshold value, and endpoint year. Still, these differences were generally smaller than the observed differences across the 10 modeled study streams, which covered most of the range of stream chemistry of the WASS streams (Figure 9). Dynamic CLs were consistently high (ranging from approximately 250 to 500 meq m^{-2} yr^{-1}) for two study streams (watersheds 24001 and 28030). For five streams (i.e., watersheds 27020, 27026, 35014, and both Buck Creek tributaries), CL values were often estimated to be zero (threshold not attainable by the endpoint year even with zero acidic deposition) and were consistently less than 60 meq m^{-2} yr^{-1} for various combinations of chemical criterion, critical threshold value, and end year. The calculated CL to prevent mobilization of Al_i by the year 2050, based on keeping the BCS above 0, ranged from 0 meq m^{-2} yr^{-1} for

Table 2. Simulated dynamic critical load results for 10 study watersheds to achieve various ANC and BCS criteria values by the years 2050 and 2100 using the MAGIC model.

| | Critical Load of S Deposition (meq m^{-2} yr^{-1}) | | | | | | | |
| Stream Name | ANC=20 µeq L^{-1} | | ANC=50 µeq L^{-1} | | BCS=0 µeq L^{-1} | | BCS=25 µeq L^{-1} | |
End Year	2050	2100	2050	2100	2050	2100	2050	2100
Watershed 24001	507	359	489	344	495	349	480	337
Watershed 24002	115	93	82	68	94	76	63	54
Watershed 27020	0	12	0	0	0	9	0	0
Watershed 27026	0	6	0	0	0	0	0	0
Watershed 28011	187	135	125	93	189	137	138	102
Watershed 28014	58	53	13	24	65	59	31	35
Watershed 28030	341	278	317	257	327	265	307	248
Watershed 35014	23	23	0	0	0	0	0	0
Buck Creek North	33	33	0	0	0	0	0	0
Buck Creek South	49	44	0	3	54	47	6	15

four study streams, to over 175 meq m^{-2} yr^{-1} for three study streams. The remaining three study streams had CLs to maintain BCS > 0 in the year 2050 between 54 and 94 meq m^{-2} yr^{-1}.

There was not a clear relationship between the model estimates of dynamic CL, using the various ANC and BCS threshold values and soil B horizon BS (Figure 10). Base saturation measures total exchangeable bases as a percent of total exchangeable cations and in most soil horizons is generally related to BCS and ANC in surface waters (Lawrence et al., 2008b; Warby et al., 2009). Nevertheless, the result in Figure 10 was not unexpected, based on WASS results that showed a stronger relationship between stream water BCS and Oa horizon BS as compared with B horizon BS (Figure 11). The use of base-flow chemistry rather than high-flow chemistry to calculate the dynamic CL likely weakened the relationship in Figure 10 because base flow tends to reflect subsoil neutralization processes. In general terms, the simulated dynamic CL was lower at lower levels of BS, but the relationship was very noisy (Figure 10). Nevertheless, Figure 10 shows that a CL below 75 meq m^{-2} yr^{-1} was only found to occur in streams having watershed soil BS below about 12% in the B horizon.

The BCS-BS relationship from WASS results indicated that without accounting for variations in deposition, the BCS equaled zero at a B horizon BS of about 12.2% (Figure 11). Similarly, Sullivan et al. (2008) found that stream ANC in Shenandoah National Park was below about 20 µeq L^{-1} only in watersheds having soil BS less than about 12%. Because DOC concentrations in Shenandoah streams are low, this ANC value approximately equals the BCS value. A similar result was found for Adirondack lakes by Sullivan et al. (in review b). These results suggest that acid sensitivity near the threshold of Al$_i$ mobilization is generally associated with streams that drain soils having BS in the B horizon below about 12%. Figure 11 further indicates that if the BS of the Oa horizon is used, the critical BS value is near 40%.

Figure 10. Simulated dynamic critical load for the 10 study sites needed to achieve designated stream chemistry targets for ANC and BCS in the year 2100 versus measured watershed soil percent base saturation of the mineral B soil horizon. Results are shown for the study watersheds modeled using MAGIC relative to four critical ANC/BCS values (ANC = 20, 50 µeq L⁻¹; BCS = 0, 25 µeq L⁻¹).

Figure 11. Mean soil base saturation of the Oa horizon and upper 10 cm of the BS horizon in the 10 watersheds where soils were sampled during the WASS project, plotted as a function of base cation surplus in the streams of these watersheds during the March-April 2004 survey.

Dynamic CLs calculated for the 10 study watersheds modeled using MAGIC are mapped in Figures 12 through 15, based on the various chemical criteria, threshold values, and endpoint years. Calculated dynamic CL values were highly variable across a limited spatial extent. This result suggests considerable heterogeneity of soil, glacial till, and/or geology, which is well known in the Adirondack region (cf., Driscoll et al., 1991).

3.3   Scenario Modeling

MAGIC model hindcast simulations suggested that all of the modeled streams had ANC above 0 µeq L^{-1} in 1900. Nevertheless, five of the modeled streams had simulated pre-industrial ANC below 50 µeq L^{-1} and one had pre-industrial ANC below 20 µeq L^{-1} (Table 3). Simulated chemistry suggests that three of the modeled streams had an ANC ≤ 0 µeq L^{-1} in the year 2000. All except one of those streams were simulated to attain positive ANC by the year 2050 under existing and expected emissions regulations. Under increased emissions controls, beyond those already enacted and expected, all modeled streams were projected to have positive ANC by the year 2050. Improvements were largest for the Aggressive Emissions Controls scenario, especially if one considers improvements out to the year 2100 (Table 3).

Under the most aggressive of the emissions control scenarios considered, all of the study streams were projected to attain ANC above 20 µeq L^{-1}, but the year of attainment was variable from 2004 to beyond the year 2300 (Table 4). Four of the streams were projected to be unable to attain ANC above 50 µeq L^{-1} over

Table 3.   Projected stream ANC (in µeq L^{-1}) for the 10 study streams at different times in the past and the future, based on four scenarios of future emissions controls.

Stream	Hindcast and Recent Estimates		No Change Scenario		Existing Regulations Scenario[1]		Moderate Emissions Controls Scenario		Aggressive Emissions Controls Scenario	
	1900	2000	2050	2100	2050	2100	2050	2100	2050	2100
Watershed 24001	571	542	535	528	540	536	544	545	548	552
Watershed 24002	116	68	76	74	83	84	90	95	96	105
Watershed 27020	26	-13	-5	-6	0	2	6	12	11	20
Watershed 27026	12	-26	-14	-15	-7	-6	2	5	9	15
Watershed 28011	94	75	77	75	79	79	82	84	85	88
Watershed 28014	72	13	22	20	32	33	42	48	51	61
Watershed 28030	376	332	330	327	336	337	343	348	349	357
Watershed 35014	20	-9	-5	-8	5	4	18	18	30	32
Buck Creek North	32	8	15	13	19	19	25	26	29	33
Buck Creek South	48	16	20	16	27	25	34	36	40	44

[1]   Existing Regulations Scenario is based on full implementation of the Clean Air Act Title IV rules plus emissions reductions expected under controls proposed by the Clean Air Interstate Rule (CAIR).

Figure 12. Map showing simulated dynamic critical load to achieve ANC = 20 μeq L^{-1} by the year 2100 in the 10 modeled study streams.

Figure 13. Map showing simulated dynamic critical load to achieve ANC = 50 µeq L^{-1} by the year 2100 in the 10 modeled study streams.

Figure 14. Map showing simulated dynamic critical load to achieve BCS = 0 µeq L^{-1} by the year 2100 in the 10 modeled study streams.
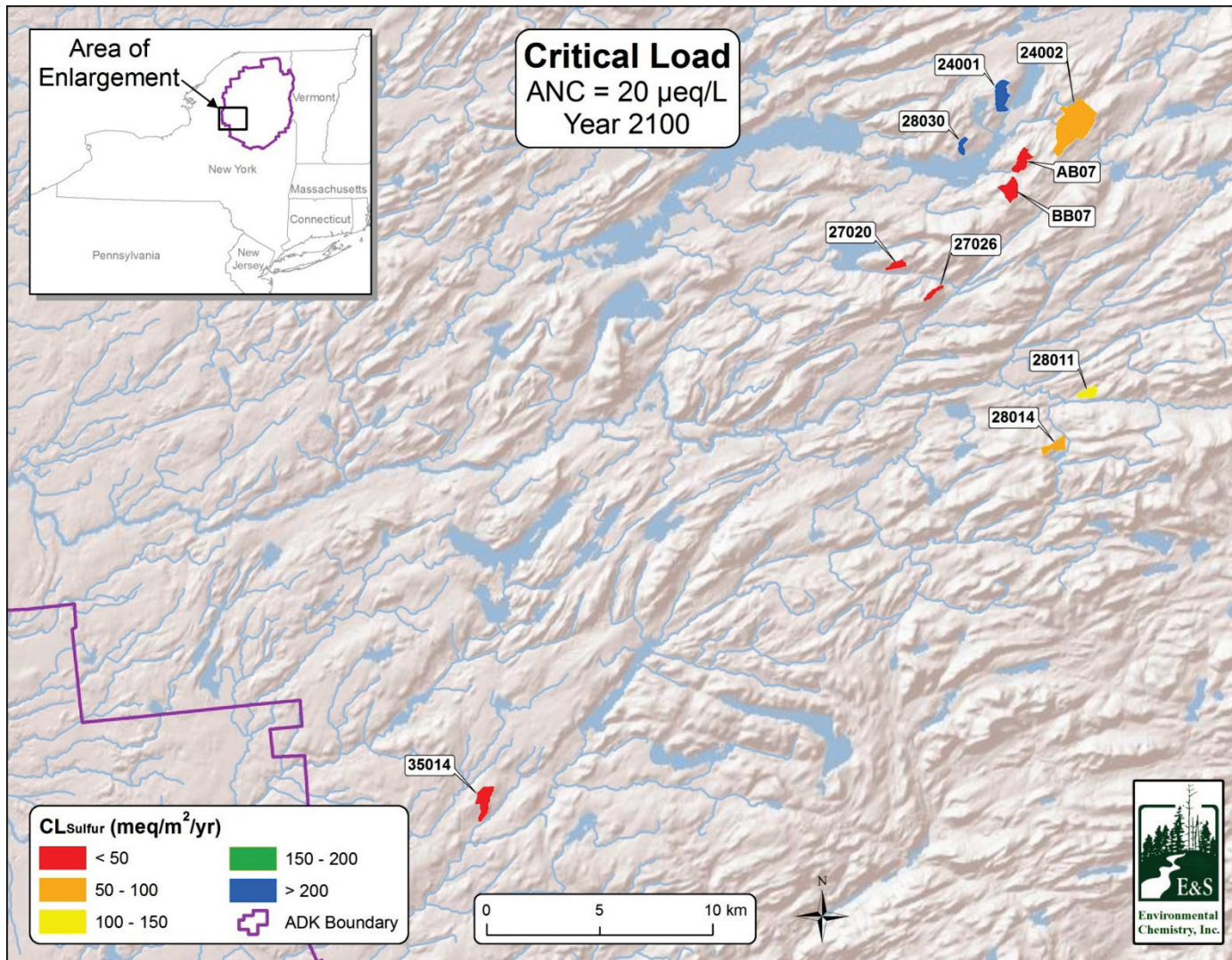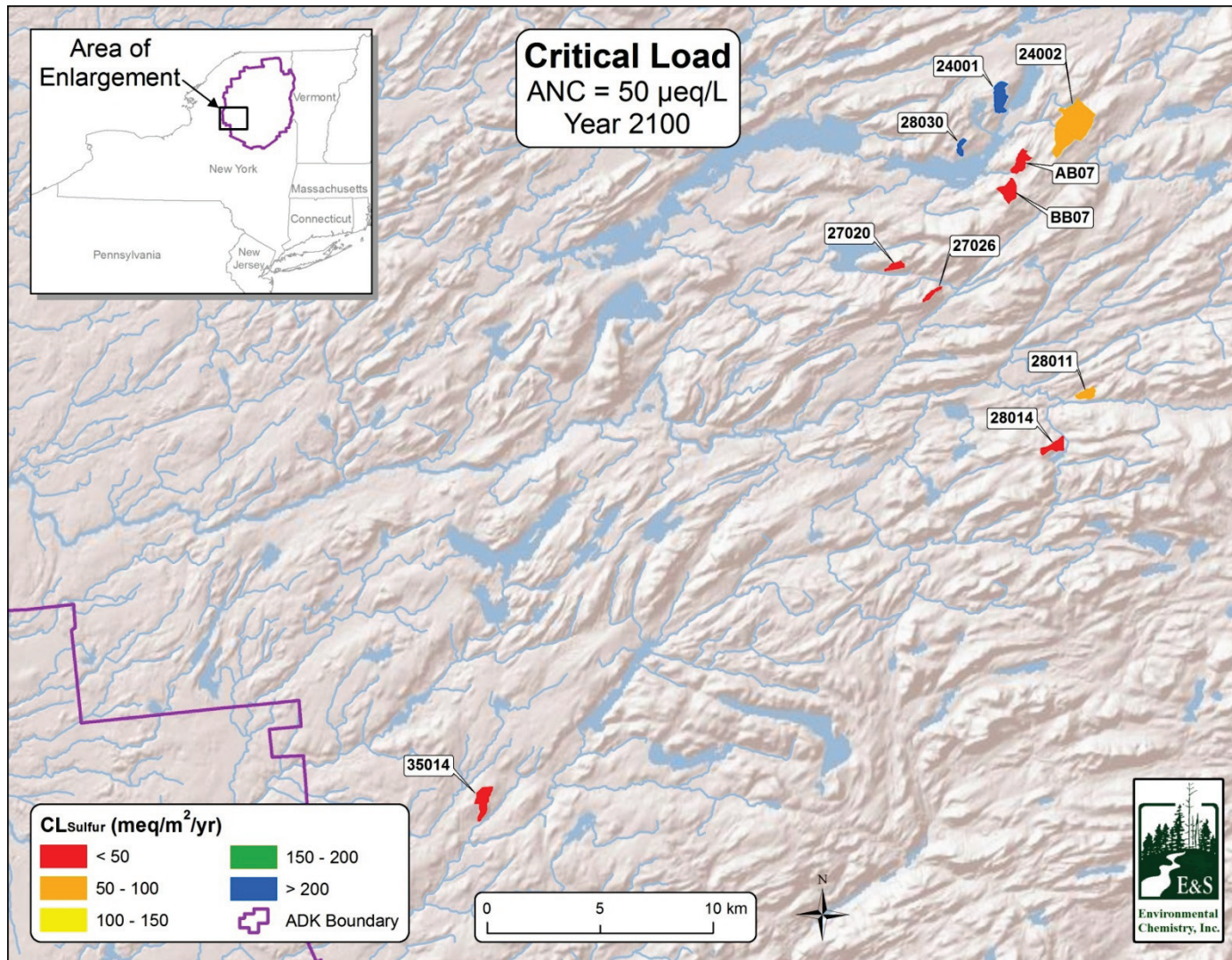
Figure 15. Map showing simulated dynamic critical load to achieve BCS = 25 µeq L^{-1} by the year 2100 in the 10 modeled study streams.

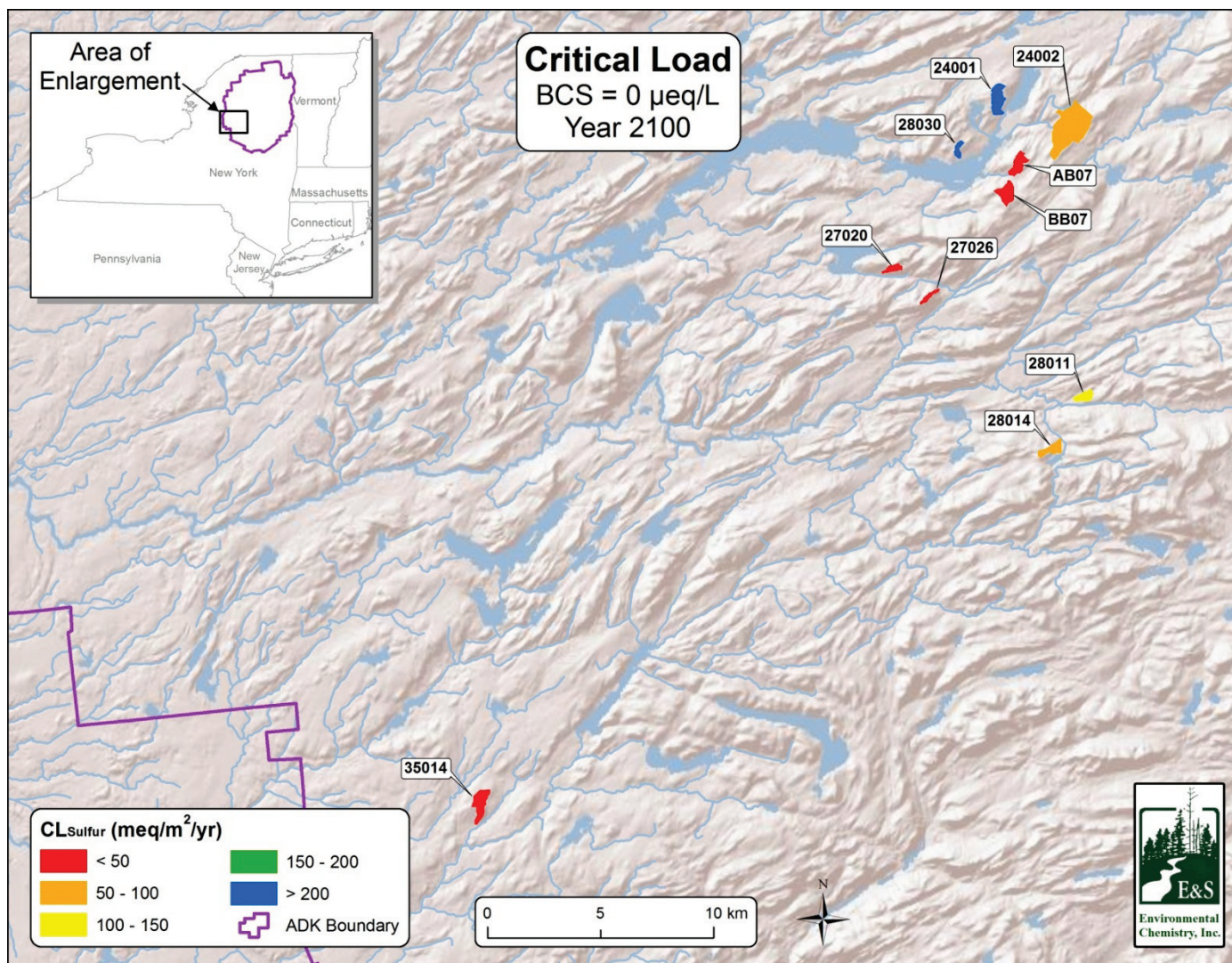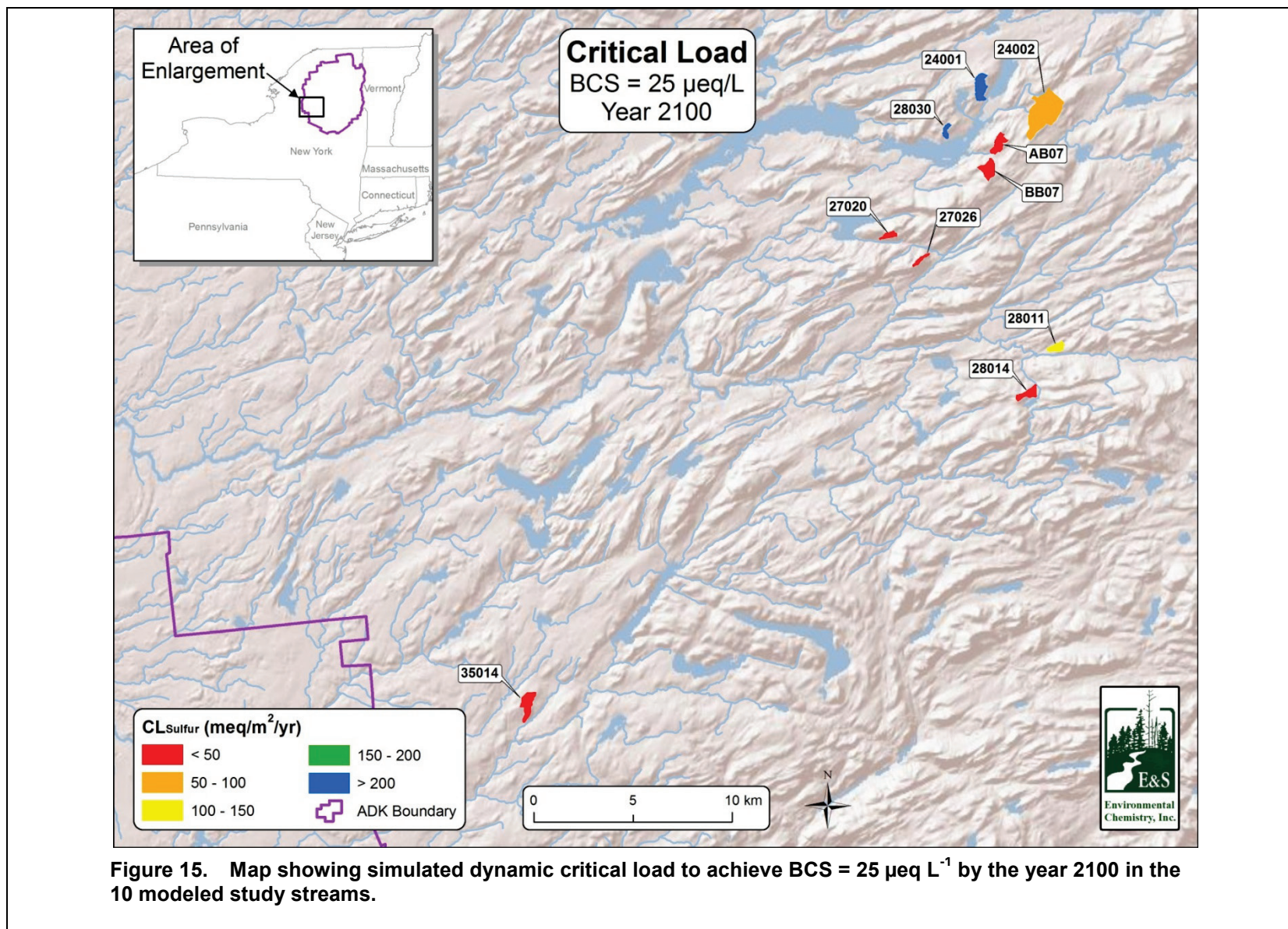**Table 4.** Time in the future at which the ANC of study streams is projected to reach or exceed certain benchmark values under the Aggressive Emissions Controls scenario.

| | Future Year at which Benchmark Chemistry is Achieved[1] | | | |
| | ANC Benchmark (μeq L^{-1}) | | BCS Benchmark (μeq L^{-1}) | |
Stream	20	50	0	25
Watershed 24001	NA	NA	NA	NA
Watershed 24002	NA	NA	NA	NA
Watershed 27020	2100	--	2125	--
Watershed 27026	> 2300	--	--	--
Watershed 28011	NA	NA	NA	NA
Watershed 28014	2010	2050	NA	2025
Watershed 28030	NA	NA	NA	NA
Watershed 35014	2020	--	--	--
Buck Creek North	2020	--	--	--
Buck Creek South	2010	>2300	NA	2065

[1] NA – not applicable. For these streams, ANC or BCS in the year 2000 was already above the designated benchmark value. Dashed line indicates that the benchmark cannot be attained even if acidic deposition is reduced to zero and held at that level for 300 years.

the next 300 years. These same four streams were projected to be unable to attain BCS above 25 μeq L^{-1} and three were projected to be unable to attain BCS above 0 μeq L^{-1}.

3.4 Exceedance

Critical load exceedance was calculated as the extent to which current acidic deposition exceeds the dynamic CL within a given watershed. Varying with chemical criterion, threshold value, and endpoint year, many of the study watersheds were found to be in exceedance (Figures 16 through 19). In some cases, study watersheds were in exceedance by more than 75% of ambient deposition (those colored red on the figures).

3.5 Comparison of Results from Empirical Critical Loads Modeling, Dynamic Critical Loads Modeling, and Scenario Modeling

The three methods presented for evaluating chemical effects of acidic deposition provided different, but related information. This was in part due to differences in the way deposition values were used to determine CLs. The empirical CL method used the sum of S and N deposition, whereas the dynamic CL values listed in Table 2 are for S deposition, although CAIR levels of N deposition were used as constant background levels to model the S CLs. Therefore, if the output from the dynamic CL modeling included the background levels of N, rather than just S, the dynamic CL values shown in Table 2 would be higher than presented.

Figure 16. Map showing simulated dynamic CL exceedance in the modeled study streams, based on achieving ANC = 20 µeq L^{-1} by the year 2100 and ambient deposition estimated for 2002.

Figure 17. Map showing simulated dynamic CL exceedance in the modeled study streams, based on achieving ANC = 50 µeq L^{-1} by the year 2100 and ambient deposition estimated for 2002.

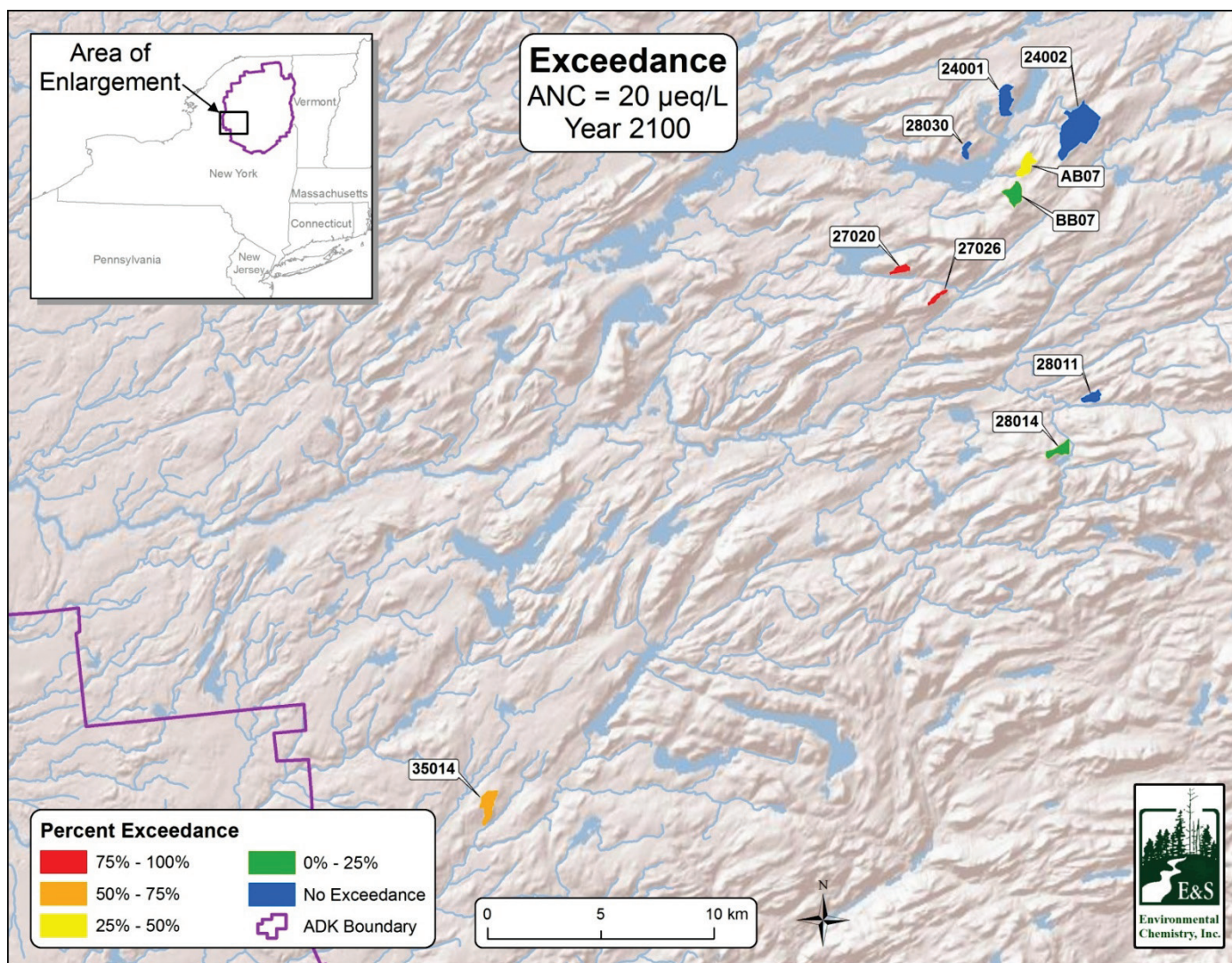**Figure 18.** Map showing simulated dynamic CL exceedance in the modeled study streams, based on achieving BCS = 0 µeq L^{-1} by the year 2100 and ambient deposition estimated for 2002.

Figure 19. Map showing simulated dynamic CL exceedance in the modeled study streams, based on achieving BCS = 25 µeq L^{-1} by the year 2100 and ambient deposition estimated for 2002.
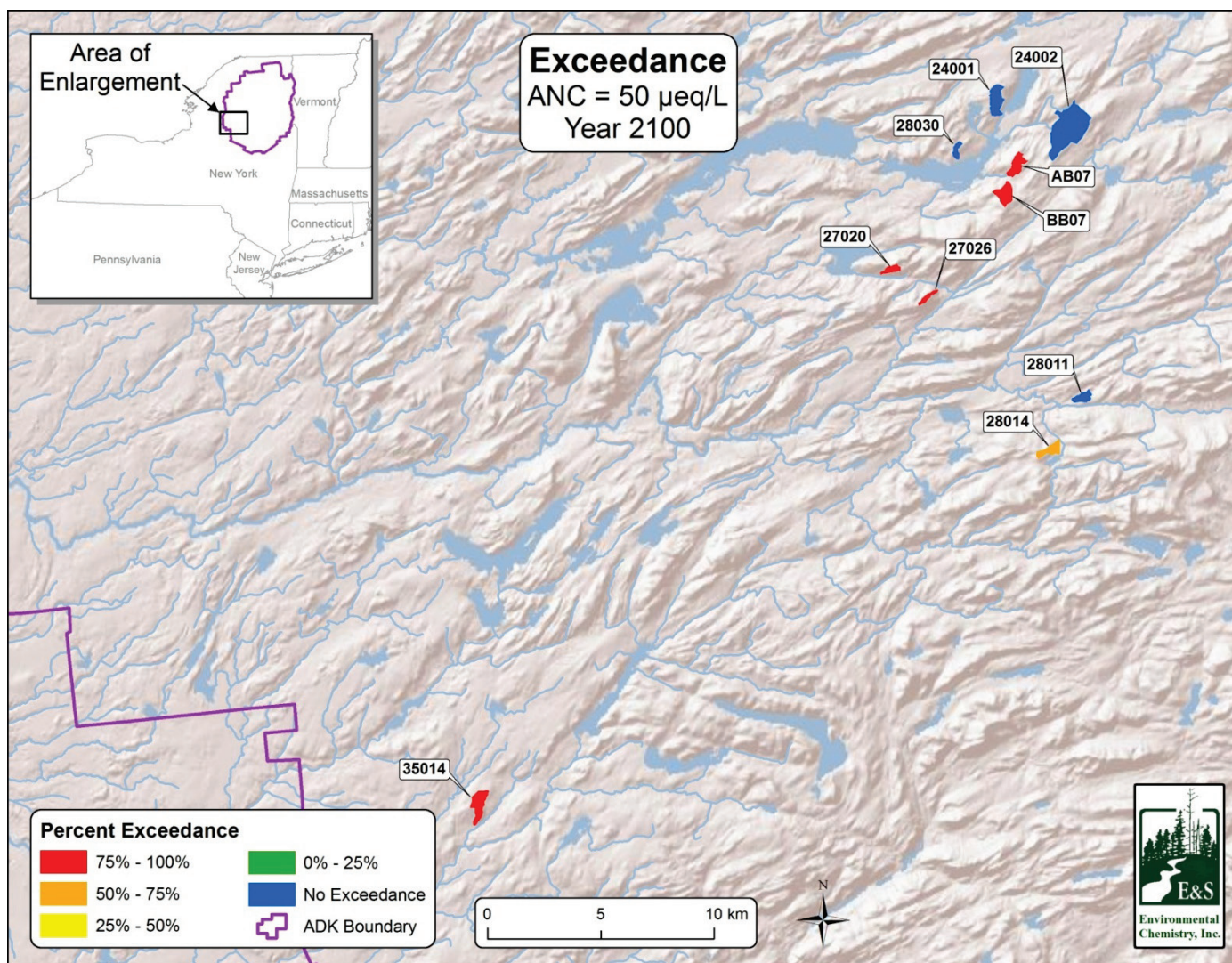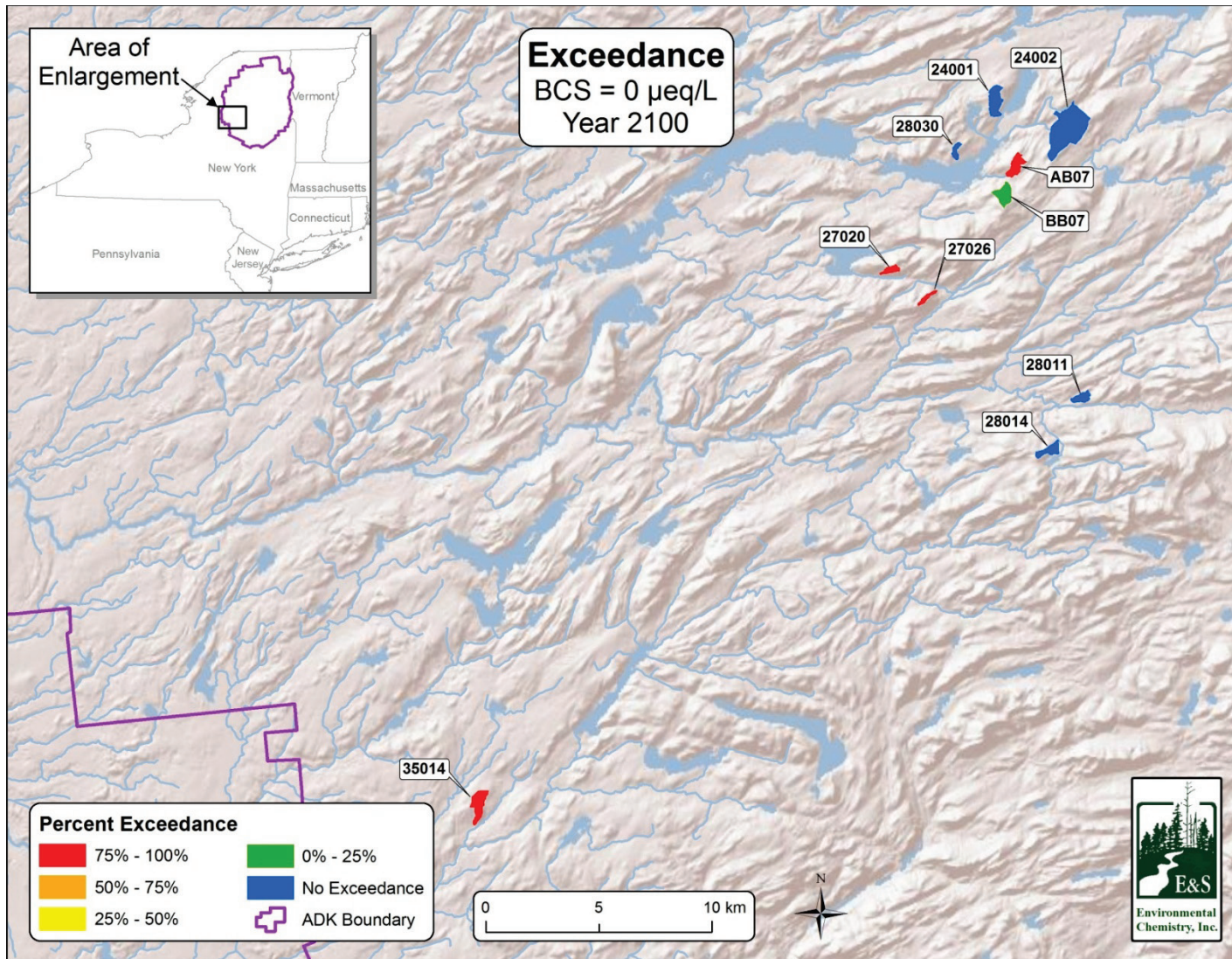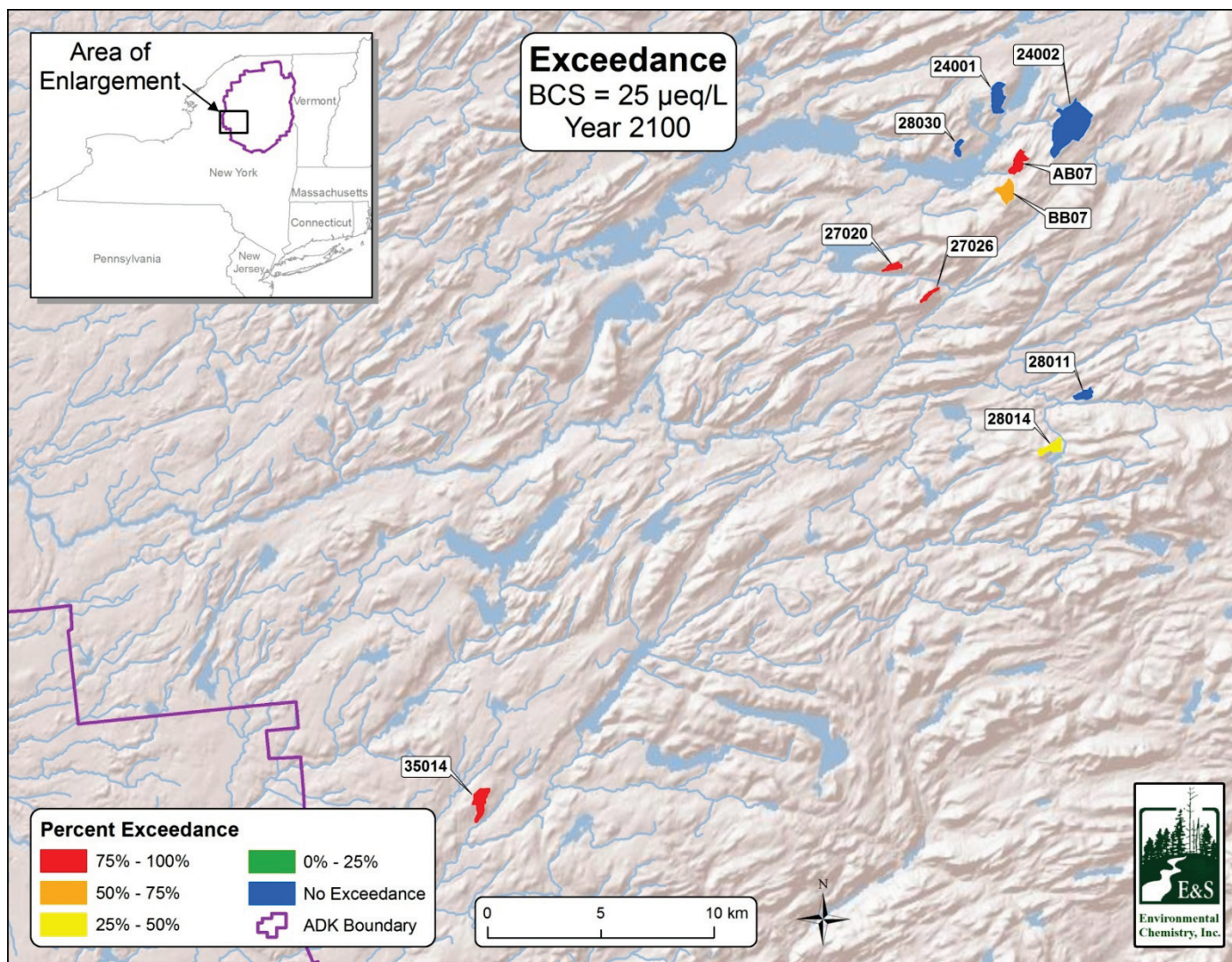
The empirical CL method provides information on the current neutralization status and suggests that if deposition levels were approximately 10 meq m^{-2} yr^{-1} lower than ambient values, the percentage of these watersheds mobilizing Al$_i$ would decrease from 77 % to 23%. This does not address future conditions that could include changes in soil BS. The MAGIC dynamic CL modeling provides the CL at which a certain condition of stream chemistry could be achieved within 50 or 100 years. Results indicated that four of ten streams would not achieve a BCS of zero by 2050 even if deposition were zero, and two other sites would require deposition to be nearly halved to achieve this BCS level. Although not directly comparable, the empirical CL results were consistent with the MAGIC dynamic CL results in suggesting that six of these streams are currently receiving acidic deposition above their CL for Al$_i$ mobilization, and that would not be expected to change by 2050 (Table 2). All of the streams in these watersheds were severely acidified (BCS values of -54 to -146 in the March-April 2004 survey).

Dynamic CL estimates from the MAGIC modeling for the three most strongly buffered watersheds (watersheds 24001, 28011, and 28030) indicated that current deposition could be increased by approximately two-to-five times through the year 2050 without causing Al$_i$ mobilization (Table 2, BCS < 0). Nevertheless, the empirical approach indicated that two of these sites were receiving deposition that was only 1 to 3 meq m^{-2} yr^{-1} below the CL for Al$_i$ mobilization, and one site was already in exceedance of the CL. This apparent discrepancy was likely related to differences in the CL calculation depending on whether base-flow or high-flow chemistry was modeled, and would have been larger had the dynamic CL results been expressed as S + N. In watersheds with substantial till deposits, base flow is controlled by subsoil neutralization as water passes through the till en route to surface waters, whereas during high flow, acidic upper soil horizons exert important control over stream chemistry. Till deposits, where they exist, vary in thickness and neutralization capacity, but are likely to have a much greater neutralization capacity than the upper soil.

The S deposition rate to avoid Al$_i$ mobilization up to the year 2050 in watershed 24001 was estimated by the dynamic S CL modeling to equal 495 meq m^{-2} yr^{-1} (Table 2). With soil data available for this watershed (Oa thickness = 9.9 cm; bulk density = 0.25 g cm^{-3}, average Oa exchangeable Ca concentration = 7.2 cmol$_c$ kg^{-1}), the total pool of exchangeable Ca in the Oa horizon was determined to be approximately 2200 meq m^{-2}. This pool size equates to about 4.5 years of Ca at a leaching rate of 495 meq m^{-2} yr^{-1} if all of the leaching occurs in the Oa horizon and no replenishment occurs. Certainly, replenishment at some rate does occur through root uptake in the mineral soil followed by redistribution back to the soil via litterfall, throughfall, and stemflow. Some leaching would occur in the B horizon, but this would be a small fraction of total leaching because the concentration of exchangeable Ca in this horizon is only 1.1 cmol$_c$ kg^{-1}. Data on Ca cycling are not available for watershed 24001, but inputs of litterfall, stemflow, and throughfall at the Hubbard Brook Experimental Forest, a mature northern hardwood forest similar to watershed 24001, were estimated to be approximately 240 meq m^{-2} yr^{-1} (Likens et al., 1998). If it is assumed that all of this Ca resulted from uptake in the mineral soil, then this rate of input would still only equal about half of the leaching rate. Still, much of the uptake does undoubtedly occur in the forest floor (Dijkstra, 2003), which

suggests that the rate of Ca replenishment in the Oa horizon is well below the value of 240 meq m^{-2} yr^{-1} and even farther below the estimated CL of 495 meq m^{-2} yr^{-1}. Although baseflow stream chemistry could continue to be neutralized under a relatively high CL, this would be at the expense of the upper soil, through which acidic deposition first passes, depleting Ca and making the stream more susceptible to episodic acidification.

The comparative magnitude of these numbers suggests that the Oa Ca pool size would not be sustained under a deposition level of 495 meq m^{-2} yr^{-1}. The discrepancy between this deposition level and the Ca availability in the forest floor is most likely the result of using base-flow stream chemistry in the dynamic CL modeling and comparing these results with the Ca pool in the upper O_a horizon, which is most closely tied to stream chemistry during high-flow conditions. The Ca concentration in stream water during base flow reflects relatively deep flow paths that are likely to be intercepting subsoil materials that are much more enriched in Ca than the upper soil horizons that are better reflected in stream chemistry during high flow. The BCS in watershed 24001 during the March-April 2004 high-flow sampling was 212 μeq L^{-1}, whereas the concentration during low flow in August 2003 was 563 μeq L^{-1}. These results emphasize the importance of using high-flow stream chemistry for assessing processes of acidification and recovery in the ecologically significant upper soil horizons. The overall comparison between the MAGIC dynamic CL estimates and the empirical CL estimates indicates a consistency for watersheds that are acidic most, if not all, of the year (chronically or near chronically acidic). These watersheds are likely to have little or no till to provide substantial neutralization during base flow. For watersheds that do have more substantial till deposits, estimates of the CL become more dependent on whether base flow or high flow is modeled.

The scenario modeling can be coupled with the empirical CL modeling to provide estimates of the mechanisms and timing of chemical recovery. Under the most aggressive emissions controls considered, only the three most highly buffered streams achieved ANC values significantly above 50 μeq L^{-1} by 2050. These are the three watersheds that are currently receiving deposition below or just above their CL based on the dynamic and empirical CL estimates. The watersheds currently receiving more S deposition than their CL showed limited recovery response even under the most aggressive emission reductions.

The comparison of the empirical CL results with the scenario results was complicated by effects of using base-flow chemistry versus high-flow chemistry. The scenario estimates of stream water ANC suggested that only three of the ten watersheds had negative ANC in 2000 (Table 3), whereas all of the watersheds, with the exception of Watershed 24001, had negative ANC values during the March-April 2004 survey. As in the comparison with dynamic CL modeling, these results suggest that the current empirical CL results are most relevant to scenario modeling in chronically acidified watersheds.

Additional research is ongoing to quantify CL values for protecting both ANC and soil BS to various critical threshold values in Adirondack watersheds (Sullivan et al., in review a, b). Results of these various CL and exceedance modeling efforts will aid in the management of acid-sensitive aquatic and terrestrial resources in New York.

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Comparison of Methods for Estimating Critical Loads of Acidic Deposition in the Western Adirondack Region of New York

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