Final Report

Modeling the Timeline for Acidification from Excess Nitrogen Deposition in Rocky Mountain National Park

Rocky Mountain National Park
Intermountain Region
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Contact Information:
Dennis S. Ojima[1] and Jill S. Baron[1,2]
[1]Natural Resource Ecology Laboratory
Colorado State University
Fort Collins CO 80523-1499
dennis@nrel.colostate.edu
jill@nrel.colostate.edu
970-491-1968
[2]U.S. Geological Survey

Project Summary

Excess nitrogen (N) deposition has two effects on ecosystems, eutrophication and acidification. Eutrophication occurs before acidification, and is the consequence of stimulating plant and microbial growth by adding a nutrient that had previously only been available in limited amounts. Nitrogen saturation occurs when more N is available than plants and microbes can take up and store, causing excess mobile nitrate to flush through soils into surface and groundwaters. Leaching of the strong acid anion nitrate, or nitrogen saturation, leads to reduction of soil base cations and acidification. Previous research by us and others has shown the occurrence of nitrogen saturation at high elevations of the Colorado Front Range. Among the consequences noted already from excess nitrogen has been nutrient enhancement, or eutrophication, of terrestrial and aquatic ecosystems. For this project, cooperatively funded by NPS and EPA, we asked when and at what levels of atmospheric N deposition did eutrophication occur in the past, and when and at what levels of atmospheric N deposition will acidification occur in the future under current and potential rates of nitrogen deposition. We performed two activities: estimating past atmospheric deposition of both N and S based on emissions, population growth records, and correlations of current deposition with emissions; and development and application of a model, DayCent-Chem, a hybrid of an ecosystem biogeochemical model, DAYCENT, with a soil chemical equilibrium model, PHREEQC (Figure 1; Hartman et al. in revision). DayCent-Chem was applied in hindcasting mode to look at changes in biogeochemistry over the past century, and in forecasting mode to ask how much N deposition must occur for soil buffering to fail, causing alpine ROMO lakes to acidify.

An N deposition history was reconstructed using historic VEMAP climate and exponential equations that correlated well with EPA-reported NO_x emissions from Colorado, from the sum of emissions of 11 western states, and with population growth rates in Colorado from 1900 to 2000. The mean wet N deposition value for the period 1950-1964, corresponding to the reported time of alteration of diatom assemblages in alpine lakes in Rocky Mountain National Park, was approximately 1.5 kg N ha^{-1} yr^{-1}. This value becomes the critical load defining the

threshold for ecological change from eutrophication (Baron in press).

Sulfate deposition histories were reconstructed from EPA emissions estimates and daily historic VEMAP climate. The combined N and S reconstructions were used as inputs to DayCent-Chem to investigate the changes in soil and stream water chemistry that may have occurred in an alpine ecosystem since 1900 (Figure 2). Simulations were run for Andrews Creek, an alpine sub-catchment of Loch Vale Watershed in Rocky Mountain National Park (Figures 3 and 4). The model estimated that mean annual stream pH and ANC were highest in 1900, and that annual dynamics were highly responsive to SO_4 deposition. Minimum pH and ANC occurred in conjunction with the highest SO_2 emissions in the late 1960s-70s, before measurements began. Soil base saturation was higher in 1900 compared to the late 1990's. Over the past century, simulated stream [NO_3^-], like precipitation [NO_3^-], increased exponentially with NO_x emissions, while stream [SO_4^{2-}] reflected the interannual variability of SO_2 emissions that peaked between 1960 and 1980 for the western U.S.

DayCent-Chem forecasts predicted episodic acidification when total nitrogen deposition averaged 6.6 kg N ha^{-1} yr^{-1} (range of 6.3-7.1 kg N ha^{-1} yr^{-1}) for Andrews Creek. Episodic acidification was simulated to occur 10-19 years, 28-30 years, or 44-45 years into future if annual deposition increased at rates of 5.0%, 2.5%, or 1.25% yr^{-1} from 2003 to 2048 (Figure 5). The model predicted acidification to happen yearly when nitrogen deposition exceeds 7-8 kg N ha^{-1} yr^{-1}; this deposition rate occurred after 26-33 years in the +5.0% yr^{-1} scenarios, and after 43-45 years in the +2.5% yr^{-1} scenarios. Deposition rates of 14 kg N ha^{-1} yr^{-1} were predicted to cause chronic acidification in Andrews Creek (Figure 6). Simulated alpine tundra production and soil organic matter turnover was limited by air temperature and duration of snow cover and did not respond to increasing nitrogen deposition (Hartman et al. in prep.).

Project Description

Problem Purpose: In this project we addressed three questions: 1) what was the N and S deposition history to Loch Vale Watershed in Rocky Mountain National Park; 2) what were biogeochemical and ecological responses to deposition since 1900; and 3) how much additional N deposition is necessary to depress soil base saturation and cause surface waters to acidify? The third question was proposed and funded; the first two were added in later in order to address subsequent questions posed by the National Park Service. High elevation ecosystems of Rocky Mountain National Park (RMNP) are sensitive to atmospheric deposition, due to slow-weathering granitic bedrock, harsh climate, sparse vegetation, and high quantities of precipitation (Figure 3; Baron 1992). Nitrogen wet deposition of 3-5 kg N ha^{-1} to the east side of the Colorado Front Range in RMNP, in the form of nitrate and ammonium, is among the highest measured in the State. Precipitation pH values are more acidic than is natural (NADP 2000, Baron et al. 2000). Stream chemical records from the Green Lakes south of Rocky Mountain National Park suggest acidification of headwaters during spring snowmelt (Williams and Tonnessen 2000). Studies of the ecological response to elevated N deposition reveal that significant terrestrial and aquatic responses have already occurred (Baron et al. 2005). Fertilization experiments in alpine tundra show a response at the plant community level, where more N favors the dominance of grasses, in particular *Deschampsia caespitosa* (L.) P. Beauv. over what is currently the dominant flowering plant *Acomosytlis rossii* (R. Br.) Greene (Bowman et al. in press). Old-growth Englemann spruce show significant increases in forest nutrient cycling rates and soil microbial activity where N deposition is high (Rueth and Baron 2002, Baron et al. 2000). Alpine lake algal diatom communities show a significant shift toward mesotrophic disturbance species over the past 50 years in lakes with high nitrate concentrations, but not in lakes with low nitrate concentrations (Wolfe et al.2001, 2003). And, a forest fertilization experiment in Loch Vale watershed has shown a significant trend of increased leaching of nitrate, ammonium, and base cations in treatment plots (Rueth et al. 2003). It is clear that excess N from atmospheric deposition has altered tundra, forest, and lake ecosystems (Baron et al. 2005).

Continued N deposition on terrestrial and aquatic systems has the potential to cause lake and stream acidification. The acidification process will be somewhat similar to that caused by sulfate, in that the processes are mediated through the soils. There is an important difference, however. Because nitrogen is a critical, and often unavailable, plant nutrient, any realistic projection of nitrogen-caused acidification must include understanding ecosystem nutrient cycling. Great Smoky Mountains National Park is an example of an area where N saturation has caused acidification. The park receives extremely high amounts of both nitrogen and sulfur pollution, and has reported fish kills in downstream fish hatcheries related to episodic acidification from nitrogen flushing from nitrogen-saturated soils (Cook et al. 1994).

Soils control the potential for lake and stream acidification, through soil base cations availability. Base cations, such as calcium and magnesium, leach from soils with acid anions such as sulfate and nitrate. Long-term loss of soil base cations in the northeastern U.S. is thought to have been initiated with the onset of acid rain between 1950 and 1955 (Likens et al. 1996). In the Colorado Front Range, lake sediment records show that algal communities began to change during this same time period. This is commensurate with in increase in human population, synthetic fertilizer use, and industrial livestock operations (Baron et al. 2000). Although the total input of strong acid anions in Colorado precipitation is far less than that recorded from sites in the eastern U.S., the Rockies are more sensitive than eastern ecosystems because of strong climatic limits on microbial and plant N uptake abilities (Fenn et al. 1998). This proposed research brings Loch Vale watershed research full circle back to its origins in acid rain research. Nitrogen deposition is not acid rain, *per se*, but it will lead to acidification of aquatic systems as mediated by soil biogeochemistry.

Objectives: The initial research objective was to project, both in time, and in deposition amounts, the rate of change in soil buffering capacity until capacity is depleted to the point of causing episodic or chronic lake acidification. We added an additional objective in response to requests from NPS to address questions about ecological critical loads. Since wet and dry deposition have only been measured in the US for 25 years, but nitrogen-caused eutrophication of high elevation lakes in RMNP occurred approximately 50 years ago, we developed proxy methods for estimating deposition amounts since 1900. The 1950-1964 deposition values corresponding to a shift in algal diatom assemblages define the threshold, or critical load, below which no observable ecological change is observed.

Methods for determining past deposition: The Loch Vale National Atmospheric Deposition Program (NADP) site, CO98, is located at 3159 m in a subalpine forest clearing. Annual inorganic wet nitrogen concentrations (mg N L^{-1}) of NO_3 and NH_4 were obtained from NADP (http://nadp.sws.uiuc.edu/). Loch Vale data from calendar year 1988 were excluded due to four months of missing data. Annual inorganic wet N deposition was calculated by multiplying measured NO_3-N and NH_4-N concentrations with measured precipitation from NADP. Pre-measurement NO_3-N and NH_4-N concentrations were extrapolated from measured concentrations using both linear and exponential functions with least squares regressions (Microsoft Excel 2002). Pre-measurement NO_3-N and NH_4-N depositions were calculated by multiplying both the linearly and exponentially estimated concentrations with two methods of estimating past precipitation: the mean annual 1984-2002 annual precipitation (1055 mm); and VEMAP-derived precipitation for 1900-1983 (Kittel et al. 1996). A pre-industrial "anchor" deposition value of 0.5 kg N ha^{-1} yr^{-1} was set for 1900 (Holland et al. 1999). Of that, 80% was assigned as NO_3-N, and 20% was assigned as NH_4-N, after Holland et al. (1999).

Pre-measurement SO_4 deposition was calculated from EPA NEI SO_2 emissions estimates and VEMAP-derived precipitation from 1900-1983. Since SO_2 can be transported long distances, several combinations of state emissions were tested against measured 1984-2001 SO_4 deposition to determine the best source area match. Correlations were highest for emissions from Arizona alone (0.73), moderately high (0.65) for the six states surrounding Colorado plus Colorado, slightly lower (0.55) for all western states, and negatively related to Colorado SO_2 emissions alone (-0.55). In all emissions estimates, SO_4 deposition was greatest in 1969, the year of peak smelter emissions from AZ.

The combined N and S deposition scenarios show deposition was lowest in 1900. High N and S deposition have persisted, with interannual variability, since the late 1960s, but whereas the values in the 60s and 70s could be attributed to SO_2 emissions, increasing NO_x and NH_3 emissions have kept the strong acid anion input high even as SO_2 emissions declined (Figure 2).

The hindcasting work was conducted jointly by Jill Baron and Melannie Hartman. The nitrogen hindcasting manuscript was written by Baron.

<u>Methods for determining biogeochemical responses to deposition:</u> We developed a non-spatial biogeochemical model to simulate soil and surface water chemistry by linking the daily version of the CENTURY ecosystem model (DayCent) with a low temperature aqueous geochemical model, PHREEQC. The coupled model, DayCent-Chem, implements a multi-layered soil system and simulates the daily dynamics of plant production, soil organic matter, soil water and temperature, cation exchange, mineral weathering, elution, stream discharge, and solute concentrations in soil water and stream flow (Figure 1). We applied the model to Andrews Creek in RMNP (Figures 3 and 4). By aerially weighting the contributions of separate bedrock/talus and tundra simulations, the model was able to replicate the measured seasonal and annual stream chemistry for most solutes (Hartman et al. in revision). Simulated soil chemistry, net primary production, live biomass, and soil organic matter for tundra matched well with measurements.

Model development was conducted by Melannie Hartman, with constructive advice by Dennis Ojima and Jill Baron. Manuscripts were written by Hartman, with substantive and editorial advice from Baron and Ojima.

Accomplishments

The major accomplishments of the project were to 1) develop and apply the DayCent-Chem model to past, present, and future ecosystem biogeochemistry, and 2) reconstruct plausible past deposition values and use them to define the ecological critical load for lake trophic state and 100 years of stream biogeochemistry.

Four 48-year future N deposition scenarios were tested: "control" runs where deposition amounts were kept similar to measured values, "low" runs where N deposition ramped up at a rate of 1.25%/yr, "medium" runs with a rate of increase of 2.5%/yr, and "high" runs where deposition increased at 5%/yr. The rate of increase determined the approximate year in which acidification would occur, but the amount of annual N deposition that caused acidification was similar across scenarios. Episodic acidification occurred in some, but not all, years at deposition values of 6.6 kg N ha^{-1} yr^{-1}. Episodic acidification occurred every year when deposition values reached 7.5 kg N ha^{-1} yr^{-1}, and chronic acidification with annual ANC <0 occurred at 14 kg N ha^{-1} yr^{-1} (Figures 5, 6). The soonest episodic acidification would begin with the 5% annual rate of N deposition increase is 2015, or ten years into the future. Slower rates of increase would cause a delay of up to several decades before acidification would begin, and the model shows that maintenance of deposition rates at their current values prevents acidification from occurring at all.

The hindcasting exercise produce a paper that will be published in January or February 2006. Using the methods described above, it was determined that 1.5 kg N ha^{-1} yr^{-1} is sufficient deposition to alter the trophic state of alpine lakes in Rocky Mountain National Park. Independent lines of evidence or inference from experimental studies, ecosystem modeling, and paleolimnological records from northern Wyoming added credibility to the determination from hindcasting.

Manuscripts produced from this project:

Baron, J.S. 2005. Hindcasting nitrogen deposition to determine an ecological critical load. Ecological Applications, in press.

Baron, J.S., M.D. Hartman, and D.S. Ojima, 2005. Determining critical loads for eutrophication and acidification for alpine ecosystems of the Colorado Rocky Mountains. Extended abstract for proceedings of the Open Science Conference on Global Change in Mountain Regions, Perth, Scotland, in press.

Hartman, M.D., J.S. Baron, and D. S. Ojima. 1995. Application of a coupled ecosystem-chemical equilibrium model, DayCent-Chem, to stream and soil chemistry in an alpine watershed. Ecological Modeling, in revision.

Hartman, M.D., J.S. Baron, and D. S. Ojima. Modeling the timeline to stream acidification from excess nitrogen deposition in an alpine watershed in Rocky Mountain National Park, Colorado. In prep.

Presentations given as part of this project:

Hartman, M.D. Modeling the Timeline for Lake and Stream Acidification from Excess Nitrogen Deposition for Rocky Mountain National Park. Natural Resource Ecology Laboratory departmental seminar, Fort Collins, CO November 2004.

Baron, J.S., An update on Loch Vale watershed research. Departmental seminar, Department of Civil and Environmental Engineering, Syracuse University, November 2004.

Jill Baron, Melannie Hartman, Dennis Ojima, Brenda Moraska Lafrancois, Koren Nydick, Heather Rueth, Alex Wolfe, Jorin Botte. Nitrogen deposition in the Rocky Mountains: causes and consequences. Symposium on nitrogen eutrophication in xeric and agricultural systems, January 2005, Riverside CA, invited speaker.

Hartman, M.D. Jill S. Baron, Dennis S. Ojima, William J. Parton. Modeling the Timeline for Lake and Stream Acidification from Excess Nitrogen Deposition for Rocky Mountain National Park. George Wright Society, Philadelphia, PA, March 2005.

Baron, J.S., Consequences of nitrogen deposition in Rocky Mountain National Park. Colorado Air Quality Control Commission, Estes Park, CO, April 2005, invited speaker.

Baron, J.S., Consequences of nitrogen deposition in Rocky Mountain National Park. Presentation and field trip, Scripps Howard Institute on the Environment, Boulder and Rocky Mountain National Park CO, May 2005.

Baron, J.S., Consequences of nitrogen deposition in Rocky Mountain National Park. Colorado Institute for Leadership Training, Fort Collins , CO, June 2005, invited speaker.

Baron, J.S., Consequences of nitrogen deposition to Rocky Mountain National Park. Colorado Departments of Environmental Health annual meeting, Aspen, CO, July 2005, invited speaker.

Hartman, M.D. Jill S. Baron, Dennis S. Ojima. Calculating pre-measurement atmospheric deposition, stream chemistry, and soil chemistry for an alpine watershed in Rocky Mountain National Park, Colorado. Ecological Society of America annual meeting, Montreal, Canada, August 2005.

Hartman, M.D. Jill S. Baron, Dennis S. Ojima. Calculating pre-measurement atmospheric deposition, stream chemistry, and soil chemistry for an alpine watershed in Rocky Mountain National Park, Colorado. Poster presented at the NADP annual meeting, Jackson WY, September 2005.

Baron, J.S., Hindcasting nitrogen to determine and ecological critical load. Poster presented at the NADP annual meeting, Jackson WY, September 2005.

Baron, J.S., M.D. Hartman, and D.S. Ojima. Determining critical loads for eutrophication and acidification for alpine ecosystems of the Colorado Rocky Mountains. Open Science Conference on Global Change in Mountain Regions, Perth, Scotland, October 2005.

Failures

1. We have not yet developed a user-friendly interface for DayCent-Chem, although many parts are in place. There is a Century Model Interface available at http://www.nrel.colostate.edu/projects/century5/, although it does not include the PHREEQC portions of DayCent-Chem. A detailed list of necessary data and formats for input values and output validation values has been compiled and is available from Melannie

Hartman (melannie@nrel.colostate.edu) or Jill Baron (jill@nrel.colostate.edu). We are currently in the process of parameterizing the model for 12 other sites, including three national parks, and this is teaching us much about the difficulty of introducing others to the model. A "user-friendly interface" to such a complex model may not be possible.

2. A manuscript describing the timeline for acidification for Andrews Creek was rejected from ES&T. Some reviewer comments will be helpful for a revision of the paper, while others were not applicable. We plan to revise and submit to a different journal.

3. Andrews Creek sub-catchment was a poor choice for demonstrating the importance of terrestrial nutrient cycling on stream biogeochemistry. Only 11% of the area has vegetation, and it is tundra and alpine meadow. Cold temperatures prevent much plant response to nitrogen. We expect the role of vegetation in affecting N cycling to greatly increase in areas with greater plant cover and more moderate climates.

Figures:

1) DayCent-Chem conceptual model

2) Estimated N and S deposition to Loch Vale Watershed, 1900-2001

3) Photo of Andrews Creek sub-catchment looking uphill from Andrews Tarn, Loch Vale Watershed.

4) Photo of Andrews Creek sub-catchment looking downhill from Andrews Tarn, Loch Vale Watershed.

5) Model output showing daily stream ANC over time with N deposition similar to current rates of 3.0-5.0 kg N ha/yr (red) and a 5% annual increase in N deposition (blue) for Andrews Creek. Episodic acidification occurs for the first time in 2015 when the average N deposition rate is 6.6 kg N ha/yr and ANC falls to negative values (first yellow arrow). By 2033 acidification occurs yearly (second yellow arrow) when the average deposition rate reaches 7.5 kg N ha/yr.

6) Model outputs depicting a) annual ANC at different annual N deposition rates for Andrews Creek, and b) number of days with ANC <0 at different N deposition rates for Andrews Creek.

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NPS-ACID2
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17.50%, TD

MODELING THE TIMELINE FOR ACIDIFICATION FROM EXCESS NITROGEN DEPOSITION IN ROCKY MOUNTAIN NATIONAL PARK

Jill Baron - Dennis Ojima
6/1/2004 to 3/31/2006

Subcode	Description	Budget	Current Month Expenses	Spent through 11/30/05	Month End Balance	Projection	Projected Balance
2111	ADMINISTRATIVE PRO SALARY	6,531.00	0.00	0.00	6,531.00	0.00	6,531.00
2111	HARTMAN,MELANNIE	0.00	66.15	6,254.85	-6,254.85	264.60	-6,519.45
Subtotal for Salaries and Wages		6,531.00	66.15	6,254.85	276.15	264.60	11.55
2112	BENEFITS - ADMIN PROF SALARY	1,313.00	13.43	1,257.92	55.08	53.72	1.36
Subtotal for Fringe Benefits		1,313.00	13.43	1,257.92	55.08	53.72	1.36
Subtotal for Salary, Wages & Benefits:		7,844.00	79.58	7,512.77	331.23	318.32	12.91
3000	DOMESTIC TRAVEL ALLOTMENT	1,300.00	0.00	0.00	1,300.00	0.00	1,300.00
Subtotal for Travel		1,300.00	0.00	0.00	1,300.00	0.00	1,300.00
3810	COMPUTER HARDWARE/SOFTWARE	731.00	0.00	0.00	731.00	0.00	731.00
Subtotal for Supplies		731.00	0.00	0.00	731.00	0.00	731.00
4090	PRINT/COPY/PUBL CHARGES	1,955.00	0.00	0.00	1,955.00	0.00	1,955.00
4130	NREL NETWORK/SYSTEMS SUPPORT	340.00	2.76	310.00	30.00	11.04	18.96
Subtotal for Other Direct Costs		2,295.00	2.76	310.00	1,985.00	11.04	1,973.96
Subtotal for Subcontracts		0.00	0.00	0.00	0.00	0.00	0.00
Subtotal for Equipment		0.00	0.00	0.00	0.00	0.00	0.00
Expense Total:		12,170.00	82.34	7,822.77	4,347.23	329.36	4,017.87
9500	Indirect Costs	2,130.00	14.41	1,369.01	760.99	57.64	703.35
Subtotal for Indirect Costs		2,130.00	14.41	1,369.01	760.99	57.64	703.35
TOTAL		14,300.00	96.75	9,191.78	5,108.22	387.00	4,721.22
SPENDABLE BALANCE							4,018.06

Contains 532901 NPS-ACID2 2004