



# Global Biogeochemical Cycles

## RESEARCH ARTICLE

10.1002/2015GB005137

### Key Points:

- Anthropogenic emissions of phosphorus and nitrogen are globally disproportionate
- N:P ratios in precipitation are reflected in alpine Lakes worldwide
- Phosphorus deposition appears to be driving alpine Lake nutrient status

### Supporting Information:

- Figures S1–S3
- Data Set S1
- Data Set S2

### Correspondence to:

J. Brahney,  
Janice.Brahney@ubc.ca;  
jbrahney@gmail.com

### Citation:

Brahney, J., N. Mahowald, D. S. Ward, A. P. Ballantyne, and J. C. Neff (2015), Is atmospheric phosphorus pollution altering global alpine Lake stoichiometry?, *Global Biogeochem. Cycles*, 29, 1369–1383, doi:10.1002/2015GB005137.

Received 4 MAR 2015

Accepted 5 AUG 2015

Accepted article online 9 AUG 2015

Published online 9 SEP 2015

## Is atmospheric phosphorus pollution altering global alpine Lake stoichiometry?

Janice Brahney<sup>1</sup>, Natalie Mahowald<sup>2</sup>, Daniel S. Ward<sup>2</sup>, Ashley P. Ballantyne<sup>3</sup>, and Jason C. Neff<sup>4</sup>

<sup>1</sup>Department of Geological Sciences, University of Colorado Boulder, Boulder, Colorado, USA, <sup>2</sup>Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, New York, USA, <sup>3</sup>Department of Ecosystem and Conservation Science, University of Montana, Missoula, Montana, USA, <sup>4</sup>Department of Geological Sciences, University of Colorado Boulder, Boulder, Colorado, USA

**Abstract** Anthropogenic activities have significantly altered atmospheric chemistry and changed the global mobility of key macronutrients. Here we show that contemporary global patterns in nitrogen (N) and phosphorus (P) emissions drive large hemispheric variation in precipitation chemistry. These global patterns of nutrient emission and deposition (N:P) are in turn closely reflected in the water chemistry of naturally oligotrophic lakes ( $r^2 = 0.81$ ,  $p < 0.0001$ ). Observed increases in anthropogenic N deposition play a role in nutrient concentrations ( $r^2 = 0.20$ ,  $p < 0.05$ ); however, atmospheric deposition of P appears to be major contributor to this pattern ( $r^2 = 0.65$ ,  $p < 0.0001$ ). Atmospheric simulations indicate a global increase in P deposition by 1.4 times the preindustrial rate largely due to increased dust and biomass burning emissions. Although changes in the mass flux of global P deposition are smaller than for N, the impacts on primary productivity may be greater because, on average, one unit of increased P deposition has 16 times the influence of one unit of N deposition. These stoichiometric considerations, combined with the evidence presented here, suggest that increases in P deposition may be a major driver of alpine Lake trophic status, particularly in the Southern Hemisphere. These results underscore the need for the broader scientific community to consider the impact of atmospheric phosphorus deposition on the water quality of naturally oligotrophic lakes.

## 1. Introduction

Over the last century, human activities have altered the global cycles of nitrogen (N) and phosphorus (P), which has led to an increased flux of these elements through the atmosphere [Galloway *et al.*, 2004; Mahowald *et al.*, 2008]. However, the spatial patterns and the rates of historical change in emissions for these two elements are not parallel. Primary sources of reactive N are industry, transportation, and agriculture; thus, areas with high deposition rates and large changes in deposition since the 1950s tend to be in the Northern Hemisphere where human populations are dense and industry has undergone considerable expansion [Galloway *et al.*, 2004]. Nitrogen deposition and its effects on alpine Lake ecosystems have been widely considered [Elser *et al.*, 2009a], and nitrogen deposition is routinely measured by many national-scale atmospheric deposition networks. However, these national-scale networks typically only sample wet deposition, and only aerosol particles smaller than 10  $\mu\text{m}$ . Because a large fraction of deposited P tends to be in the dry fraction [Tipping *et al.*, 2014], and total dust or P deposition is not routinely measured, we are only starting to appreciate potential changes in regional phosphorus deposition rates and their impacts on aquatic ecosystems [Camarero and Catalán, 2012; Morales-Baquero *et al.*, 2006].

The most important sources of P to the atmosphere are soils and vegetation emissions, ash from biomass burning, and to a lesser extent industrial and mining emissions [Mahowald *et al.*, 2008]. Land use practices and climate change are contributing to regional increases in soil dust emissions [Ginoux *et al.*, 2012; Neff *et al.*, 2008]. Similarly, biomass burning, both from naturally occurring fires and tropical deforestation, is an important source of P emissions to the atmosphere [Crutzen and Andreae, 1990]. Major dust and ash sources tend to be closer to the equator and/or in the Southern Hemisphere. Dust is known to contribute phosphorus to terrestrial ecosystems over millennial time scales [Okin *et al.*, 2004], and recent studies have shown that atmospheric transport of P can be an important mechanism for nutrient delivery to contemporary lake ecosystems [Brahney *et al.*, 2014; Camarero and Catalán, 2012; Reche *et al.*, 2009; Sickman *et al.*, 2003; Vicars *et al.*, 2010]. Despite these advances, studies that evaluate changes in phosphorus deposition over large spatial scales and through recent history are rare.

Both nitrogen and phosphorus are key limiting nutrients in terrestrial and freshwater ecosystems, in fact primary productivity in most lakes is thought to be colimited and their relative availability determines ecosystem productivity and species composition. Lake ecosystems respond rapidly to nutrient alterations, particularly in oligotrophic alpine lakes where a small change in absolute concentration can mean a large change in relative availability. Here we examine the nutrient status (i.e., N:P) of naturally oligotrophic lakes in both hemispheres and compare these results to nutrient deposition rates. We then use a global atmospheric chemistry model to evaluate changes and potential major drivers in deposition across space and time.

## 2. Methods

### 2.1. Compilation of Deposition and Lake Data

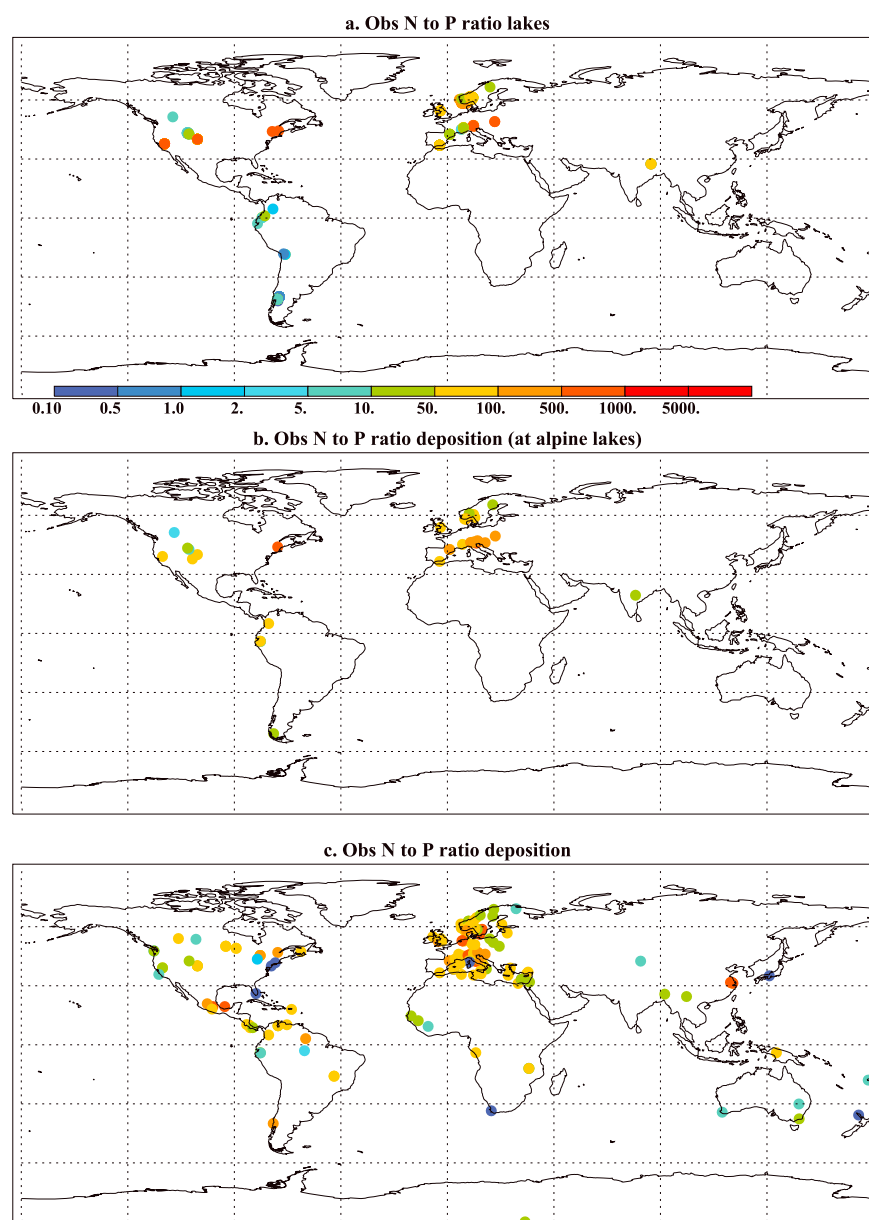
To evaluate the role of atmospherically transported nutrients on lake ecosystems, we conducted an extensive literature search to examine regional differences in both N and P deposition rates, and the degree to which these ratios are mirrored in lake water nutrient status. We focus on naturally oligotrophic alpine lakes as these settings should be most sensitive to variations in atmospheric input [Psenner, 1999; Pulido-Villena *et al.*, 2006]. Alpine lakes are typically nutrient poor with little to no catchment vegetation and receive proportionally a larger fraction of nutrients from the atmosphere than lowland lakes. Consequently, they are often sensitive to small changes in nutrient inputs [Brahney *et al.*, 2015; Reche *et al.*, 2009]. These lakes are also, in general, less affected by other anthropogenic activities. We compiled a database of over 700 upland lakes across 21 alpine regions with corresponding deposition data from each area (supporting information).

To account for possible dilution effects in both precipitation and lake reservoirs, we focus mainly on nutrient ratios, though we also consider absolute concentrations. We evaluate independently, and as a ratio, the biologically available nutrient fractions, including dissolved inorganic nitrogen (DIN), total phosphorus (TP), and soluble reactive phosphorus (SRP), where DIN is the sum of nitrate, nitrite, and ammonia, and TP is the SRP from an unfiltered sample that has been acid/persulfate digested. The reasoning behind the use of DIN instead of total nitrogen (TN) is because TN includes the measurement of dissolved organic nitrogen, which may not be a reliable indicator of the amount of nitrogen available for aquatic organisms because much of the organic N is tied up in high molecular weight compounds that are difficult to break down [Morris and Lewis, 1988]. In contrast, it has been found that TP is the most reliable indicator of P availability to aquatic species [McMaster and Schindler, 2005; Morris and Lewis, 1988]. The reason that the use of TP, rather than SRP, is more physiologically appropriate is because aquatic organisms (algae, bacteria, and zooplankton) have evolved numerous ways to rapidly acquire P from organic molecules [Jansson *et al.*, 1988], mineral sources [Schaperdoth *et al.*, 2007; Smith *et al.*, 1978], and this measurement includes internal reserves [Pettersson, 1980]. With respect to deposition, TP rather than  $\text{PO}_4^{3-}$  is predominantly used because biological uptake of  $\text{PO}_4^{3-}$  is so rapid that without the acid/persulfate digestions, deposition SRP measurements would be relatively small and not truly reflective of the full atmospheric load. In only two instances, the Sierra Nevada Mountains in Spain and the French Alps, the dry P fraction is included in the TP deposition estimate. All lake and deposition data and metadata can be found in the supporting information.

The strength of the relationship between N, P, and N:P in deposition and lakes is evaluated through regression analysis. We ascertain the coefficients of determination ( $r^2$ ) by regressing the mean lake values against the mean deposition values in each region. In Figure 1, we show the range of potential regression lines based on 1000 random samples from each region's distribution based on the mean and standard deviation of the available lake data. This way, we also account for within-site variation.

### 2.2. Atmospheric Modeling

To evaluate the potential drivers behind large-scale changes in the N and P deposition rates, and regional N:P ratios of deposition, we simulate nitrogen and phosphorus deposition using the Community Atmospheric Model (CAM4) and online (climate model derived) winds with slab ocean model [Neale *et al.*, 2013]. Simulations were conducted for 5 years, with the last 4 years used for analysis. By using the prescribed aerosols for radiative transfer calculations, the meteorology in all the simulations was identical. The model simulates three-dimensional transport and wet and dry deposition for gases and aerosols, as described in Lamarque *et al.* [2011], Mahowald *et al.* [2006a], and Rasch *et al.* [2000]. Model simulations were set up such that boundary conditions for N and P were comparable and differences are due to changes in emissions, and



**Figure 1.** Observed N:P ratios in deposition and lakes. Note that the map scale cannot adequately show all 700 lakes used in the study.

not meteorology. For example, simulations did not include changes in transport or chemistry due to climate change, which are usually smaller than changes in emissions [Mahowald *et al.*, 2010].

For nitrogen, the CAM-chem model was used [Lamarque *et al.*, 2011], which simulates tropospheric chemistry including ozone and organic compounds for current and preindustrial emissions using the emission data sets from Lamarque *et al.* [2010], except for fires. Because it is commonly observed that bottom-up emissions used in these chemical transport models do not capture the amount of aerosol optical depth (AOD) observed in biomass burning regions (as well as some industrial regions) [Bian *et al.*, 2007; Bond *et al.*, 2013; Chin *et al.*, 2009], and because of the importance of biomass burning to this study, we calibrate the emissions in different regions to better match available observations, and thus modify the black carbon (BC) and organic carbon (OC) emissions to obtain the observed AOD. The baseline fire emissions are the observation-based Global Fire Emission Database version 3 (GFED3) [Randerson *et al.*, 2013; van der Werf *et al.*, 2006]. We use the tuning methodology as in Johnston *et al.* [2012] and Ward *et al.* [2012] in which GFED fire emissions are scaled to

ground and space-based observations of AOD for 14 regions by identifying high-fire emission and low-fire emission months for each region. The tuning factors are applied to all the species emitted by fire, including nitrogen and phosphorus species. Here we make the assumption that biases in the GFED3 are due to error in the total C emitted and not from errors in emission factors for the noncarbon containing species.

In order to make the preindustrial estimates of emissions associated with fires consistent with the current climate, we use the same tuning factors in the preindustrial climate as in the current climate. Emissions from fires for the year 1870 from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) [Lamarque *et al.*, 2010] are scaled by the ratio of the tuned GFED3 fire emissions to the untuned ACCMIP fire emissions from the present day. Note that ACCMIP fires in preindustrial times versus current were previously scaled based on observations [Mieville *et al.*, 2010]. Scale factors are computed for total fire emissions in each of the 14 regions used for the AOD tuning, not for global totals, and the factors are computed for each individual fire-emitted species. After applying this scaling, the global fire emissions of BC increase 38% by mass from the year 1870 to the year 2000.

Phosphorus was modeled following Mahowald *et al.* [2008] with some improvements. Desert dust particles are assumed to contain  $720 \mu\text{g g}^{-1}$  of phosphorus. The model includes four size bins, which are transported and subject to deposition separately. The model sized bins are 0.1–1, 1–2.5, 2.5–5, and 5–10  $\mu\text{m}$ . Distribution of dust in the sources follows a fixed distribution into the four bins following Kok [2011] of 1%, 11%, 17%, and 69%. Dust is tuned to match observations. Preindustrial dust is likely to be lower in most regions, and the deposition ratios from Mahowald *et al.* [2010] are used to tune the emissions in different source areas to represent these changes. Industrial combustion sources of P in both the fine and coarse fraction are modeled following Mahowald *et al.* [2008], which used emission factors and the spatially explicit emissions from the Speciated Emission Wizard [Bond *et al.*, 2007, 2004; Mahowald *et al.*, 2008]. We assume preindustrial fossil fuel emissions are equal to 20% of modern fossil fuel emissions in the current climate based on trends in black carbon in Bond *et al.* [2007]. The exact fraction is not known, but it is likely to be small [e.g., Lamarque *et al.*, 2010]. Biomass burning aerosols are assumed to have a P/BC ratio of 0.0029 and 0.02 in fine and coarse modes, with 20% of the BC occurring in the coarse mode, based on observations in the Amazon [Mahowald *et al.*, 2008, 2005]. Biomass burning emissions from GFEDv3 are used but tuned to better match observations of aerosols using the methods of Ward *et al.* [2012], as described above for nitrogen emissions. Biofuel emissions are based on the same emission factors of P/BC as for biomass burning, since there is no data, and the biofuel emission map of Lamarque *et al.* [2010] is used. For these emissions, we model them within the same mechanism as the dust, using four size bins. We assume preindustrial P emissions from biofuels are equal to 50% of P emissions from present day based on BC trends shown in Bond *et al.* [2007].

Here we use satellite retrieved leaf area indices [Zhu *et al.*, 2013] to estimate above ground biomass for our prediction of primary biogenic particles (PBP). While leaf area index (LAI) and above ground vegetation show a significant relationship [Madugundu *et al.*, 2008], they may not be linear across all ecosystems. We adjust the emission rate of PBP to match the observation that approximately 30% of the aerosol mass less than 10  $\mu\text{m}$  over the Amazon is PBP and obtain a similar global emission rate as seen in Mahowald *et al.* [2008], although there is more mass in higher latitudes than in that study. This is consistent with P data in high latitudes, so this is likely to be an improvement in our simulation compared to Mahowald *et al.* [2008]. We distribute the P in PBP throughout the four bins, using a similar size distribution as P in dust. Though this is a large assumption, there is no other available information to inform the model. We do not include a change in leaf area index between preindustrial and current, as this should be a small change and is not well known.

Sea salts do not represent a large source of phosphorus to land regions [Graham and Duce, 1979; Mahowald *et al.*, 2008], so we make a simplifying assumptions that phosphorus concentrations in sea water are  $0.08 \mu\text{g P kg}^{-1}$  of salt and use the prognostic sea salt algorithm in CAM [Mahowald *et al.*, 2006b]. We use the same methodology as Mahowald *et al.* [2008] for simulating volcanic P emissions based on sulfur emission ratios from volcanoes only in the fine mode.

A detailed comparisons of the atmospheric concentrations, fine versus coarse comparisons for atmospheric concentrations, and source apportionment studies (e.g., combustion versus dust) for the phosphorus are included in the Mahowald *et al.* [2008] study, and thus not repeated here. But in order to simulate deposition close to the source areas, additional sources need to be considered.

Most model simulations include only the  $<10 \mu\text{m}$  fraction of aerosols, because most of the data are available for this size fraction [Mahowald *et al.*, 2008], and for many purposes, for example, climate or air quality, the

**Table 1.** Atmospheric Nitrogen Budgets Based On Simulations Here, Using Emissions From *Lamarque et al.* [2010], With Modifications Described in Methods<sup>a</sup>

	Current	Preindustrial	(Current/Preindustrial)
<i>NO<sub>x</sub></i> (Tg N/yr)			
Anthropogenic	32	1	26
Biomass burning	15	10	1.5
Biofuels	1.2	0.2	8
Soils	8	8	1
Lightning	4	4	1
Aircraft	0.5	0	
Total	61	24	26
<i>NH<sub>x</sub></i> (Tg N/yr)			
Anthropogenic	31	6.1	5
Biomass burning	11	8.5	1.3
Soils	2	2	1
Ocean	6.7	6.7	1
Total <i>NH<sub>x</sub></i>	50	23	2.2
Primary biogenic and very coarse mode N	25	25	1
Total N	136	71	1.9

<sup>a</sup>*NO<sub>x</sub>* represents nitrogen oxide emissions, while *NH<sub>x</sub>* represents ammonia emissions.

smaller fractions are thought to be more important [Mahowald *et al.*, 2011]. However, for biogeochemical questions, especially for dust, the larger size fraction is very important and can represent the dominant fraction of local to regional aerosol transport [Lawrence and Neff, 2009; Neff *et al.*, 2013]. For phosphorus in dust we follow the limited observations [Neff *et al.*, 2013] and assume that only 10% of the mass that travels through the atmosphere is within the <10  $\mu\text{m}$  size fraction [Neff *et al.*, 2013]. Not having any other information, we use a similar size assumption for PBP and sea-salt aerosols as well. We assume that the C:N:P ratios of foliage of 1200:28:1 are representative for both P and N in PBP [McGroddy *et al.*, 2004]. We assume that particles in the >10  $\mu\text{m}$  are emitted and deposited in the same grid box due to their short atmospheric lifetime [Seinfeld and Pandis, 1998].

We include N in fine, coarse, and ash fractions, as well as P (described below from Mahowald *et al.* [2008]). Approximately 65–90% of the N in above ground vegetation is lost in fires [Kauffman *et al.*, 1995; Pivello and Coutinho, 1992], a simple budget analysis suggests that most of this is seen in the emission of gases [Andreae and Merlet, 2001]. If 10% of the 50% released of the N is in ash particles, with an atomic ratio of 1200:28:1 for C:N:P [McGroddy *et al.*, 2004], (C:N:P mass ratio of 1000:24:1), this implies 1  $\text{gN gP}^{-1}$  in particulate form. For phosphorus, it is estimated that about 50% of the phosphorus in biomass is released in fires [e.g., Pivello and Coutinho, 1992; Kauffman *et al.*, 1995, 1998]. Simple budget analysis suggests that most of the phosphorus from biomass burning is released as ash [Mahowald *et al.*, 2005], although we include the fine and coarse mode aerosols which will travel farther as described above. Adding these extra terms carried in the >10  $\mu\text{m}$  fraction (PBP, fires, and biofuels) makes the N emission budgets increase from 111 to 136  $\text{Tg N yr}^{-1}$  for current and 47 to 71  $\text{Tg N yr}^{-1}$  for preindustrial climate, so these terms are not important globally for the N budget (Table 1) but are important for the phosphorus budget [Mahowald *et al.*, 2005] (Table 2). The inclusion of large particles (>10  $\mu\text{m}$ ) is required in order to match the observations of phosphorus deposition synthesized here. We include in both the N and P modeling and budgets to be consistent. Comparisons of the deposition simulated using these assumptions suggest that the model has some ability to simulate phosphorus and nitrogen, but that improvements in the simulation of phosphorus, especially, could be made.

Based on a new emission inventory and modeling study, Wang *et al.* [2015] propose a very different atmospheric P budget with a much larger combustion source. In contrast to our approach here, with explicit treatment of fine, coarse, and very coarse (>10  $\mu\text{m}$ ) particles considered, for transport they simulate one mode focused on 3.5  $\mu\text{m}$  mass median diameter, which is typical for dust long-range transport [Schulz *et al.*, 1996], and use this mode for all types of aerosols considered here [Wang *et al.*, 2015]. This approach is very appropriate for simulations of long-range transport or aerosol optical depth, as it was developed; however, it deliberately neglects larger modes which contain substantial mass [e.g., Neff *et al.*, 2013; Schulz *et al.*, 1998]. For emissions,



**Table 2.** Current and Preindustrial Budgets of Total P in Deposition for the Atmospheric Modeling Study

TP (Tg P/yr)	Current Climate		Preindustrial		(Current/Preindustrial)
	(<10 $\mu\text{m}$ )	(<100 $\mu\text{m}$ )	(<10 $\mu\text{m}$ )	(<100 $\mu\text{m}$ )	
Dust	2.4	2	1.7	17	1.4
Primary biogenic particles	0.18	1.8	0.18	1.8	1
Fires	0.029	0.29	0.021	0.2	1.4
Fossil fuels	0.024	0.024	0.0048	0.0048	5
Biofuels	0.011	0.011	0.0056	0.0056	2
Volcanoes	0.011	0.011	0.011	0.011	1
Sea salt	0.00046	0.0046	0.00046	0.0046	1
Total P	2.7	26	1.9	19	1.4

*Wang et al.* [2015] assumes that 35%, 16%, and 6% of the P is emitted in the  $>10\ \mu\text{m}$  mode for the combustion, primary biogenic, and dust particles, respectively. These assumptions are quite different than the assumptions made here (described above). For combustion, *Wang et al.* [2015] treats the aerosol size distribution in detail, while ignoring available data and theory which would argue that mechanically generated aerosols (such as primary biogenic or dust) should tend to be more in the coarse mode than combustion particles (e.g., based on the limited observations of primary biogenic and dust P) [e.g., *Neff et al.*, 2013; *Tipping et al.*, 2014]. The discrepancy between deposition simulated in the model for the long-range transported mode, which here or in *Tipping et al.* [2014] is attributed to the large particles emitted locally ( $>10\ \mu\text{m}$ ), is in *Wang et al.* [2015] attributed to an underestimate in the combustion sources, resulting in the suggestion that the combustion sources should be  $1.1\ \text{Tg P yr}^{-1}$ , compared here with  $0.06\ \text{Tg P yr}^{-1}$  for the same size fraction (Table 3). That study also did not compare their model simulation to available atmospheric concentrations, as done in detail in *Mahowald et al.* [2008]. Since combustion-sourced aerosols should be predominately in the fine fraction [e.g., *Seinfeld and Pandis*, 1998], the hypothesis of a larger-combustion source is not consistent with the dominance of coarse P over fine P in the observations in many industrialized regions (Table S3b in *Mahowald et al.* [2008]). In addition, an observationally based source apportionment study using the ratio of P to BC also supports a relatively small source of combustion to the P cycle [*Mahowald et al.*, 2008, 2005]. Our simulation of deposition is just as good (or poor) as *Wang et al.* [2015] (see supporting information Figure S2 for our model); however, here we are able to capture the observed concentration distributions, fine versus coarse fraction, and source apportionment, which is not shown in the *Wang et al.* [2015] study. Thus, the budget used here represents an atmospheric P cycle that is more consistent with the available observations.

The differences between *Wang et al.* [2015] and our study illustrate the large uncertainties in the atmospheric P cycle and thus can be used to construct a sensitivity study to examine how very different assumptions about the size of P particles, as well as the sources of P, impact our results. We modify our model results such that there are no very large particles ( $>10\ \mu\text{m}$ ), increase our combustion sources to  $1.1\ \text{Tg P yr}^{-1}$ , as postulated in that paper, and show the results of our P budget using these assumptions in Table 2. We also change the N budget, by removing also the very large particles in the N budget as well, which, as noted above, is less important than in the P budget. Note that because our source distributions and transport model are slightly different, our results differ slightly from *Wang et al.* [2015] but contain the majority of the differences between

**Table 3.** Current and Preindustrial Budgets of Total P in Deposition From Sensitivity Study Using High Combustion P (Based on Assumptions in *Wang et al.* [2015], as Discussed in Methods and Text)

TP (Tg P/yr)	Current Climate		Preindustrial		(Current/Preindustrial)
	(<10 $\mu\text{m}$ )	(<100 $\mu\text{m}$ )	(<10 $\mu\text{m}$ )	(<100 $\mu\text{m}$ )	
Dust	2.4	2	1.7	17	1.4
Primary biogenic particles	0.18	1.8	0.18	1.8	1
Fires	0.029	0.29	0.021	0.2	1.4
Fossil fuels	0.024	0.024	0.0048	0.0048	5
Biofuels	0.011	0.011	0.0056	0.0056	2
Volcanoes	0.011	0.011	0.011	0.011	1
Sea salt	0.00046	0.0046	0.00046	0.0046	1
Total P	2.7	26	1.9	19	1.4

studies which are due to emissions. These sensitivity studies are included in the supporting information and discussed in the text below. Notice that our approach will tend to minimize the impact of humans on the atmospheric P cycle as we attribute much of the atmospheric P to local ecosystem emissions, while their approach will tend to maximize the impact of humans, because of the predominance of the combustion aerosols to the P cycle (see Table 3). Thus, these two studies with very different assumptions represent an excellent bound on the atmospheric P cycle.

### 3. Results

#### 3.1. Database Synthesis and Regression Analyses

Measured N deposition rates ranged from 80 to 7000 mg m<sup>-2</sup> yr<sup>-1</sup>, and P deposition from 4 to 400 mg m<sup>-2</sup> yr<sup>-1</sup> (supporting information). The N:P ratio in deposition ranged from 4 to 382 molar ratio, and in lakes from 1 to 594 molar N:P. Nitrogen deposition rates were highest near industrialized areas of Europe, China, and North America. In contrast, observed total phosphorus deposition rates were highest, >100 mg m<sup>-2</sup> yr<sup>-1</sup>, in the Southern Hemisphere in several locations close to areas of biomass burning, (East Africa, Ecuador, Northern Brazil, and Venezuela), in areas downwind of major deserts, (northwest Africa and southeast Australia), and in some areas close to industrial sources (England and Germany). Mean regional deposition and lake N:P ratios are presented in Table 4, and observed regional data are shown in Figure 1.

Contemporary measured nutrient deposition rates and ratios are clearly reflected in the alpine Lake water composition and stoichiometry (Table 4 and Figure 2). Because a variety of factors will influence an individual lake response to N or P deposition, including the size of the catchment, the type of vegetation, and whether or not the lake is open or closed [Ballantyne *et al.*, 2010; Morales-Baquero *et al.*, 1999], some variability among the lakes in each region is expected. For this reason, we calculated 1000 regression lines from a random selection of the data. The mean relationship between the TIN:TP of deposition and that of the lakes was strong with an  $r^2$  of 0.82,  $p < 0.0001$  (Figure 1). If we consider only SRP measurements (filtered lake water samples), which are available from ~170/700 lakes across 12 regions, then the relationship remains strong at an  $r^2$  of 0.87,  $p < 0.0001$ . Regressing each nutrient independently, the correlation between deposition and lake water nutrient content is stronger for P ( $r^2 = 0.64$ ,  $p < 0.0001$ ) than for N ( $r^2 = 0.20$ ,  $p < 0.05$ ).

In considering the potential role of P deposition leading to intermittent or persistent N limitation, we divided the data set into two groups. We assume that, where the molar ratio of deposition averages <20 N:P, there is the potential for atmospherically induced intermittent or persistent N limitation [Camarero and Catalán, 2012]. Within the available data, there are five regions with a mean deposition ratio below 20 and 480 lakes with data. Of these lakes, 450, or 94%, have average molar ratios below the Redfield ratio of 16. For regions with a deposition ratio above 20, only 5% of the lakes have N:P values below 16. These results provide suggestive evidence that the chemistry of atmospheric deposition plays a role in the nutrient limitation of naturally oligotrophic alpine Lakes.

#### 3.2. Atmospheric Modeling

Though the atmospheric model used here only captures relatively large scale processes, the observed patterns in global N and P deposition are reasonably well reflected in the model runs. Modeled nitrogen deposition (supporting information Figure S1) was correlated to observed nitrogen deposition with a correlation coefficient of 0.45 and a Spearman's rank coefficient of 0.58. Modeled phosphorus deposition (supporting information Figure S2) was correlated to observed phosphorus deposition with a correlation coefficient of 0.10 and a Spearman's rank coefficient of 0.01. Modeled N:P ratios are correlated with observed N:P ( $r$  of 0.01 and a Spearman's rank coefficient of 0.05) (supporting information Figure S3). Because of the importance of large particles in the observed atmospheric P budget, low-correlation coefficients are not unexpected as global atmospheric models are designed to capture the large-scale effects and average over small-scale processes and highly heterogeneous sources that may dominate in a given region.

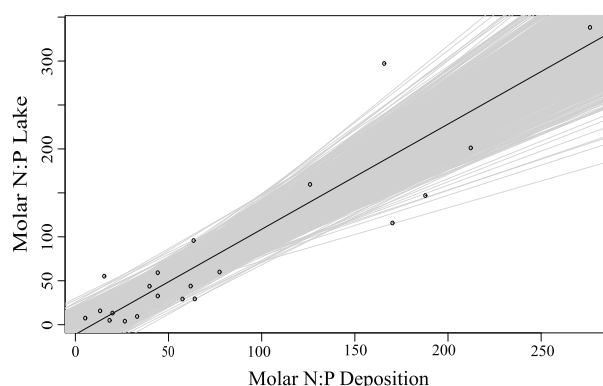
Modeling results indicate that while N deposition has increased globally by 1.9 times the preindustrial rate, P deposition has also increased by an average of 1.4 times (Tables 1 and 2). The largest increases in P occurred over regions of Africa and Australia, with up to a fivefold increases in regions of South America (Figure 3a).

**Table 4.** Paired N:P Ratios in Deposition and Regional Alpine Lakes for Paired Sites Around the World<sup>a</sup>

Area	Measurement			Mean Regional		References	Elevation	# of Sites	Mean Regional		References
	Type	Longitude	Latitude	N:P Weight	N:P Molar				N:P Weight	N:P Molar	
North (Area 12)	Wet	19.14	65.36	9.1	20.1	Bergstrom et al. [2005], Knulst [2001]	Unknown	344	6.0	13.3	Bergstrom et al. [2005]
Central	Bulk	9.39	60.42	20.1	44.5	Solberg et al. [1998]	703–1050	19	14.8	32.7	Elser et al. [2009a]
Southern	Bulk	7.64	58.12	56.8	125.6	Solberg et al. [1998]	59–384	18	72.2	159.6	Elser et al. [2009a]
Alps	Bulk glacier	6.38	45.22	28.9	63.8	Maupetit and Delmas [1994], DeAngelis and Gaudichet [1991], Guieu et al. [2002]	1945–2173	6	13.3	29.4	Birck et al. [2013], Lepori and Robin [2014]
Ave. Northeast Italy	Bulk	11.05	46.43	96.1	212.5	Mosello et al. [2002]	2384–2540	2	91.0	201.2	Tait and Thaler [2000]
Alps	Bulk	12.70	47.10	85.0	187.9	Psenner [1989]	2483–2830	3	66.5	146.9	Psenner [1999]
South lake district (Merlewood)	Bulk	−2.87	53.90	25.9	57.2	APIS [2014], Carlisle et al. [1967]	290–528	5	13.2	29.2	Maberly et al. [2002]
St. Nicholas Valley, 1990	Bulk	1.00	42.67	18.3	40.4	Camerero and Catalan [1996]	2300	~67	17.6	38.9	Catalan et al. [1993]
St. Nicholas Valley, 1997–1998	Bulk	0.77	42.63	77.1	170.5	Ventura et al. [2000]	2240	1	52.4	115.8	Ventura et al. [2000]
Sierra Nevada	Wet+Dry	−3.28	36.57	34.8	77.0	Morales-Baquero et al. [2006]	2790–3060	31	27.1	60.0	Morales-Baquero et al. [1999]
Tatra Mountains	Bulk	20.23	49.46	75.0	165.8	Kopacek et al. [2000], Kopáček et al. [2011]	1395–2145	33	132.0	291.7	Kopáček et al. [2011]
Himalays	Bulk	79.46	19.38	16.8	37.1	Pandey et al. [1983]	4500–5600	11	15.1	33.4	Tartari et al. [1998], Lami et al. [2010], Ghimire et al. [2013]
Banff National Park	Bulk	−113.62	54.01	21.2	46.9	Porter [2012]	2320	28	3.6	8.0	McMaster and Schindler [2005]
Hubbard Brook, New Hampshire	Bulk	−71.69	43.95	124.8	275.7	Likens [2013]	unk. - 1548	35	120.0	265.2	DFWI [2014], Brahney [2012]
Colorado Rockies, Green Lakes	Bulk	−105.59	40.05	28.7	63.4	Mladenov et al. [2012], Brahney [2012]	3104–3616	22	40.3	89.0	Mladenov et al. [2012], Elser et al. [2009b]
San Juan Mountains, Colorado	Bulk	−107.71	37.84	28.0	61.9	Brahney, 2012	3331–3845	13	19.9	44.0	Elser et al. [2009b]
S. Wind River Range, Wyoming	Bulk	−109.16	42.73	2.4	5.3	Brahney [2012]	2958–3086	4	4.8	10.7	Environmental Protection Agency
N. Wind River Range, Wyoming	Bulk	−109.76	43.36	8.1	17.8	Brahney [2012]	3178–3553	7	25.0	55.3	(EPA) [1985], Brahney [2012]
Lake Tahoe	Bulk	−120.34	39.11	7.2	16.0	Sahoo et al. [2010], Vicars et al. [2010], Boy et al. [2008], Fabian et al. [2009], Veneklaas [1990]	1898	1	7.1	15.7	Sickman et al. [2013]
Ecuador, Cordillera Real	Bulk	−79.08	−4.00	6.0	13.3	Galloway et al. [1996]	2660–4545	40	1.5	3.3	Guzman [2005], Gunkel and Beulker [2009]
Torres del Paine (Patagonia)	Wet	−73.41	−50.94	8.3	18.3		700–1950	20	2.5	5.5	Rogora et al. [2008], Diaz et al. [2007]

<sup>a</sup>Data used to derive mean values and all metadata can be found in the supporting information.





**Figure 2.** Paired N:P molar ratios of deposition and lake water from mountain ranges around the world. The gray lines represent 1000 regression lines fitted to randomly drawn values from the distributions of lake chemistry data by region. The black line represents the mean of the regression lines and has a slope of 1.185 and an intercept of  $-11.038$ . Open circles represent the mean lake value in each region.

These changes are unevenly distributed across the globe such that certain regions have been disproportionately affected by changes in N deposition while others have been most impacted by P deposition (Figure 3b).

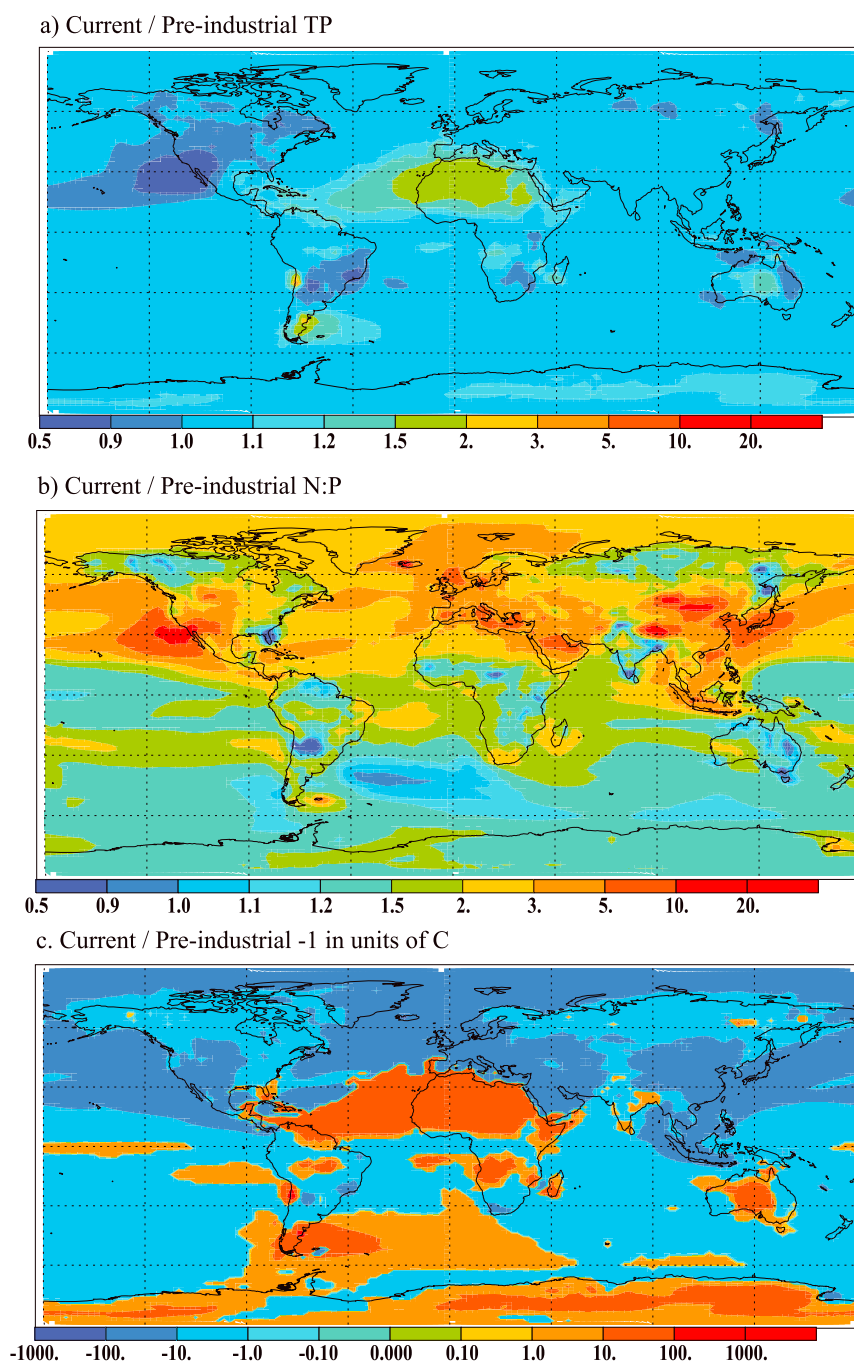
Although the overall changes in the mass flux of P are smaller than the changes in N, the biological impacts may, under some circumstances, be higher. We use the Redfield molar ratios of C:N:P (106:16:1) because they are broadly reflective of nutrient limitation of primary productivity in marine and freshwater ecosystems. Taken at face value, this indicates that a 1 M change in P deposition has 16 times the stoichiometric effect of 1 mol of N. Using this generalized relationship, we find that the increase in P deposition is equal

to or greater than the impact of N deposition in various regions of the world (Figure 3c). These model results conform to the few examples of historical measurements of N and P deposition in areas that have experienced large changes in P deposition [Bootsma and Hecky, 2003; Pandey *et al.*, 2014]. For example, the earliest recorded N:P ratio in deposition is from Lake Victoria, Africa, measured at  $\sim 1207$  M ratio in 1958. By 1991, the ratio had dropped to 13 [Bootsma and Hecky, 1993].

Because of the uncertainty in the atmospheric P budget, we include a sensitivity study with very different assumptions about the sources of P, following Wang *et al.* [2015], where combustion sources of P are as large as dust sources (discussed more in section 2). This very different set of assumptions about P deposition suggests even larger anthropogenic increases in P deposition than assumed here [Wang *et al.*, 2015] (Table 2 versus Table 3). That study also suggests that the location for the P deposition increases is similar to those for N deposition increases because combustion is a large source for both, which is different than our discussion above. On the other hand, the increased combustion source of Wang *et al.* [2015] argues for an even larger role of P deposition on aquatic systems, since the P deposition changes dominate over N deposition changes in stoichiometry over much of the globe (contrast Figure 3 with supporting information Figure S4). As we argue in the section 2, because our modeled atmospheric P cycle has been compared in detail to available atmospheric concentration observations, and includes more details about the size distribution of atmospheric P cycle, we think it represents better the atmospheric P cycle.

#### 4. Discussion

Because dust is on average enriched with respect to the upper continental crust by a factor of 1.6 [Lawrence and Neff, 2009], dry deposition has the capacity to enrich most aquatic and terrestrial environments. Similarly, biomass burning can enrich environments through P deposition. Though biomass burning releases both N and P, a study in Ecuador found the relative increases in P was greater, causing a reduction in the N:P of deposition during periods of biomass burning [Boy *et al.*, 2008]. The strong relationships between deposition and alpine Lake stoichiometry and nutrient content strongly suggest that relative nutrient availability in alpine ecosystems may be tightly coupled to atmospheric transport and subsequent deposition of nutrients. This, in combination with the simulations, suggests that humans may be altering both the N and P availability differentially in the North and South Hemispheres. Several studies have shown the effects of N deposition on alpine Lake N:P ratios in the industrialized areas of Europe and the United States [Elser *et al.*, 2009b; Wolfe *et al.*, 2001]. Here we show that a similar effect appears to be occurring with increases in P deposition for alpine Lakes proximal to areas of moderate to high dust and ash deposition. However, unlike N that can be relatively rapidly flushed from the catchment [Kopáček *et al.*, 2002; Rogora *et al.*, 2012], phosphorus has a tendency to remain within the lake ecosystem for decades or longer after pollution has abated due to



**Figure 3.** (a) Community Atmospheric Model (CAM) (v4) results of the ratio of current to preindustrial TP deposition. (b) CAM (v4) results of the current to preindustrial N:P ratios in deposition. The hemispheric difference in the mass flux changes of N versus P is clearly shown. (c) Stoichiometric representation of the relative impact of P versus N displayed as a ratio of the current to preindustrial deposition rates based on results from the CAM (v4). Values are calculated as  $\text{Current/Preindustrial} - 1$  in units of C, such that P is represented as  $P \times 10^6$ , and N as  $N \times 6.625$ . Values are shown as positive (reds) when increases in P deposition dominate, and negative (blues) when increases in N dominate.

internal recycling between the water column and sediments [Gachter and Meyer, 1993; Golterman et al., 1998], suggesting that recent increases in P deposition will affect long-term changes in lake biogeochemistry.

The implications of increased phosphorus deposition on naturally oligotrophic lake ecosystems are several fold. Because natural sources of nutrients to these waters are low, even small magnitude increases in P deposition can

result in significant ecosystem changes. Dust associated P deposition to the Sierra Nevada Mountains in Spain is relatively low at  $24\text{--}38\ \mu\text{g P m}^{-2}\text{ d}^{-1}$  [Morales-Baquero *et al.*, 2006], yet in these areas, dust P has been shown to increase chlorophyll *a* concentrations, bacterial abundance, and decrease plankton diversity [Morales-Baquero *et al.*, 2006; Pulido-Villena *et al.*, 2008; Reche *et al.*, 2009]. Similarly, in the Wind River Mountains of the United States, dust P has led to the eutrophication of lakes and the proliferation of low-food quality phytoplankton [Brahney *et al.*, 2015, 2014]. In both the Sierra Nevada Mountains of California and the Spanish Pyrenees, the atmospheric deposition of phosphorus is overwhelming the effects of N deposition leading to increasing N limitation of phytoplankton growth [Camarero and Catalán, 2012; Vicars *et al.*, 2010]. In addition, there is some evidence and rationale to suggest that enhanced P deposition would in some instances favor phytoplankton of high-food quality [Elser *et al.*, 2000]. Regardless of the food web consequences, our analyses show the potential for anthropogenic control on the nutrient supply to modify lakes in the absence of human disturbance in the catchment.

In addition to changes in nutrient ratios, the absolute supply of nutrients to the lake ecosystem from atmospheric sources can both increase productivity and influence plankton species composition. Because lakes are typically colimited by N and P, enhanced N deposition can lead to increases in productivity but only until a threshold where P limitation restricts growth, at which point N will accumulate in lake basins [Bergstrom and Jansson, 2006]. For this reason, relatively high N deposition rates can lead to high N:P ratios in lakes. The opposite relationship will not always hold because N-fixing bacteria can compensate for N limitation [Levine and Schindler, 1999]. Though this produces a weaker linear relationship at low N:P deposition rates, it likely results in a stronger ecosystem response from which it is harder to recover [Schindler *et al.*, 2008].

Beyond alpine oligotrophic lakes, the atmospheric deposition of phosphorus appears to control freshwater nutrient concentrations across a large range of water bodies, even those with human disturbance in the catchment. This relationship was noted in several small lakes in Ontario [Linsey *et al.*, 1987; Scheider *et al.*, 1979], in rivers in southeastern Australia [Leys and McTainsh, 1999], India [Pandey *et al.*, 2014], and in the large African Lakes [Bootsma and Hecky, 2003; Tamatamah *et al.*, 2005]. The African Lakes are well studied and illustrate the impacts from this nonpoint source of pollution; in these lakes, the atmospheric pathway is estimated to contribute 50–90% of the annual load of new phosphorus [Bootsma and Hecky, 2003; Tamatamah *et al.*, 2005]. In this extreme instance, the high P concentrations have subsequently led to toxic algal blooms, eutrophication, and fish kills [Bootsma and Hecky, 2003; Tamatamah *et al.*, 2005]. Because flushing rates in these lakes are long ( $10^2\text{--}10^4$  years), recovery is likely to be a slow and inefficient process.

Nitrogen deposition has increased continuously with population growth, industry, and agriculture in the twentieth century [Galloway *et al.*, 2004]. Many of the major sources of nitrogen emissions can be regulated via technological means, and for this reason, nitrogen deposition rates are dropping over much of the industrialized world and recovery from acid deposition in these regions already underway [Driscoll *et al.*, 2003; Kopáček *et al.*, 2006]. In contrast, P emissions to the atmosphere result from land use and climate changes that influence the wind erosion of soils, increases in food production, use of grazing lands, and changes in the frequency and severity of droughts that influence biomass burning [Foley *et al.*, 2005; Hudson, 2011; Pandey and Pandey, 2013; Trenberth *et al.*, 2014]. Though N deposition is decreasing in the industrialized world, N deposition continues to rise in other parts of the developing world [Galloway *et al.*, 2004; Pandey *et al.*, 2014; Wilcke *et al.*, 2013]. Given a rising population, increased demand for food, and increased frequency and severity of drought, it is reasonable to expect continued increases in P emission and deposition in both the industrialized and developing world. This study provides evidence that these changes may have already influenced the chemistry of precipitation and lake surface waters in many regions of the world. These changes may become progressively more important in the coming decades. To better protect our freshwater resources, deposition rates of phosphorus ought to be considered more widely in national deposition monitoring networks. To date, very few studies have directly examined the effects of atmospheric P deposition on aquatic and terrestrial ecosystem function and nutrient budgets, and there is growing need for these types of analyses.

#### Acknowledgments

Support was provided by NSF DEB Award 0948823, Niwot Ridge LTER Site (NSF 1027341), NSF EaSM (1049033), NSF ETBC (102163), and NSERC (PGS-D). We would like to thank Holly Hughes, Chris Seibold, and Noah Pollock for analytical and field assistance, the Editors, two anonymous reviewers, and Jeff Curtis for valuable discussion and commentary. Data supporting Figure 1 and Table S1 are available in the supporting information.

#### References

- Andreae, M. O., and P. Merlet (2001), Emission of trace gases and aerosols from biomass burning, *Global Biogeochem. Cycles*, 15(4), 955–966, doi:10.1029/2000GB001382.
- APIS (2014), *Air Pollution Information System*, Center for Ecol. and Hydrol., U. K.
- Ballantyne, A., J. Brahney, D. Fernandez, C. Lawrence, J. Saros, and J. Neff (2010), Biogeochemical response of alpine lakes to recent changes in dust deposition, *Biogeosciences*, 7, 8723–8761.

- Bergstrom, A.-K., and M. Jansson (2006), Atmospheric nitrogen deposition has caused nitrogen enrichment and eutrophication of lakes in the Northern Hemisphere, *Global Change Biol.*, 12(4), 635–643.
- Bergstrom, A.-K., P. Blomqvist, and M. Jansson (2005), Effects of atmospheric nitrogen deposition on nutrient limitation and phytoplankton biomass in unproductive Swedish Lakes, *Limnol. Oceanogr.*, 50(3), 987–994.
- Bian, H., M. Chin, S. R. Kawa, B. Duncan, A. Arellano, and P. Kasibhatla (2007), Sensitivity of global CO simulations to uncertainties in biomass burning sources, *J. Geophys. Res.*, 112, D23308, doi:10.1029/2006JD008376.
- Birck, C., I. Domaizon, and F. Rimet (2013), Monitoring of French altitude lakes in multi-stressors situations: Focus on 5 lakes in Haute-Savoie, in *5th Symposium for Research in Protected Areas*, pp. 59–64, Mittersill.
- Bond, T. C., D. G. Streets, K. F. Yarber, S. M. Nelson, J.-H. Woo, and Z. Klimont (2004), A technology-based global inventory of black and organic carbon emissions from combustion, *J. Geophys. Res.*, 109, D14203, doi:10.1029/2003JD003697.
- Bond, T., E. Bhardwaj, R. Dong, R. Jogani, S. Jung, C. Roden, D. Streets, and N. Trautman (2007), Historical emissions of black and organic carbon aerosol from energy-related combustion, 1850–2000, *Global Biogeochem. Cycles*, 21, GB2018, doi:10.1029/2006GB002840.
- Bond, T., et al. (2013), Bounding the role of black carbon in the climate system: A scientific assessment, *J. Geophys. Res. Atmos.*, 21, 5380–5552, doi:10.1002/jgrd.50171.
- Bootsma, H. A., and R. E. Hecky (1993), Conservation of the African Great Lakes: A limnological perspective conservación de los Grandes Lagos Africanos: Una perspectiva limnológica, *Conserv. Biol.*, 7(3), 644–656.
- Bootsma, H. A., and R. E. Hecky (2003), A comparative introduction to the biology and limnology of the African Great Lakes, *J. Great Lakes Res.*, 29(Supplement 2), 3–18.
- Boy, J., R. Rollenbeck, C. Valarezo, and W. Wilcke (2008), Amazonian biomass burning-derived acid and nutrient deposition in the north Andean montane forest of Ecuador, *Global Biogeochem. Cycles*, 22, GB4011, doi:10.1029/2007GB003158.
- Brahney, J. (2012), The influence of anthropogenic dust emissions on precipitation chemistry and lake biogeochemistry, PhD thesis, 190 pp, Univ. of Colo., Boulder.
- Brahney, J., A. Ballantyne, P. Kociolek, S. A. Spaulding, M. Otu, T. Porwoll, and J. C. Neff (2014), Dust mediated transfer of phosphorus to alpine lake ecosystems of the Wind River Range, Wyoming, *Biogeochemistry*, 120(1–3), 259–278.
- Brahney, J., A. P. Ballantyne, P. Kociolek, P. R. Leavitt, G. L. Farmer, and J. C. Neff (2015), Ecological changes in two contrasting lakes associated with human activity and dust transport in western Wyoming, *Limnol. Oceanogr.*, 60(2), 678–695.
- Camarero, L., and J. Catalán (2012), Atmospheric phosphorus deposition may cause lakes to revert from phosphorus limitation back to nitrogen limitation, *Nat. Commun.*, 3, 1118, doi:10.1038/ncomms2125.
- Camarero, L., and J. Catalan (1996), Variability in the chemistry of precipitation in the Pyrenees (northeastern Spain): Dominance of storm origin and lack of altitude influence, *J. Geophys. Res.*, 101, 29,491–29,498, doi:10.1029/96JD01816.
- Carlisle, A., A. H. F. Brown, and E. J. White (1967), The nutrient content of tree stem flow and ground flora litter and leachates in a Sessile Oak (*Quercus Petraea*) woodland, *J. Ecol.*, 55(3), 615–627.
- Catalan, J., E. Ballesteros, E. A. Gacia, A. Palau, and L. Camarero (1993), Chemical composition of disturbed and undisturbed high-mountain lakes in the Pyrenees: A reference for acidified sites, *Water Res.*, 27(1), 133–141.
- Chin, M., et al. (2009), *Atmospheric Aerosol Properties and Climate Impacts*, Natl. Aeronaut. and Space Admin., Washington, D. C.
- Crutzen, P. J., and M. O. Andreae (1990), Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, 250(4988), 1669–1678.
- DeAngelis, M., and A. Gaudichet (1991), Saharan dust deposition over Mont Blanc (French Alps) during the last 30 years, *Tellus B*, 43(1), 61–75.
- DFWI (2014), Adirondack Effects Assessment Program (AEAP), edited, Darrin Fresh Water Institute, Rensselaer.
- Diaz, M., F. Pedrozo, C. Reynolds, and P. Temporetti (2007), Chemical composition and the nitrogen-regulated trophic state of Patagonian Lakes, *Limnol. Ecol. Manage. Inland Waters*, 37(1), 17–27.
- Driscoll, C. T., K. M. Driscoll, K. M. Roy, and M. J. Mitchell (2003), Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition, *Environ. Sci. Technol.*, 37(10), 2036–2042.
- Elser, J. J., et al. (2000), Nutritional constraints in terrestrial and freshwater food webs, *Nature*, 408(6812), 578–580.
- Elser, J. J., M. Kyle, L. Steger, K. R. Nydick, and J. S. Baron (2009a), Nutrient availability and phytoplankton nutrient limitation across a gradient of atmospheric nitrogen deposition, *Ecology*, 90(11), 3062–3073.
- Elser, J. J., T. Andersen, J. S. Baron, A. K. Bergstrom, M. Jansson, M. Kyle, K. R. Nydick, L. Steger, and D. O. Hessen (2009b), Shifts in lake N:P stoichiometry and nutrient limitation driven by atmospheric nitrogen deposition, *Science*, 326(5954), 835–837.
- Environmental Protection Agency (EPA) (1985), Western Lakes Survey, edited, U.S. Environmental Protection Agency.
- Fabian, P., R. Rollenbeck, N. Spichtinger, L. Brothers, G. Dominguez, and M. Thieme (2009), Sahara dust, ocean spray, volcanoes, biomass burning: Pathways of nutrients into Andean rainforests, *Adv. Geosci.*, 22, 85–94.
- Foley, J. A., et al. (2005), Global consequences of land use, *Science*, 309(5734), 570–574.
- Gachter, R., and J. S. Meyer (1993), The role of microorganisms in mobilization and fixation of phosphorus in sediments, *Hydrobiologia*, 253(1–3), 103–121.
- Galloway, J. N., W. C. Keene, and G. E. Likens (1996), Processes controlling the composition of precipitation at a remote southern hemispheric location: Torres del Paine National Park, Chile, *J. Geophys. Res.*, 101(D3), 6883–6897, doi:10.1029/95JD03229.
- Galloway, J. N., et al. (2004), Nitrogen cycles: Past, present, and future, *Biogeochemistry*, 70(2), 153–226.
- Ghimire, N., P. Jha, and G. Caravello (2013), Water quality of high-altitude lakes in the Sagarmatha (Everest) National Park, Nepal, *J. Environ. Prot.*, 4(7A), 22–28.
- Ginoux, P., J. M. Prospero, T. E. Gill, N. C. Hsu, and M. Zhao (2012), Global-scale attribution of anthropogenic and natural dust sources and their emission rates based on MODIS deep blue aerosol products, *Rev. Geophys.*, 50, RG3005, doi:10.1029/2012RG000388.
- Golterman, H., J. Paing, L. Serrano, and E. Gomez (1998), Presence of and phosphate release from polyphosphates or phytate phosphate in lake sediments, *Hydrobiologia*, 364, 99–104.
- Graham, W. F., and R. A. Duce (1979), Atmospheric pathways of the phosphorus cycle, *Geochim. Cosmochim. Acta*, 43, 1195–1208.
- Guieu, C., M. D. Loje-Pilot, C. Ridame, and C. Thomas (2002), Chemical characterization of the Saharan dust end-member: Some biogeochemical implications for the western Mediterranean Sea, *J. Geophys. Res.*, 107(D15), 4258, doi:10.1029/2001JD000582.
- Gunkel, G., and C. Beulker (2009), Limnology of the Crater Lake Cuicocha, Ecuador, a cold water tropical lake, *Int. Rev. Hydrobiol.*, 94(1), 103–125.
- Guzman, J. (2005), Limnological investigations in Lake San Pablo, a high mountain lake in Ecuador, PhD thesis, Technischen Universitat Berlin, Berlin.
- Hudson, M. (2011), Facing the heat, *Nature Clim. Change*, 1(6), 282–284.
- Jansson, M., H. Olsson, and K. Pettersson (1988), Phosphatases: origin, characteristics and function in lakes, *Hydrobiologia*, 170(1), 157–175.



- Johnston, F. H., S. B. Henderson, Y. Chen, J. R. Randerson, M. Marlier, R. S. DeFries, P. Kinney, D. M. Bowman, and M. Brauer (2012), Estimated global mortality attributable to smoke from landscape fires, *Environ. Health Perspect.*, **120**, 695–701.
- Kauffman, J. B., D. L. Cummings, D. E. Ward, and R. Babbitt (1995), Fire in the Brazilian Amazon: 1 Biomass, nutrient pools, and losses in slashed primary forests, *Oecologia*, **104**, 397–408.
- Kauffman, J. B., D. L. Cummings, and D. E. Ward (1998), Fire in the Brazilian Amazon: 2 Biomass, nutrient pools and losses in cattle pastures, *Oecologia*, **113**, 415–427.
- Knulst, J. C. (2001), Phosphorus in precipitation—results from measurements during the 1990's, *Rep. B1442, IVL Rep.*, Swedish Environmental Research Institute.
- Kok, J. (2011), A scaling theory for the size distribution of emitted dust aerosols suggests climate models underestimate the size of the global dust cycle, *Proc. Natl. Acad. Sci. U.S.A.*, **108**, 1016–1021.
- Kopacek, J., E. Stuchlik, V. Straskrbova, and P. Psenakova (2000), Factors governing nutrient status of mountain lakes in the Tatra Mountains, *Freshwater Biol.*, **43**(3), 369–383.
- Kopáček, J., E. Stuchlík, J. Veselý, J. Schaumburg, I. C. Anderson, J. Fott, J. Hejzlar, and J. Vrba (2002), Hysteresis in reversal of central European Mountain Lakes from atmospheric acidification, *Water, Air, Soil Pollut. Focus*, **2**(2), 91–114.
- Kopáček, J., E. Stuchlík, and D. Hardekopf (2006), Chemical composition of the Tatra Mountain lakes: Recovery from acidification, *Biologia*, **61**, S21–S33.
- Kopáček, J., J. Hejzlar, J. Vrba, and E. Stuchlik (2011), Phosphorus loading of mountain lakes: Terrestrial export and atmospheric deposition, *Limnol. Oceanogr.*, **56**(4), 1343–1354.
- Lamarque, J.-F., et al. (2010), Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: Methodology and application, *Atmos. Chem. Phys.*, **10**, 7017–7039.
- Lamarque, J.-F., et al. (2011), CAM-chem: Description and evaluation of interactive atmospheric chemistry in CESM, *Geosci. Model Dev.*, **4**, 2199–2278.
- Lami, A., A. Marchetto, S. Musazzi, F. Salerno, G. Tartari, P. Guizzoni, M. Rogora, and G. Tartari (2010), Chemical and biological response of two small lakes in the Khumbu Valley, Himalayas (Nepal) to short-term variability and climatic change as detected by long-term monitoring and paleolimnological methods, *Hydrobiologia*, **648**(1), 189–205.
- Lawrence, C. R., and J. Neff (2009), The contemporary physical and chemical flux of Aeolian dust: A synthesis of direct measurements of dust deposition, *Chem. Geol.*, **257**, 46–63.
- Lepori, F., and J. Robin (2014), Nitrogen limitation of the phytobenthos in alpine Lakes: Results from nutrient-diffusing substrata, *Freshwater Biol.*, **59**(8), 1633–1645.
- Levine, S. N., and D. W. Schindler (1999), Influence of nitrogen to phosphorus supply ratios and physicochemical conditions on cyanobacteria and phytoplankton species composition in the Experimental Lakes Area, Canada, *Can. J. Fish. Aquat. Sci.*, **56**(3), 451–466.
- Leys, J. F., and G. H. McTainsh (1999), Dust and nutrient deposition to riverine environments of south-eastern Australia, *Z. Geomorph. Suppl.*, **116**, 59–76.
- Likens, G. E. (2013), Chemistry of bulk precipitation at HBRF (1995–2010) in the White Mountain National Forest, Durham, NH. Hubbard Brook Data Archive [Database].
- Linsey, G. A., D. W. Schindler, and M. P. Stainton (1987), Atmospheric deposition of nutrients and major ions at the Experimental Lakes Area in Northwestern Ontario, 1970 to 1982, *Can. J. Fish. Aquat. Sci.*, **44**(S1), s206–s214.
- Maberly, S. C., L. King, M. M. Dent, R. I. Jones, and C. E. Gibson (2002), Nutrient limitation of phytoplankton and periphyton growth in upland lakes, *Freshwater Biol.*, **47**(11), 2136–2152.
- Madugundu, R., V. Nizalapur, and C. Jha (2008), Estimation of LAI and above ground biomass in deciduous forests: Western Ghats of Karnataka India, *Int. J. Appl. Earth Observ. Geoinf.*, **10**, 211–219.
- Mahowald, N., P. Artaxo, A. Baker, T. Jickells, G. Okin, J. Randerson, and A. Townsend (2005), Impact of biomass burning emissions and land use change on Amazonian atmospheric cycling and deposition of phosphorus, *Global Biogeochem. Cycles*, **19**, GB4030, doi:10.1029/2005GB002541.
- Mahowald, N. M., J.-F. Lamarque, X. X. Tie, and E. Wolff (2006a), Sea-salt aerosol response to climate change: Last Glacial Maximum, preindustrial, and doubled carbon dioxide climates, *J. Geophys. Res.*, **111**, D05303, doi:10.1029/2005JD006459.
- Mahowald, N. M., D. Muhs, S. Levis, P. Rasch, M. Yoshioka, and C. Zender (2006b), Change in atmospheric mineral aerosols in response to climate: Last glacial period, pre-industrial, modern and doubled-carbon dioxide climates, *J. Geophys. Res.*, **111**, D10202, doi:10.1029/2005JD006653.
- Mahowald, N. M., et al. (2008), The global distribution of atmospheric phosphorus deposition and anthropogenic impacts, *Global Biogeochem. Cycles*, **22**, GB4026, doi:10.1029/2008GB003240.
- Mahowald, N., et al. (2010), Observed 20th century desert dust variability: Impact on climate and biogeochemistry, *Atmos. Chem. Phys.*, **10**, 10,875–10,893.
- Mahowald, N., D. S. Ward, S. Kloster, M. G. Flanner, C. L. Heald, N. G. Heavens, P. G. Hess, P. Y. Chuang, and J.-F. Lamarque (2011), Aerosol impacts on climate and biogeochemistry, *Ann. Rev. Environ. Resour.*, **36**, 45–74.
- Maupetit, F., and R. J. Delmas (1994), Snow chemistry of high altitude glaciers in the French Alps, *Tellus B*, **46**, 304–324.
- McGroddy, M., T. Daufresne, and L. Hedin (2004), Scaling of C:N:P stoichiometry in forests worldwide: Implications of terrestrial Redfield-type ratios, *Ecology*, **85**(9), 2390–2401.
- McMaster, N. L., and D. W. Schindler (2005), Planktonic and epipelagic algal communities and their relationship to physical and chemical variables in alpine Ponds in Banff National Park, Canada, *Arct. Antarct. Alp. Res.*, **37**(3), 337–347.
- Mieville, A., C. Granier, C. Liousse, B. Guillaume, F. Mouillot, J.-F. Lamarque, J.-M. Grégoire, and G. Pétron (2010), Emissions of gases and particles from biomass burning during the 20th century using satellite data and historical reconstruction, *Atmos. Environ.*, **44**, 1469–1477.
- Mladenov, N., M. W. Williams, S. K. Schmidt, and K. Cawley (2012), Atmospheric deposition as a source of carbon and nutrients to an alpine catchment of the Colorado Rocky Mountains, *Biogeosciences*, **9**(8), 3337–3355.
- Morales-Baquero, R., R. Carrillo, I. Reche, and P. Sanchez-Castillo (1999), Nitrogen-phosphorus relationship in high mountain lakes: Effects of the size of catchment basins, *Can. J. Fish. Aquat. Sci.*, **56**(10), 1809–1817.
- Morales-Baquero, R., E. Pulido-Villena, and I. Reche (2006), Atmospheric inputs of phosphorus and nitrogen to the southwest Mediterranean region: Biogeochemical responses of high mountain lakes, *Limnol. Oceanogr.*, **51**(2), 830–837.
- Morris, D. P., and W. M. Lewis (1988), Phytoplankton nutrient limitation in Colorado Mountain Lakes, *Freshwater Biol.*, **20**(3), 315–327.
- Mosello, R., M. C. Brizzio, D. Kotzias, A. Marchetto, D. Rembges, and G. Tartari (2002), The chemistry of atmospheric deposition in Italy in the framework of the National Programme for Forest Ecosystems Control (CONECOFOR), *J. Limnol.*, **61**, 77–92.
- Neale, R., J. Richter, S. Park, P. Lauritzen, S. Vavrus, P. Rasch, and M. Zhang (2013), The mean climate of the Community Atmosphere Model (CAM4) in forced SST and fully coupled experiments, *J. Clim.*, **26**(14), 5150–5168.

- Neff, J. C., A. P. Ballantyne, G. L. Farmer, N. M. Mahowald, J. L. Conroy, C. C. Landry, J. T. Overpeck, T. H. Painter, C. R. Lawrence, and R. L. Reynolds (2008), Increasing eolian dust deposition in the western United States linked to human activity, *Nat. Geosci.*, *1*(3), 189–195.
- Neff, J., M. P. Reynolds, S. Munson, D. Fernandez, and J. Belnap (2013), The role of dust storms in total atmospheric particle concentration at two sites in the western U.S., *J. Geophys. Res. Atmos.*, *118*, 11,201–11,222, doi:10.1002/jgrd.50855.
- Okin, G. S., N. Mahowald, O. A. Chadwick, and P. Artaxo (2004), Impact of desert dust on the biogeochemistry of phosphorus in terrestrial ecosystems, *Global Biogeochem. Cycles*, *18*, GB2005, doi:10.1029/2003GB002145.
- Pandey, A. N., P. C. Pathak, and J. S. Singh (1983), Water, sediment and nutrient movement in forested and non-forested catchments in Kumaun Himalaya, *For. Ecol. Manage.*, *7*(1), 19–29.
- Pandey, J., U. Pandey, and A. Singh (2014), Impact of changing atmospheric deposition chemistry on carbon and nutrient loading to Ganga River: Integrating land-atmosphere-water components to uncover cross-domain carbon linkages, *Biogeochemistry*, *119*(1–3), 179–198.
- Pandey, U., and J. Pandey (2013), Impact of DOC trends resulting from changing climatic extremes and atmospheric deposition chemistry on periphyton community of a freshwater tropical lake of India, *Biogeochemistry*, *112*(1–3), 537–553.
- Pettersson, K. (1980), Alkaline phosphatase activity and algal surplus phosphorus as phosphorus-deficiency indicators in Lake Erken, *Arch. Hydrobiol.*, *89*(1/2), 54–87.
- Pivello, V. R., and L. M. Coutinho (1992), Transfer of macronutrients to the atmosphere during experimental burnings in an open cerrado (Brazilian savanna), *J. Trop. Ecol.*, *8*, 487–497.
- Porter, L. L. (2012), Benthic responses to nitrogen and phosphorus deposition on alpine Ponds in Banff National Park: A replicated whole-ecosystem experiment, MSc thesis, Univ. of Alberta.
- Psenner, R. (1989), Chemistry of high mountain lakes in siliceous catchments of the Central Eastern Alps, *Aquat. Sci.*, *51*(2), 108–128.
- Psenner, R. (1999), Living in a dusty world: Airborne dust as a key factor for alpine Lakes, *Water, Air, Soil Pollut.*, *112*, 217–227.
- Pulido-Villena, E., I. Reche, and R. Morales-Baquero (2006), Significance of atmospheric inputs of calcium over the southwestern Mediterranean region: High mountain lakes as tools for detection, *Global Biogeochem. Cycles*, *20*, GB2012, doi:10.1029/2005GB002662.
- Pulido-Villena, E., I. Reche, and R. Morales-Baquero (2008), Evidence of an atmospheric forcing on bacterioplankton and phytoplankton dynamics in a high mountain lake, *Aquat. Sci.*, *70*(1), 1–9.
- Randerson, J. T., G. R. van der Werf, L. Giglio, G. J. Collatz, and P. S. Kasibhatla (2013), Global Fire Emissions Database, Version 3 (GFEDv3.1), <http://daac.ornl.gov/>, Oak Ridge Natl. Lab. Distributed Active Archive Center, Oak Ridge, Tenn., doi:10.3334/ORNLDAAAC/1191.
- Rasch, P. J., W. D. Collins, and B. E. Eaton (2000), Understanding the Indian Ocean Experiment INDOEX aerosol distributions with an aerosol assimilation, *J. Geophys. Res.*, *106*(D7), 7337–7355, doi:10.1029/2000JD900508.
- Reche, I., E. Ortega-Retuerta, O. Romera, E. Pulido-Villena, R. Morales-Baquero, and E. O. Casamayor (2009), Effect of Saharan dust inputs on bacterial activity and community composition in Mediterranean lakes and reservoirs, *Limnol. Oceanogr.*, *54*(3), 869–879.
- Rogora, M., J. Massafiero, A. Marchetto, G. Tartari, and R. Mosello (2008), The water chemistry of some shallow lakes in Northern Patagonia and their nitrogen status in comparison with remote lakes in different regions of the globe, *J. Limnol.*, *67*(2), 75–86.
- Rogora, M., S. Arisci, and A. Marchetto (2012), The role of nitrogen deposition in the recent nitrate decline in lakes and rivers in Northern Italy, *Sci. Total Environ.*, *417–418*, 214–223.
- Sahoo, G. B., S. G. Schladow, and J. E. Reuter (2010), Effect of sediment and nutrient loading on Lake Tahoe optical conditions and restoration opportunities using a newly developed lake clarity model, *Water Resour. Res.*, *46*, W10505, doi:10.1029/2009WR008447.
- Schaperdoth, I., L. J. Liermann, and S. L. Brantley (2007), The effect of polymeric substances on apatite reactivity in the presence of a freshwater cyanobacterium, *Geomicrobiol. J.*, *24*, 79–91.
- Scheider, W. A., W. R. Snyder, and B. Clark (1979), Deposition of nutrients and major ions by precipitation in south-central Ontario, *Water, Air, Soil Pollut.*, *12*(2), 171–185.
- Schindler, D. W., R. E. Hecky, D. L. Findlay, M. P. Stainton, B. R. Parker, M. J. Paterson, K. G. Beaty, M. Lyng, and S. E. M. Kasian (2008), Eutrophication of lakes cannot be controlled by reducing nitrogen input: Results of a 37-year whole-ecosystem experiment, *Proc. Natl. Acad. Sci. U.S.A.*, *105*(32), 11,254–11,258.
- Schulz, M., Y. Balkanski, W. Guelle, F. Dulac, C. Moulin, and C. E. Lambert (1996), Model components necessary to capture a dust plume pattern over the Mediterranean Sea, in *The Impact of Desert Dust Across the Mediterranean*, edited by S. Guerzoni and R. Chester, pp. 51–58, Kluwer Acad., Netherlands.
- Schulz, M., Y. J. Balkanski, W. Guelle, and F. Dulac (1998), Role of aerosol size distribution and source location in a three-dimensional simulation of a Saharan dust episode tested against satellite-derived optical thickness, *J. Geophys. Res.*, *103*(D9), 10,579–10,592, doi:10.1029/97JD02779.
- Seinfeld, J., and S. Pandis (1998), *Atmospheric Chemistry and Physics*, 1326 pp., John Wiley, New York.
- Sickman, J., D. Bennett, D. Lucero, T. Whitmore, and W. Kenney (2013), Diatom-inference models for acid neutralizing capacity and nitrate based on 41 calibration lakes in the Sierra Nevada, California, USA, *J. Paleolimnol.*, *50*(2), 159–174.
- Sickman, O. J., M. J. Melack, and W. D. Clow (2003), Evidence for nutrient enrichment of high-elevation lakes in the Sierra Nevada, California, *Limnol. Oceanogr.*, *48*(5), 1885–1892.
- Smith, E. A., C. I. Mayfield, and P. T. S. Wong (1978), Naturally occurring apatite as a source of ortho-phosphate for growth of bacteria and algae, *Microb. Ecol.*, *4*(2), 105–117.
- Solberg, S., K. Breivik, N. Clarke, T. Groeggen, I. Rosberg, K. Torseth, D. Aamlid, and W. Aas (1998), Intensive skogovervåkingslater. resultater fra 1998. Forest monitoring plots, results 1998, Norsk institutt for skogforskning.
- Tait, D., and B. Thaler (2000), Atmospheric deposition and lake chemistry trends at a high mountain site in the eastern Alps, *J. Limnol.*, *59*(1), 61–71.
- Tamatamah, R. A., R. E. Hecky, and H. Duthie (2005), The atmospheric deposition of phosphorus in Lake Victoria (East Africa), *Biogeochemistry*, *73*(2), 325–344.
- Tartari, G. A., G. Tartari, and R. Mosello (1998), Water chemistry of high altitude lakes in the Kumbu and Imja Kola valleys (Nepalese Himalayas): Limnology of high altitude lakes in the Mt Everest Region (Nepal), *Mem. Ist. ital. Idrobiol.*, *27*, 51–76.
- Tipping, E., et al. (2014), Atmospheric deposition of phosphorus to land and freshwater, *Environ. Sci. Processes Impacts*, *16*(7), 1608–1617.
- Trenberth, K. E., A. Dai, G. van der Schrier, P. D. Jones, J. Barichivich, K. R. Briffa, and J. Sheffield (2014), Global warming and changes in drought, *Nat. Clim. Change*, *4*(1), 17–22.
- van der Werf, G. R., J. T. Randerson, L. Giglio, G. J. Collatz, P. S. Kasibhatla, and A. F. Arellano Jr. (2006), Interannual variability in global biomass burning emissions from 1997 to 2004, *Atmos. Chem. Phys.*, *6*(11), 3423–3441.
- Veneklaas, E. J. (1990), Nutrient fluxes in bulk precipitation and throughfall in two montane tropical rain forests, Colombia, *J. Ecol.*, *78*(4), 974–992.
- Ventura, M., L. Camarero, T. Buchaca, F. Bartumeus, D. M. Livingstone, and J. Catalan (2000), The main features of seasonal variability in the external forcing and dynamics of a deep mountain lake (Redó, Pyrenees), *J. Limnol.*, *59*(1s), 97–108.



- Vicars, W. C., J. O. Sickman, and P. J. Ziemann (2010), Atmospheric phosphorus deposition at a montane site: Size distribution, effects of wildfire, and ecological implications, *Atmos. Environ.*, *44*(24), 2813–2821.
- Wang, R., Y. Balkanski, O. Boucher, P. Ciais, J. Penuelas, and S. Tao (2015), Significant contribution of combustion-related emissions to the atmospheric phosphorus budget, *Nat. Geosci.*, *8*, 48–54.
- Ward, D. S., S. Kloster, N. M. Mahowald, B. M. Rogers, J. T. Randerson, and P. G. Hess (2012), The changing radiative forcing of fires: Global model estimates for past, present and future, *Atmos. Chem. Phys.*, *12*(22), 10,857–10,886.
- Wilcke, W., S. Leimer, T. Peters, P. Emck, R. Rollenbeck, K. Trachte, C. Valarezo, and J. Bendix (2013), The nitrogen cycle of tropical montane forest in Ecuador turns inorganic under environmental change, *Global Biogeochem. Cycles*, *27*, 1194–1204, doi:10.1002/2012GB004471.
- Wolfe, A. P., J. S. Baron, and R. J. Cornett (2001), Anthropogenic nitrogen deposition induces rapid ecological changes in alpine lakes of the Colorado Front Range (USA), *J. Paleolimnol.*, *25*(1), 1–7.
- Zhu, Z., J. Bi, Y. Pan, S. Ganguly, A. Anav, L. Xu, A. Samanta, S. Piao, R. Nemani, and R. Myneni (2013), Global data sets of vegetation leaf area index (LAI)3g and fraction of photosynthetically active radiation (FPAR)3g derived from global inventory modeling and mapping studies (GIMMS) normalized difference vegetation index (NDVI3g) for the period 1981 to 2011, *Remote Sens.*, *5*(2), 927–948.