AGU PUBLICATIONS

Global Biogeochemical Cycles

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

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Is atmospheric phosphorus pollution altering global alpine Lake stoichiometry?

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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 μm. 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 PO_4^{3-} is predominantly used because biological uptake of 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
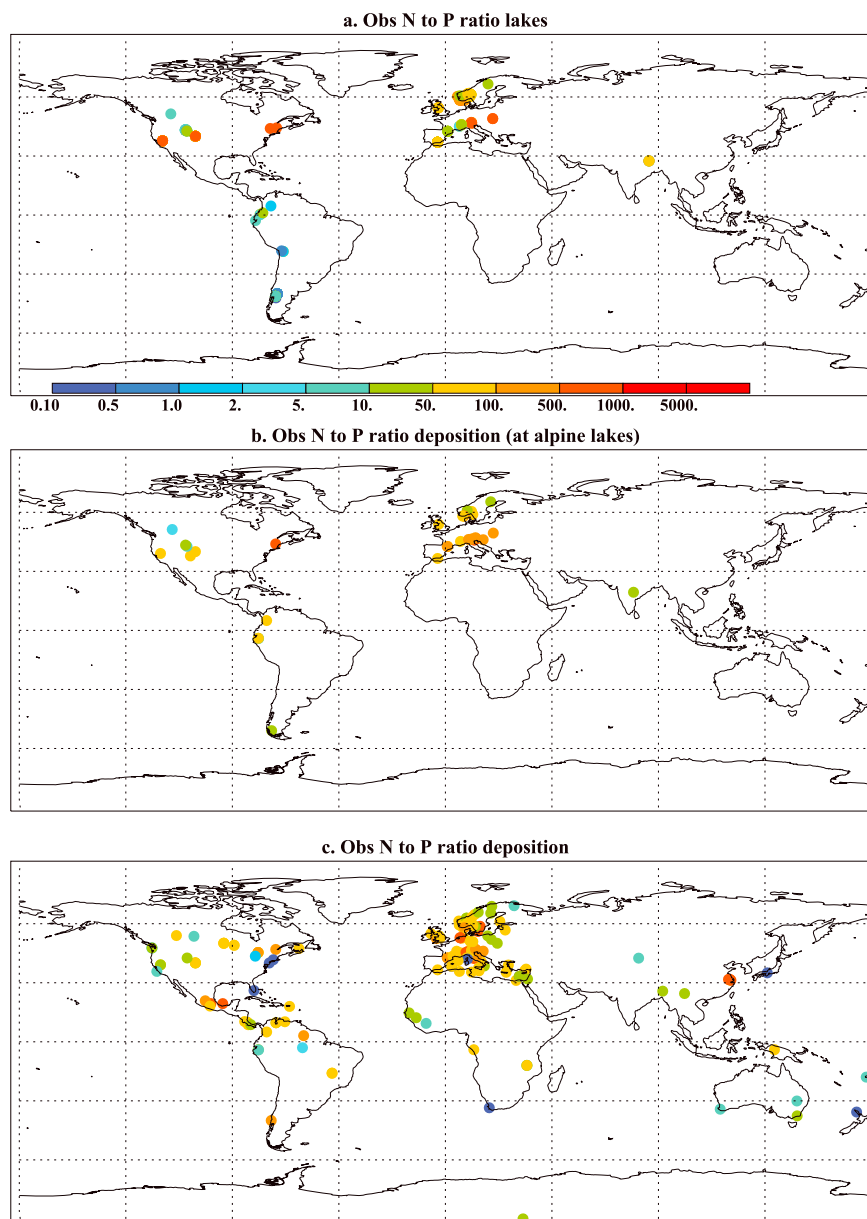
Figure 1. Observed N:P ratios in deposition and lakes. Note that the map scale cannot adequately show all 700 lakes used in the study.

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 $720 \, \mu g \, g^{-1}$ 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 μm. 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 retried 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 μm 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 $0.08 \, \mu g \, P \, kg^{-1}$ 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 μm 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[a]

	Current	Preindustrial	(Current/Preindustrial)
NO_x (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
NH_x (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 NH_x	50	23	2.2
Primary biogenic and very coarse mode N	25	25	1
Total N	136	71	1.9

[a]NO_x represents nitrogen oxide emissions, while NH_x 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 μm 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 μm 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 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 μm fraction (PBP, fires, and biofuels) makes the N emission budgets increase from 111 to 136 Tg N yr^{-1} for current and 47 to 71 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 μm) 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 μm) particles considered, for transport they simulate one mode focused on 3.5 μm 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		
	($<10\,\mu m$)	($<100\,\mu m$)	($<10\,\mu m$)	($<100\,\mu m$)	(Current/Preindustrial)
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 $>10\,\mu m$ 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 ($>10\,\mu m$), 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 Tg P yr^{-1}, compared here with 0.06 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 ($>10\,\mu m$), increase our combustion sources to 1.1 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		
	($<10\,\mu m$)	($<100\,\mu m$)	($<10\,\mu m$)	($<100\,\mu m$)	(Current/Preindustrial)
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^{-2} yr^{-1}, and P deposition from 4 to 400 mg m^{-2} yr^{-1} (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^{-2} yr^{-1}, 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[a]

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

[a]Data used to derive mean values and all metadata can be found in the supporting information.
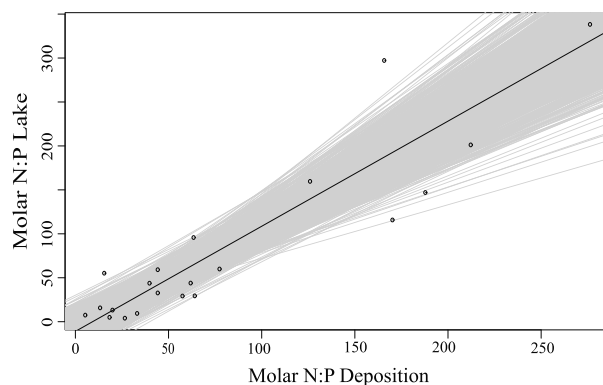
Figure 2. Paired N:P molar ratios of deposition and lake water from mountain ranges around the world. The gray lines represent 1000 regression lines fitted to randomly drawn values from the distributions of lake chemistry data by region. The black line represents the mean of the regression lines and 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 disproportionally 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 ~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
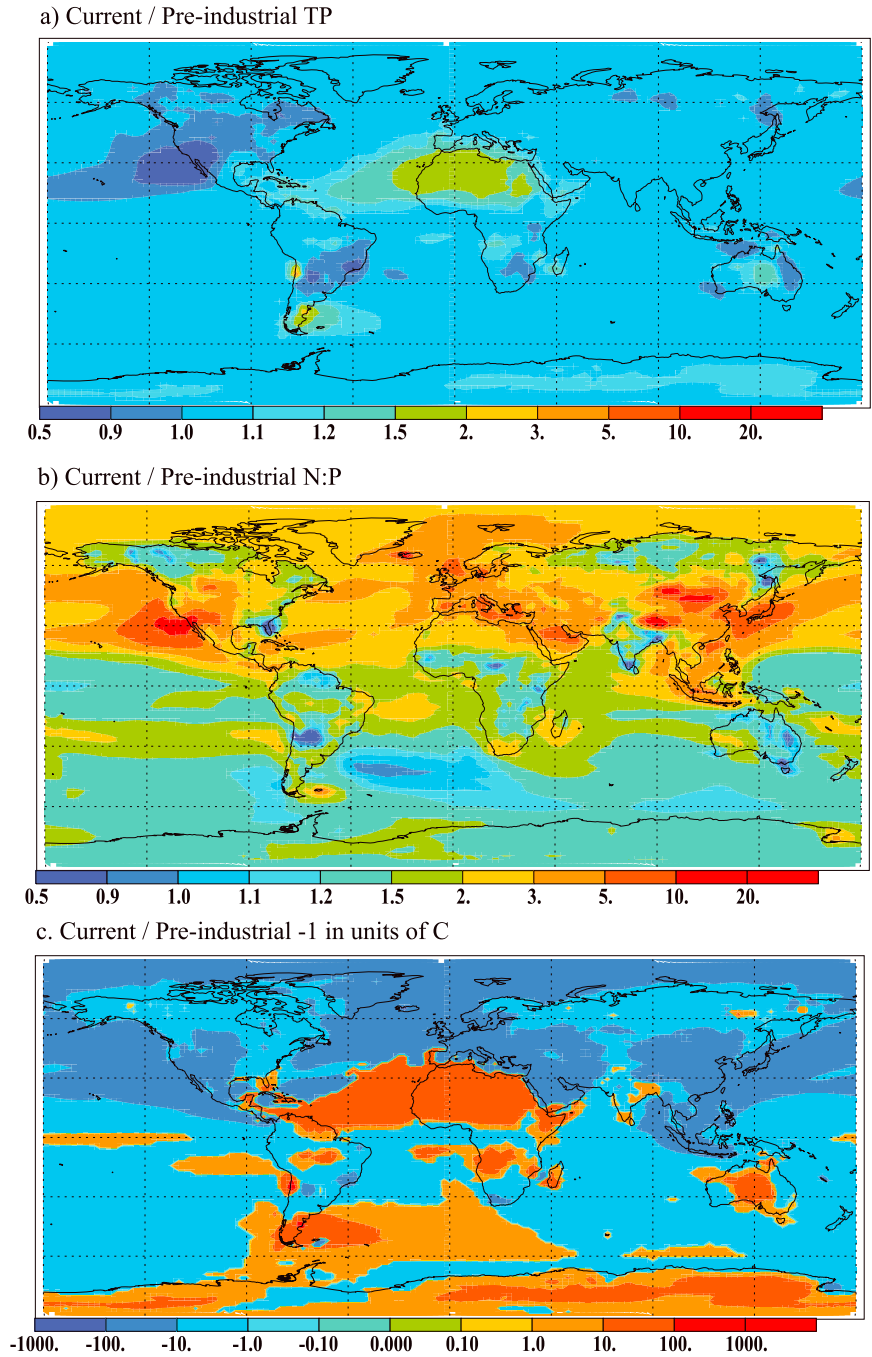
Figure 3. (a) Community Atmospheric Model (CAM) (v4) results of the ratio of current to preindustrial TP deposition. (b) CAM (v4) results of the current to preindustrial N:P ratios in deposition. The hemispheric difference in the mass flux changes of N versus P is clearly shown. (c) Stoichiometric representation 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 Current/Preindustrial -1 in units of C, such that P is represented as $P \times 106$, 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 24–38 $\mu g \, P \, m^2 \, d^{-1}$ [*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 (10^2–10^4 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.

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