Shifts in Lake N:P Stoichiometry and Nutrient Limitation Driven by Atmospheric Nitrogen Deposition

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Human activities have more than doubled the amount of nitrogen (N) circulating in the biosphere. One major pathway of this anthropogenic N input into ecosystems has been increased regional deposition from the atmosphere. Here we show that atmospheric N deposition increased the stoichiometric ratio of N and phosphorus (P) in lakes in Norway, Sweden, and Colorado, United States, and, as a result, patterns of ecological nutrient limitation were shifted. Under low N deposition, phytoplankton growth is generally N-limited; however, in high–N deposition lakes, phytoplankton growth is consistently P-limited. Continued anthropogenic amplification of the global N cycle will further alter ecological processes, such as biogeochemical cycling, trophic dynamics, and biological diversity, in the world's lakes, even in lakes far from direct human disturbance.

All of Earth's major biogeochemical cycles have been altered by human population expansion and industrialization (*1*). In particular, the total amount of circulating nitrogen (N) in the biosphere has increased by more than 100% (*2*). Much of this N is in the form of oxidized and reduced reactive N species (NO_x and NH_x), which are produced as byproducts of fossil fuel combustion and from agricultural emissions from croplands, rangelands, and industrial livestock feeding operations. Reactive N is transported regionally through the atmosphere and deposited in terrestrial and aquatic habitats via rain, snowfall, and dry deposition (*3*). Considerable previous work has evaluated the biogeochemical and ecological impacts of this atmospheric N deposition on terrestrial ecosystems (*4*) and was performed because primary production in terrestrial systems is often limited by N availability (*5*). The effects of atmospheric N deposition on freshwater ecosystems, however, have not been not widely studied, perhaps because lake primary production is generally thought to be limited by phosphorus (P) (*6*). However, the purported primacy of P limitation of lake productivity (*7*) has been challenged by some recent experimental and comparative assessments, suggesting frequent phytoplankton N- and light-limitation in lakes (*5*, *8*, *9*). The effects of atmospheric N deposition on lake phytoplankton have several important implications. For example, fundamental phytoplankton biomass–P loading relationships may be a function of atmospheric N inputs (*10*). Furthermore, increased N:P supply ratios might reduce phytoplankton diversity by favoring those relatively few species with strong competitive abilities for using P (*11*). Enhanced phytoplankton P limitation caused by elevated N loading from the atmosphere may also affect the functioning of lake food webs, because P-limited algae are known to be poor-quality food for consumers such as zooplankton (*12*).

We analyzed 2053 lakes in Norway (385 lakes) and Sweden (1668 lakes) that represent both high– and low–N deposition conditions to determine whether elevated atmospheric N inputs affect lake phytoplankton nutrient supplies in terms of concentrations and ratios of total N (TN) and total P (TP). Additionally, we performed a comprehensive study of nutrient concentrations and phytoplankton nutrient limitation (via N and P enrichment bioassay experiments) in high- and low-deposition lakes both in southern Norway and in the central Colorado Rocky Mountains, United States (*13*). These data were combined with data from previous studies on high- and low-deposition lakes in southern and northern Sweden (*14*), resulting in a overall assessment involving nearly 90 N/P enrichment experiments.

In each of the three study regions, lakes receiving elevated N deposition had significantly elevated surface-water nitrate (NO_3^-) concentrations relative to low-deposition lakes (~sevenfold higher overall, Table 1). Increased N deposition was also associated with considerably higher overall lake N concentrations and higher availability of N compared to P (Table 1 and table S1). In the lakes sampled for the bioassay studies (Table 1), average TN:TP ratios were about 2 to 5 times higher in high-deposition lakes. This pattern was confirmed in the large Scandinavian data set in which the slopes of TN versus TP relationships in Norway and Sweden were 2 to 2.5 times higher in high-deposition lakes than in lakes receiving N loading closer to background levels (Fig. 1). The slopes of the TN versus TP relationships in low-deposition lakes in the large-scale Norway and Sweden lake surveys (Fig. 1) were similar to the average TN:TP ratios observed in the lakes used in our experimental studies in Norway and Sweden (Table 1), suggesting that the low-deposition lakes involved in our bioassays were representative of the larger population of unaffected Scandinavian lakes. However, TN:TP ratios in the Scandinavian high N deposition lakes included in the experimental studies (Table 1) were somewhat higher than the slopes of the TN versus TP relationships, perhaps indicating that our experimental studies involved lakes with stronger N deposition than the overall population classified as "high deposition" in the lake survey analyses.

Changes of N:P stoichiometry indicate altered patterns of phytoplankton nutrient limitation. Nutrient enrichment bioassays demonstrated an inverse relationship between phytoplankton N and P limitation, consistent with Liebig-type resource limitation (*15*) in which significant changes are observed in response to one nutrient or the other (or neither), but not to enrichments of N or P made separately in the same experiment [Fig. 2A; lakes with high values of both response ratios (defined as the final chlorophyll levels normalized to control samples) for N (RR-N) and for P (RR-P) were not observed]. The data indicate shifts in phytoplankton nutrient limitation caused by elevated atmospheric N deposition in each of the three study regions. In Norway, no experiment in lakes receiving low levels of N deposition provided evidence of phytoplankton P limitation, but 12 of 19 experiments indicated a primary N limitation (Table 1 and table S2). In contrast, under elevated N deposition, no experiment produced any sign of N limitation, whereas 13 of 18 suggested phytoplankton P limitation. RRs representing the impact of N or P limitation on phytoplankton biomass also showed similar trends with N deposition levels (Table 1). The strength of this contrast is somewhat surprising, because N deposition levels in the low-deposition region of Norway that we studied (~4.5 kg N ha^{-1} $year^{-1}$) are actually somewhat elevated relative to natural background levels found further north (*16*).

In Colorado, similar overall trends were observed; phytoplankton growth in high N deposition lakes was P-limited, whereas in low-N deposition lakes, it was primarily N-limited (Table 1) (*17*). Although constrained to a shorter sampling time, spring and early summer experiments in Sweden (*14*) also showed signs of the same pattern seen in Norway and Colorado (Table 1). In all the sampled areas, response ratios were generally consistent with an ecological impact of distorted N:P supplies caused by atmospheric N inputs (Table 1). The relative balance of phytoplankton N versus P limitation (RR-N/RR-P) was inversely related to the lake TN:TP ratio (Fig. 2B). Below a TN:TP value of ~44.2 (by atoms), the large majority of experiments indicated N-limited phytoplankton growth (RR-N/RR-P > 1), and the lakes were entirely in low-deposition areas. Above a TN:TP value of ~110, phytoplankton were consistently P-limited, and the lakes were almost entirely (with one exception) in high-deposition areas. Alterations in lake N:P stoichiometry brought about by atmospheric N deposition have therefore produced similar shifts in phytoplankton nutrient limitation across a wide variety of lakes on two continents.

Whereas overall effects of N deposition were generally similar for the three geographic regions

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considered, the consistency and magnitude of impact did vary somewhat both between and among regions. Differences in the impact of N deposition between regions may reflect variable N-loading gradients between high- and low-deposition areas; however, the similarity in the N-deposition gradients in the three study regions (Table 1) suggests that this is unlikely to explain differences in the apparent effect of N deposition on phytoplankton nutrient limitation. It seems more likely that between-region differences reflect contrasts in the relative impact of watershed vegetation on intercepting N. In Sweden, lakes were located in forested catchments, whereas watersheds of lakes in Norway and Colorado were generally unforested. This may explain why the effects of N deposition on phytoplankton nutrient limitation in Sweden were somewhat modest compared with the effects seen in Colorado and especially Norway; differences in N/P limitation between high- and low-deposition areas in Sweden appear to be confined to the early growing season, when forest uptake of inorganic N is limited (*14*). Within-region variations may reflect various local factors that impinge on overall N and P supply and loss rates, such as those associated with geological substrata, flow paths taken by inflow water, or the extent of wetland or lake denitrification (*16*).

Our findings show that, despite the potential of watershed vegetation uptake and sediment denitrification to buffer lakes against elevated N loading, increased inputs of anthropogenic N have accumulated in receiving waters. As a result, shifts in lake N:P stoichiometry have altered ecological nutrient limitation of phytoplankton growth. Phytoplankton in lakes that are less influenced by anthropogenic inputs experience relatively balanced

Table 1. Effects of atmospheric N deposition on average nutrient concentrations and ratios as well as on quantitative and qualitative phytoplankton responses to N or P enrichment in three regions. High-and low-deposition lakes are compared for each region and overall (via *t* test for quantitative parameters or chi-squared test for type of nutrient limitation). Quantitative measures are given as the average RRs for enrichment by N or P or N and P (*13*). The type of limitation indicates the relative frequency of primary limitation or sequential colimitation by N or P as described in the supporting online material. n.s., not significant. *P* values in parentheses indicate the results of a *t* test comparing mean values for high- and low-deposition lakes for each region or for the entire study.

Country	Deposition	Number of lakes	NO_3 (μM)	TN (μM)	TP (μM)	TN:TP (atomic)	RR-N	RR-P	RR-N/RR-P	Type of limitation	
										N	P
Norway	Low (~4.5 kg/ha)	19	0.11	9.81	0.34	32.8	1.64	1.03	1.63	12/19	0/19
	High (~8.5 kg/ha)	18	20.4	26.7	0.17	165	1.04	1.86	0.60	0/18	13/18
			$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$
United States	Low (~2 kg N/ha)	20	4.27	7.54	0.16	52.9	1.32	1.35	1.24	5/20	4/20
	High (~7 kg N/ha)	16	11.9	16.5	0.15	126	0.97	1.49	0.72	1/16	9/16
			$P < 0.0001$	$P < 0.0001$	n.s.	$P < 0.0006$	$P < 0.02$	($P < 0.06$)	$P < 0.03$	($P \sim 0.12$)	$P < 0.03$
Sweden	Low (~2 kg/ha)	7	0.12	8.02	0.25	34.5	1.32	0.96	1.39	3/7	0/7
	High (~6 kg/ha)	7	0.89	14.2	0.24	60.2	1.18	1.19	1.04	0/7	3/7
			$P < 0.011$	$P < 0.01$	n.s.	$P < 0.001$	($P \sim 0.14$)	$P < 0.001$	($P < 0.09$)	($P < 0.10$)	($P < 0.10$)
Total	Low	46	2.01	8.79	0.25	42.2	1.32	1.13	1.42	20/46	4/46
	High	41	13.6	20.1	0.17	131	1.18	1.54	0.72	1/41	25/41
			$P < 0.0001$	$P < 0.0001$	$P < 0.001$	$P < 0.0001$	$P < 0.0001$	$P < 0.001$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$

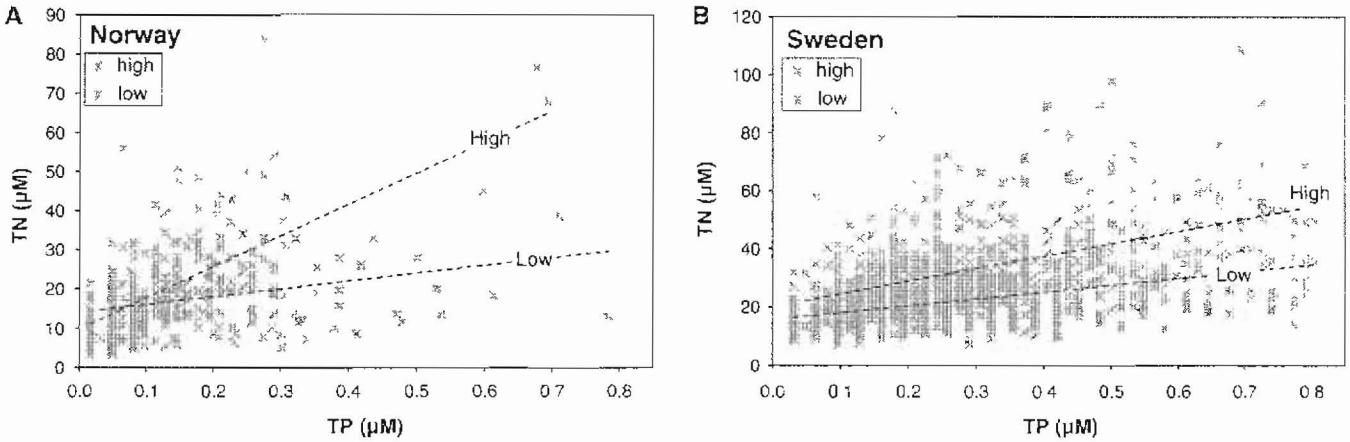

Fig. 1. The effect of atmospheric N deposition on lake N:P stoichiometry in Scandinavia. Compared to low-deposition lakes (green), lakes receiving high atmospheric N deposition (red) have higher TN concentrations for a given level of TP in both Norway (**A**) and Sweden (**B**). All relationships were highly significant ($P < 0.0001$ and $R^2 = 0.16$ to 0.40). The slopes for TN versus TP relationships for the high- and low-deposition lakes were 76 and 32, respectively (Norway) and 43 and 23, respectively (Sweden). For clarity, values for TP for high-deposition lakes were offset by −0.015 μM so that they did not overlap with low-deposition data.

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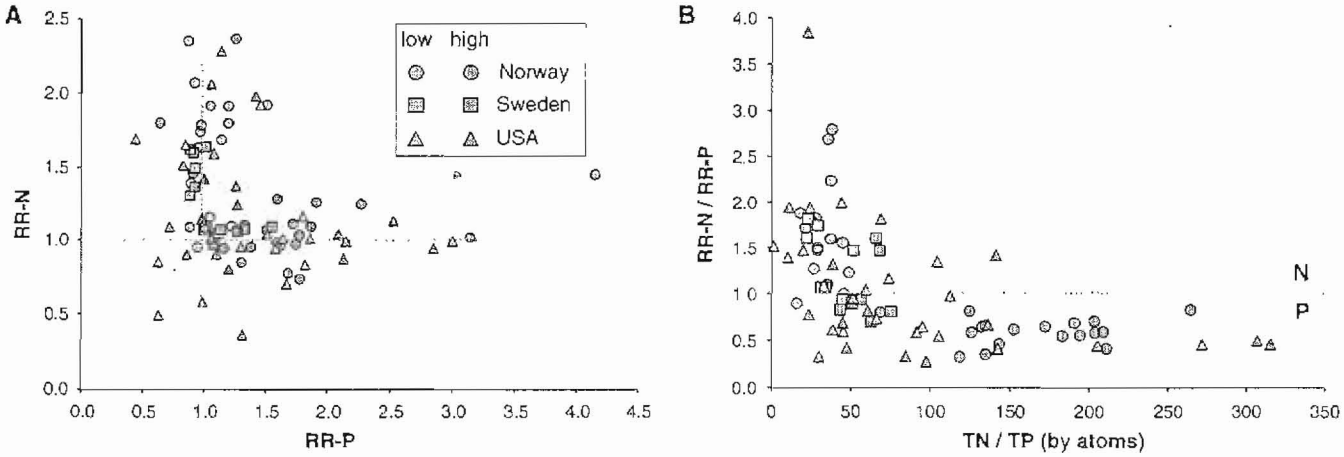

Fig. 2. Phytoplankton N and P limitation as a function of atmospheric N deposition in lakes of Norway (circles), Sweden (squares), and Colorado (triangles). Lake phytoplankton that respond strongly to N have a weak response to P and vice versa (**A**). Horizontal and vertical lines delineate response ratios of 1, indicating no response of phytoplankton biomass to enrichment of that nutrient. Results from low-deposition lakes (green) are clustered on the *y* axis, indicating primary N limitation, whereas those from high-deposition lakes (red) are clustered on the *x* axis, indicating primary P limitation. The relative phytoplankton response to N compared with P (RR-N/RR-P) is strongly dependent on lake TN:TP ratio (**B**), which itself is dependent on N deposition. Values greater than 1 indicate that N limitation predominates in that lake, whereas values less than 1 indicate that P limitation predominates.

or N-deficient nutrient supplies, but enhanced N inputs from the atmosphere during the past several decades of human industrialization and population expansion appear to have produced regional phytoplankton P limitation. Producer diversity is likely to be low when resource supply ratios are skewed in favor of one particular nutrient relative to others (*11*, *18*). Thus, increased N loading from the atmosphere may reduce lake phytoplankton biodiversity, similar to anticipated effects of N deposition on plant diversity in terrestrial ecosystems (*19*, *20*), by possibly favoring those relatively few species that are best able to compete for the limiting P. Enhanced phytoplankton P limitation may also impair food-web performance, because both laboratory and field studies (*21*) have shown that P-limited algae are poor-quality food for zooplankton because of unsuitable biochemical composition (*22*) or low P content (*23*). Indeed, this is possible in the Colorado and Norway lakes that we studied, in which particulate biomass (seston) C:P and N:P ratios were significantly higher ($P < 0.006$) in high-deposition lakes (240 versus 197 C:P by atoms, and 36.2 versus 26.7 N:P by atoms). Thus, sustained N deposition that generates stoichiometric imbalance between P-limited, low-P phytoplankton and their P-rich zooplankton consumers (*12*) may result in reduced production of higher trophic levels, such as fish. Projected increases in global atmospheric N transport during the coming decades (*24*) are likely to substantially influence the ecology of lake food webs, even in lakes far from direct human disturbance.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/326/5954/835/DC1
Materials and Methods
Tables S1 and S2
References

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Abiotic Gas Formation Drives Nitrogen Loss from a Desert Ecosystem

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In arid environments such as deserts, nitrogen is often the most limiting nutrient for biological activity. The majority of the ecosystem nitrogen flux is typically thought to be driven by production and loss of reactive nitrogen species by microorganisms in the soil. We found that high soil-surface temperatures (greater than 50°C), driven by solar radiation, are the primary cause of nitrogen loss in Mojave Desert soils. This abiotic pathway not only enables the balancing of arid ecosystem nitrogen budgets, but also changes our view of global nitrogen cycling and the predicted impact of climate change and increased temperatures on nitrogen bioavailability.

After the presence of water, nitrogen availability is the primary constraint to biological activity in many arid ecosystems (*1*). Despite the existence of large pools of soil N, arid regions such as deserts, dry shrublands, and savannas often lack bioavailable forms of N (*2*, *3*). Inputs and losses of biologically available N therefore directly affect ecosystem

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