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The Haber Bosch–harmful algal bloom (HB–HAB) link

Patricia M Glibert¹, Roxane Maranger², Daniel J Sobota³ and Lex Bouwman^{4,5}

¹ University of Maryland Center for Environmental Science, Horn Point Laboratory, PO Box 775, Cambridge, MD 21613, USA

² Groupe de Recherche Interuniversitaire en Limnologie et en Environnement Aquatique (GRIL), Département de Sciences Biologiques, Université de Montréal, Case Postale 6128, Succ. Centre-Ville, Montréal, Québec H3C 3J7, Canada

³ Environmental Solutions Division, Oregon Department of Environmental Quality, 811 SW 6th Ave., Portland, OR 97206, USA

⁴ Department of Earth Sciences—Geochemistry, Faculty of Geosciences, Utrecht University, PO Box 80021, 3508 TA Utrecht, The Netherlands

⁵ PBL Netherlands Environmental Assessment Agency, PO Box 303, 3720 AH Bilthoven, The Netherlands

E-mail: glibert@umces.edu


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Abstract

Large-scale commercialization of the Haber–Bosch (HB) process is resulting in intensification of nitrogen (N) fertilizer use worldwide. Globally N fertilizer use is far outpacing that of phosphorus (P) fertilizer. Much of the increase in N fertilizers is also now in the form of urea, a reduced form of N. Incorporation of these fertilizers into agricultural products is inefficient leading to significant environmental pollution and aquatic eutrophication. Of particular concern is the increased occurrence of harmful algal blooms (HABs) in waters receiving nutrient enriched runoff. Many phytoplankton causing HABs have physiological adaptive strategies that make them favored under conditions of elevated N : P conditions and supply of chemically reduced N (ammonium, urea). We propose that the HB-HAB link is a function of (1) the inefficiency of incorporation of N fertilizers in the food supply chain, the leakiness of the N cycle from crop to table, and the fate of lost N relative to P to the environment; and (2) adaptive physiology of many HABs to thrive in environments in which there is excess N relative to classic nutrient stoichiometric proportions and where chemically reduced forms of N dominate. The rate of HAB expansion is particularly pronounced in China where N fertilizer use has escalated very rapidly, where soil retention is declining, and where blooms have had large economic and ecological impacts. There, in addition to increased use of urea and high N : P based fertilizers overall, escalating aquaculture production adds to the availability of reduced forms of N, as does atmospheric deposition of ammonia. HABs in both freshwaters and marginal seas in China are highly related to these overall changing N loads and ratios. Without more aggressive N control the future outlook in terms of HABs is likely to include more events, more often, and they may also be more toxic.

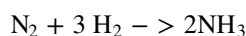
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Keywords: nitrogen, eutrophication, nitrogen fertilizer, N : P ratio, cyanobacteria, dinoflagellates, harmful algal blooms

The industrial fixation of nitrogen gas (N₂) to ammonia (NH₃), the Haber–Bosch (HB) process



is considered to be one of the most important chemical reactions in the world (e.g., Smil 2001) and ‘the greatest single experiment in global geo-engineering ever made’ (Sutton *et al* 2013, p. 4). This reaction has produced the nitrogen (N) fertilizers that have contributed to the ‘green revolution’ responsible for increased food production that has supported the expansion of human population from ~2 billion in the early 20th century to >7 billion people today (Smil 1999, Erismann *et al* 2008).

Prior to World War II, the creation of reactive N was largely due to natural processes, including biological N fixation and lightning, and population expansion kept pace with its creation (Galloway *et al* 2002). After the mid-1940s and the commercialization and scaling up of the HB process, the manufacture and use of N expanded rapidly, from <10 MT N yr⁻¹ in 1950 to >170 MT N yr⁻¹ in 2013 (MT = megatonnes; figure 1(A); Constant and Sheldrick 1992, FAO 2012, Heffer and Prud’homme 2013). In fact, 85% of all synthetic N fertilizers have been created since 1985 (Howarth 2008).

The rate of change in use of N fertilizers has eclipsed that of phosphorus (P) fertilizers in large part due to this large-scale capacity for anthropogenic synthesis. Global use of N fertilizer has increased nine-fold, while that of P has increased three-fold (Sutton *et al* 2013; figure 1(B)) and the upward trends in N : P in fertilizer application (figure 1(C)) are apparent in virtually all regions of the globe (figures 1(D)–(F)). In the US, it has been estimated that there has been at least a five-fold increase in reactive N use on average compared to pre-industrial time (Houlton *et al* 2013), but this increase is spatially variable ranging from negligible to 35-fold in different areas (Sobota *et al* 2013).

Although the HB process is the conversion of N₂ to NH₃, nearly 60% of all N fertilizer now used throughout most of the world is in the form of urea (CO(NH₂)₂; Constant and Sheldrick 1992, Glibert *et al* 2006, IFA 2014; figure 1(A). Urea production is an extension of the HB process, being produced by reacting CO₂ with anhydrous NH₃ under pressure at high temperatures. World use of urea as a fertilizer and feed additive has increased more than 100-fold in the past four decades (Glibert *et al* 2006). From 2001 to 2010, global urea use grew on average at a rate of 3.8% yr⁻¹, and it is projected that from 2012 to 2017 an estimated 55 new urea manufacturing plants will be constructed worldwide, with half of these located in China (Heffer and Prud’homme 2013), contributing to another anticipated doubling by 2050 (Glibert *et al* 2006). Multiple factors, including the less explosive nature of urea relative to ammonium-nitrate fertilizer (NH₄NO₃), make the transportation and storage of this

synthetically produced N form much safer and the preferred choice for agricultural applications.

The incorporation of agricultural N into plant biomass is extremely inefficient. Although the efficiency of N use in experimental fields may be much higher than the global average of 50% (Balasubramanian *et al* 2004), under practical conditions it is difficult to equate the N supply from fertilizer and from soil organic matter mineralization with the dynamics of crop N uptake demand (Dobermann and Cassman 2005). Considering the complete food chain, only ~10–30% of N applied actually reaches human consumers (Galloway *et al* 2002, Houlton *et al* 2013). The difficulty in improving N use efficiency in agriculture lies in the high mobility of N in the soil-plant system, and the variety of potential loss pathways ranging from NH₃ volatilization, denitrification, leaching and runoff, and other N transformation processes (Bouwman *et al* 2009). Urea inputs are typically hydrolyzed to NH₄⁺ in soil, but losses via volatilization and from runoff can be large and depend on the timing of application, weather, soil temperature and pH and other factors (Khakural and Alva 1995, Wali *et al* 2003). In regions such as China where the rate of fertilization has risen rapidly, the rate of soil retention of the excess N is actually declining (Cui *et al* 2013), leading to further environmental leakage.

The recovery of fertilizer P in crop products is also low (Syers *et al* 2008) but its biogeochemistry leads to proportionately greater retention within soils and sediments than N (e.g., Rhue and Harris 1999, Smil 2000, Bouwman *et al* 2009). The accumulation of residual soil P due to large fertilizer P surpluses over crop uptake during the 1960s, 1970s, and 1980s has led to an increased pool of plant available P in soils of most industrialized countries; a similar development was seen in later decades in India and China (Sattari *et al* 2012, 2014).

Among the various fates of the ‘leaked N’ are pathways that ultimately lead to N enrichment of lakes, rivers, and coastal waters. The major pathways for this leaked N include direct runoff, estimated to range up to 40% of inputs in large rivers (e.g., Howarth *et al* 2006) and atmospheric volatilization of NH₄⁺, and together these pathways can comprise more than half of the N input (e.g., Galloway *et al* 2004). P also runs off to receiving waters, but given the aforementioned change in patterns of fertilizer use and its biogeochemistry, the stoichiometry of the runoff has also changed in the last decades, leading to increasing N : P in receiving waters (e.g., Glibert *et al* 2013). It has been estimated that the atmospheric deposition of nutrients in the ocean is now ~20 times the Redfield ratio for N : P (Jickells 2006, Peñuelas *et al* 2012) and these changes are also having large consequences for N : P stoichiometry in lakes (Elser *et al* 2009). This change in stoichiometry has been further compounded since the mid-1980s and 1990s when the major industrialized nations began curtailing P use by removing it from detergents and by upgrading sewage treatment processes which generally are

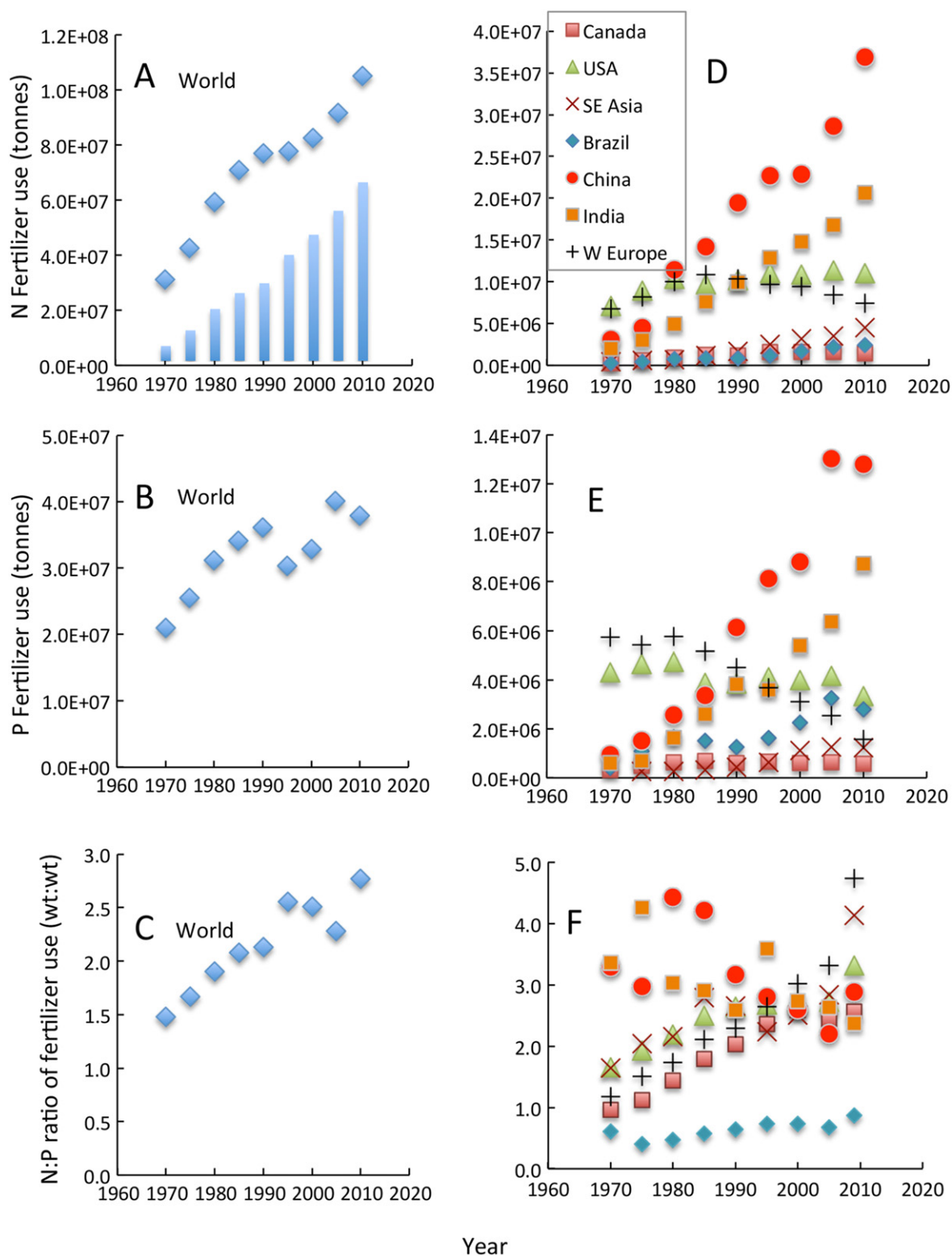


Figure 1. N and P (as P_2O_5) fertilizer use and change in N : P ratio of fertilizer use by weight for the world ((A), (B), and (C) respectively) and for selected countries or regions ((B), (D), and (E) respectively). Superimposed on the world N use graph (A) is the fraction of N use as urea (bars). Total N and P data are from FAO (2012) and data are the average of the three preceding years for each 5 yr period; urea data are from Constant and Sheldrick (1992) through 1990 and estimated at 3.8% growth per year thereafter, comparable to urea data reported from IFA (2014).

more efficient in removing P than N (Litke 1999, Van Drecht *et al* 2009).

In general, urea concentrations in aquatic ecosystems are less than those of the inorganic N forms NO_3^- and NH_4^+ , but depending on proximity of the land source to the water body, concentrations of urea in lacustrine, estuarine and coastal waters may be high, particularly when runoff occurs from heavily fertilized areas (Glibert *et al* 2005, 2006). Concentrations up to 25–50 μMN have been reported in tributaries of the Chesapeake Bay (Lomas *et al* 2002, Glibert *et al* 2005), and nearshore waters adjacent to the heavily fertilized Yaqui Valley, Mexico (Glibert *et al* 2006), among other coastal areas (Kudela *et al* 2008, Switzer 2008). Urea concentrations vary from undetectable to 150 μMN in Lake Kinneret, Israel (Berman 1974), in Polish lakes (Siuda and Chrost 2006) and in lakes of Central Canada where these concentrations also represented 10–50% of bioavailable N (Bogard *et al* 2012). Urea is also part of the dissolved organic N pool that is typically a very large component of the available N in nutrient rich waters (Glibert *et al* 2006, Solomon *et al* 2010).

Eutrophication is the process by which waters are enriched in nutrients, leading to effects such as increased algal growth and development of high biomass blooms, changes in species diversity of both the primary and secondary producers, reductions in dissolved oxygen, fish kills, and the increased frequency of harmful algal blooms (HABs; Nixon 1995, Cloern 2001). HABs are those proliferations of algae that can cause ecological harm to food webs when they accumulate in massive quantities, and they can cause ecological, human health, and economic impacts when these cells produce toxic or other bioactive compounds and when the decay of high algal biomass results in hypoxia (Hallegraeff 1993, Glibert *et al* 2005, Backer and McGillicuddy 2006). The most common HABs are either dinoflagellates or cyanobacteria, although not all dinoflagellates or cyanobacteria are harmful, and not all HABs are made up of these species groups. Cyanobacteria are the HAB functional group of proportionately greater concern in freshwater, while dinoflagellates are the HAB functional group of greater concern in estuarine and marine waters. HABs have been expanding globally, in spatial extent, in duration of blooms, and in intensity (Anderson *et al* 2002, 2008, Glibert *et al* 2005) and a critical question has been the extent to which this change is associated with eutrophication and/or accelerated by climate or other factors (e.g., Paerl and Scott 2010). There are many reports of increases in HABs associated with eutrophication or nutrient loading (e.g., Anderson *et al* 2002, 2008, Glibert *et al* 2006, 2010, Heisler *et al* 2008), but the complexity of the relationship is far from understood. Many nutrient reduction strategies are focused on reducing algal biomass (e.g., total chlorophyll), while appropriate efforts or best management practices that may specifically prevent toxic HABs have remained much more challenging (Jewett *et al* 2008).

One of the most central tenets of aquatic science is that algal biomass and production in lakes and other freshwaters is limited by the availability of P, while that in marine waters is

more often limited by the availability of N (e.g., Ryther and Dunstan 1971, Schindler 1977). However, P limitation in lakes is not universal (Lewis and Wurtsbaugh 2008) as some regions are either naturally (Finlay *et al* 2010) or culturally enriched (Bennett *et al* 2001) in P relative to N, and excess N loading is changing the nutrient stoichiometry and limiting element in some coastal areas (e.g., Sylvan *et al* 2006). It is commonly assumed that to control eutrophication the only focus should be on that nutrient which is classically considered ‘limiting.’ Such an argument is typically extended to promote enhanced P control over N control (e.g., Schindler *et al* 2008, Wang and Wang 2009) for multiple reasons, among which it is often assumed that N_2 -fixing toxic cyanobacteria will be favored when N is limiting. Contrary to this common perception, in enriched systems, some toxic cyanobacteria are more common under elevated N : P conditions or when total N (TN) concentrations are high, and several cross comparative studies show that total cyanobacterial biomass can be predicted from increasing TN concentrations and from changes in TN to total P ratios (Smith 1983, Downing *et al* 2001, Kosten *et al* 2012, Dolman *et al* 2012). Therefore, species composition is important to consider (Dolman *et al* 2012) as, in fact, some of the most toxic cyanobacteria, namely *Microcystis* sp., are not N_2 -fixing species.

Further arguments for P relative to N control are that P does not have a gaseous form and therefore cannot be permanently removed from lakes, whereas N can be lost to the atmosphere through denitrification provided conditions are optimal to favor coupled nitrification–denitrification (Seitzinger 1988, Cornwell *et al* 1999). However, rates of N_2 -fixation do not necessarily offset N limitation (Scott and McCarthy 2010, Lewis *et al* 2011) and not all N enrichment is removed through denitrification resulting in eutrophication related problems that may be spatially and temporally displaced from the nutrient source (Conley *et al* 2009, Pearl 2009, Glibert *et al* 2011).

Here we make the case that accelerated P reduction over N control is insufficient in reducing the frequency of HABs; we base this on our growing understanding of HAB physiology and we support this with long-term trend data from one of the most eutrophic regions of the world, China. We also argue that increasing N : P environments further favor HABs when the N form is disproportionately in chemically reduced form (i.e. urea, NH_4^+) relative to chemically oxidized form (i.e., NO_3^-). We thus propose that the HB-HAB link is a function of (1) the inefficiency of incorporation of N fertilizers in the food supply chain, the leakiness of the N cycle from crop to table, and the fate of the lost N to the environment as described above; and (2) adaptive physiology of many HABs to thrive in environments in which there is excess N relative to classic nutrient stoichiometric proportions and where chemically reduced forms of N are increasing. We review physiological evidence for this at the cellular level, and we highlight long-term trends in HABs and fertilizer in China demonstrating increased HAB proliferations for systems in which N : P stoichiometry has been altered due to continued N loading with P reduction and the greater proportional use of urea as the main N fertilizer.

There are a number of specific physiological strategies that allow certain types of algae to thrive under conditions of elevated N:P availability relative to classic Redfieldian proportions (Redfield 1934), but not all cells necessarily have all such adaptive strategies (Glibert and Burkholder 2011). The first strategy is a low overall requirement for P. Very small cells, such as picocyanobacteria, have a lower requirement for P due to the smaller need for structural components in the cell (Finkel *et al* 2010). The second strategy is the ability to 'make do with less' which may be accomplished by physiological substitution of a P-containing lipid with a non-P-containing lipid (sulfolipid), and many cyanobacteria are able to do this (Van Mooy *et al* 2009). Thus the cellular C:P content of *Synechococcus* is about 100, whereas this ratio in a typical diatom is about 50 (Finkel *et al* 2010). The third strategy is the ability to acquire P in organic or particulate form, via alkaline phosphatase activity or mixotrophy, which may provide some cells a source of P not available to those cells dependent on inorganic P for their nutrition. Many dinoflagellates have a comparatively high cellular P requirement, and therefore the ability to consume particulate P may be an important reason why these types of cells can thrive when some others cannot. An added competitive benefit for these cells is that there may also be a growth advantage when feeding mixotrophically, compared to pure autotrophic growth (Jeong *et al* 2004, Glibert *et al* 2009, Flynn *et al* 2013), thus mixotrophy is a major mode of nutrition by HABs in eutrophic waters (Burkholder *et al* 2008) and may help to sustain blooms when dissolved nutrients are depleted.

Of particular concern is the association of increased toxin in many HABs under condition of elevated N:P availability. Many cyanobacteria and dinoflagellate toxins are N-rich compounds and thus these cells require a supply of N in order to synthesize these metabolites. The most ubiquitous cyanotoxin in freshwater systems are microcystins (MCs), hepatotoxic compounds that can be lethal to mammals if ingested (Carmichael 1994, Chorus and Bartram 1999), some congeners of which are significantly more toxic than others (Sivonen and Jones 1999). *Microcystis* (Chroococcales), *Anabaena* (Nostocales), and *Planktothrix* (Oscillatoriales) are among the taxa that can synthesize MCs (Cronberg and Annadottir 2006). Total concentrations of MC have been strongly related to N concentrations in several comparative studies (Giani *et al* 2005, Rolland *et al* 2005, Dolman *et al* 2012, Monchamp *et al* 2014). Although negative relationships between MC and N:P ratios have been reported for lake Tai (Taihu), China (Otten *et al* 2012), but in a cross system analysis of freshwaters (Orihel *et al* 2012), the authors of the findings of negative correlations emphasize that such results are relevant only to hypereutrophic conditions in which TN concentrations are also high (>100 µM N). Furthermore, a reanalysis of the aforementioned comparative study reported highest MC concentration at intermediate N:P ratios (Scott *et al* 2013). Excess N and high N:P ratios have also been related to MC production under controlled culture conditions (e.g., Lee *et al* 2000, Oh *et al* 2000, Vézic *et al* 2002, Downing *et al* 2005, Van de Waal *et al* 2009). Some *in situ* evidence, albeit weak, suggests that increased N

availability may influence the MC congener type to more toxic variants that have higher N content (e.g., Van de Waal *et al* 2009) and that P limitation causes an increase in N-rich toxins of numerous HABs (Van de Waal *et al* 2014).

Some marine HABs also show increased toxin production under conditions of elevated N:P ratios. As examples, under conditions of elevated N:P, hemolytic activity per cell increases by up to an order of magnitude in the prymnesiophytes *Prymnesium parvum* and *Chrysochromulina* (now *Prymnesium*) *polylepis* (Johansson and Granéli 1999), and neurotoxin production increases in the diatom *Pseudo-nitzschia multiseriis* and in the dinoflagellates *Karlodinium venificum*, *Alexandrium* sp., and *Karenia brevis* (Granéli and Flynn 2006, Hardison *et al* 2013).

Recent reviews of the physiological bases of N uptake as well as molecular and metatranscriptomic data lend considerable support to the emerging conclusion that diatoms are specialists in use of oxidized forms of N, while cyanobacteria and dinoflagellates are specialists in reduced forms of N (e.g., Glibert *et al* 2014a and references therein). A considerable amount of experimental evidence supports the notion that freshwater cyanobacteria seem to favor reduced N forms (Blomqvist *et al* 1994, Berman and Chava 1999). Extensive laboratory molecular evidence of the use of both urea and NH₄⁺ by cyanobacteria (Flores and Herrero 2005), and gene expression data (Ginn *et al* 2009) also lend support to this conclusion. Mesocosm studies conducted in fresh and brackish systems further illustrate that when enriched with oxidized versus reduced forms of N, even when the TN supply remains the same, proportionately more diatoms are produced under oxidized N conditions while more cyanobacteria and cryptophytes are produced under conditions of increasing reduced forms of N (e.g., Finlay *et al* 2010, Donald *et al* 2013, Glibert *et al* 2014a). Donald *et al* (2011) found in mesocosm enrichment studies conducted in the Northern Prairie lakes of Canada, that urea additions stimulated *M. aeruginosa* growth but MC concentrations increased even more. Of the comparative field studies in freshwater, toxic cyanobacterial species appear to be favored over diatoms as a function of N availability in reduced relative to more oxidized forms in the hypereutrophic Taihu and Lake Okechobee (McCarthy *et al* 2009). In marine systems, cyanobacteria and dinoflagellates have also been associated with proportionately greater use of reduced forms of N and diatoms greater use of oxidized forms of N (e.g., Berg *et al* 2003, Heil *et al* 2007).

In situ evidence of the role of N forms in cyanobacterial community composition remain rare and influence on MC concentrations or congener composition even rarer. In Québec, Canada, the ratio of N:P in fertilizer acquisition increased steadily from 1977 to 1995, and accelerated from 1995 to peaks of >3 (on a weight basis) from 2006 to 2008 (figure 2(A)). There was a marked increase in the purchase of N fertilizer in the form of urea or products containing urea as of 2003 with a urea peak observed in 2007. That year was considered an 'exceptionally favorable' year for agricultural commodities (Heffer and Prud'homme 2008), and a sustained higher overall use of urea products has occurred since that time (figure 2(B)). Records of reported cyanobacterial incidences in lakes across

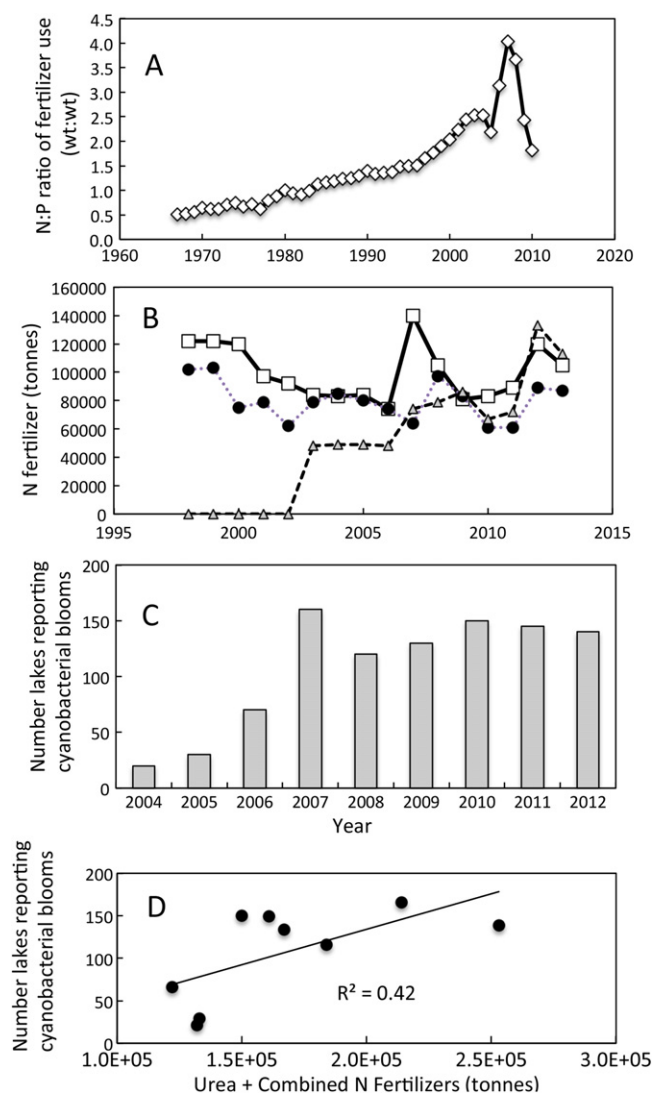


Figure 2. (A) N : P ratio of fertilizer use (by weight) in Québec since 1967 illustrating year-to-year variability superimposed on long-term trends. (B) Trends in use of different N fertilizer types since 1998 in Québec (urea-squares; NH_4NO_3 -circles; urea- NH_4 - NO_3 (UAN)-triangles); note the increasing use of UAN versus the more consistent use of urea and NH_4NO_3 . (C) Number of lakes with reported cyanobacteria blooms from over 450 systems surveyed in Québec since 2004. Note the time scale zooms in to progressively recent years from (A) to (C); also note the peaks in all panels in the year 2007. (D) Correlation between the number of lakes reporting cyanobacterial blooms from 2004 to 2012 and the use of urea plus combined N (UAN).

the province (see SI) suggest that the peak in events occurred in 2007 (figure 2(C)), when both the N : P ratio and urea use were high. Since then the incidences of blooms have remained high (figure 2(C)). The correlation of incidences of blooms in these lakes with the increase in forms of N fertilizer containing urea (figure 2(D); $r^2=0.42$, $p=0.058$) is suggestive of such an effect, although more years of data will be required to substantiate this relationship. While these patterns provide only indirect evidence, in a comparison over the course of the growing season of three lakes in Québec known to have toxic cyanobacteria, cyanobacterial community structure was

primarily influenced by the availability of chemically reduced and organic N forms (DON and NH_4^+) and temperature (Monchamp *et al* 2014). N forms and concentration however did not influence congener composition or the toxicity of the dominant variant in that study, but cyanobacterial community structure did. This suggests complex interaction between the availability of N and other environmental variables in influencing community structure with an indirect effect on congener composition and overall bloom toxicity.

Several of the more potent marine HAB species show the same trend. For *Alexandrium tamarense*, the availability of urea has also been related to toxin content of the cells: the toxin content for urea-grown cells was found to be higher than that of NO_3^- -grown cells, but not as high as cells grown on NH_4^+ (Leong *et al* 2004). Furthermore the biosynthesis of toxin when grown on urea appears to differ from that which occurs under NO_3^- or NH_4^+ growth conditions. For another dinoflagellate, *Karenia brevis*, up to six-fold increases in toxin content have been observed during growth with elevated urea availability compared to controls without urea enrichment (Shimizu *et al* 1993). For the toxic diatom, *Pseudo-nitzschia* sp., increases in toxicity in both laboratory cultures and natural field assemblages have also been found for cells growing on urea compared to those growing on NH_4^+ or NO_3^- (Cochlan *et al* 2008, Kudela *et al* 2008). On a global scale there is a simultaneous increase of total fertilizer N, particularly in the form of urea, and the frequency and extent of a number of HAB cyanobacteria and dinoflagellate species providing further, though indirect, evidence for a relationship between urea and HABs (Glibert *et al* 2006, 2008).

China presents an interesting case study in terms of the relationships between increasing HAB frequency and the changes in fertilizer use and export. All data used herein come from pre-existing data sources, industry statistics and published literature (see SI). Fertilizer N use in China has escalated from about ~ 0.5 MT in the early 1960s to 42 MT around 2010, with the fraction of urea increasing nearly five-fold over just the past two decades (figure 3(A); IFA 2014, FAO 2012, Zhang and Zhang, no date). River export of N increased from 1980 to 2010 from ~ 500 to >1200 $\text{kg N km}^{-2} \text{yr}^{-1}$ in the Changjiang River (Yantze River), from ~ 100 to ~ 200 $\text{kg N km}^{-2} \text{yr}^{-1}$ in the Huanghe River (Yellow River), and from ~ 400 to >1200 $\text{kg N km}^{-2} \text{yr}^{-1}$ in the Zhujiang River (Pearl River) basins, the latter having one of the largest N : P ratios in the world (Ti and Yan 2013). The annual N load from the Changjiang River to the coastal ocean is higher than loads from the Mississippi and the Amazon rivers (Goolsby and Battaglin 2001, Duan *et al* 2008). Atmospheric sources of NH_4^+ , which is the dominant form of inorganic N on a regional basis, and which exceeds that of oxidized N forms in the Changjiang River basin, are due primarily to livestock excretion, fertilizer N use, and human waste (52%, 33% and 13% respectively, Xiao *et al* 2010).

The number of HABs has increased in all waters of China in the past three decades and most inland and coastal waters are rated in the moderately to severely polluted range (Wang *et al* 2011, Ti and Yan 2013). In Taihu, the largest lake in the Changjiang watershed, the duration of cyanobacterial

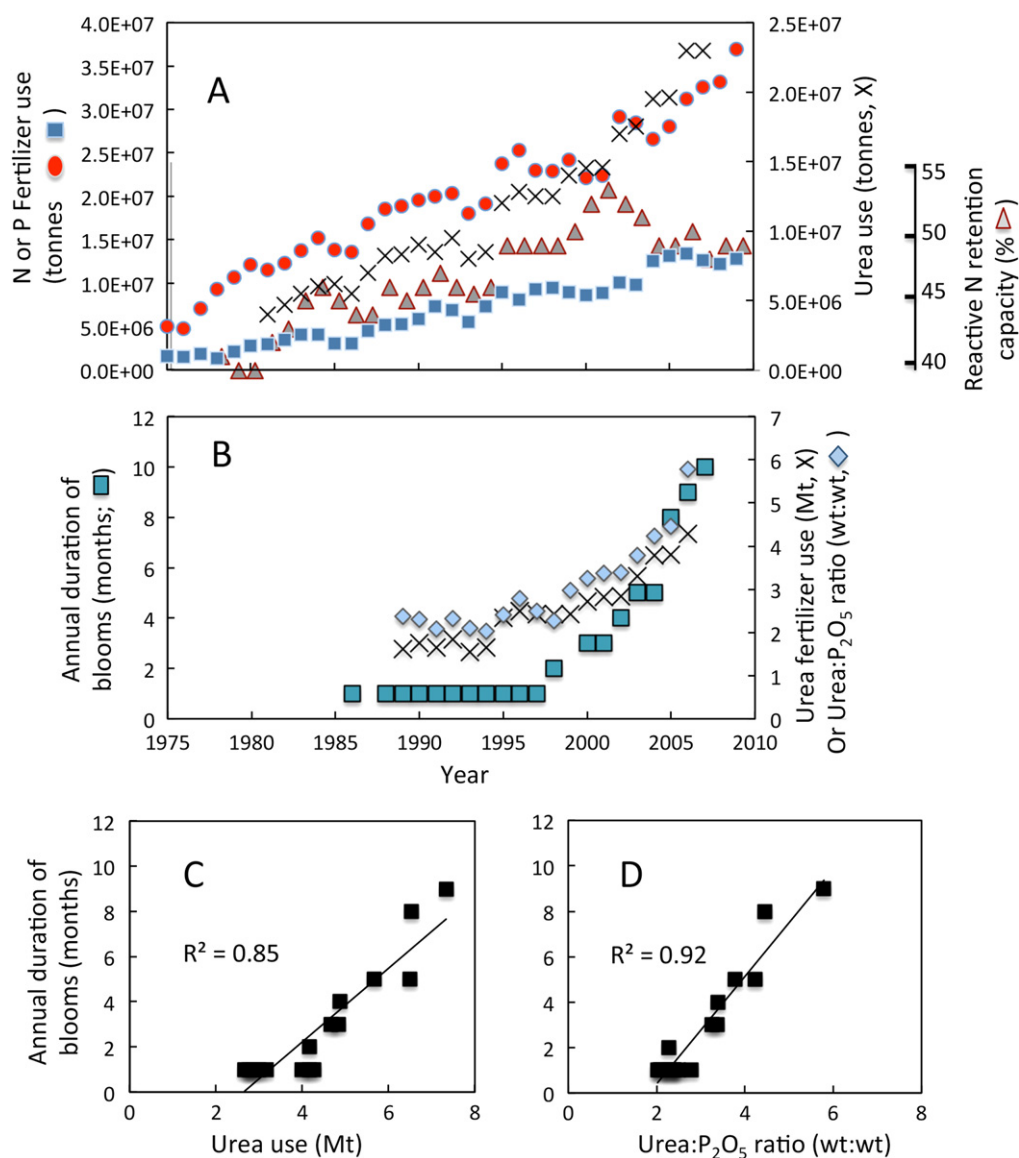


Figure 3. (A) Comparison of N (red circles) and P (blue squares) fertilizer use and the use of urea (black crosses) in China from 1975 to 2005. N and P data are from FAO (2012) while urea data are from Zhang and Zhang (no date) and represent the total of production and imports minus exports. Also shown (gray triangles) is the calculated reactive N retention capacity of the Chinese landscape as estimated by Cui *et al* (2013). (B) Change in annual duration of *Microcystis* blooms in Lake Tai (Taihu) in months, urea fertilizer use scaled to that in the Changjiang watershed and the ratio of use of urea : P₂O₅ fertilizer. *Microcystis* data are from Duan *et al* (2009) reprinted with permission of the American Chemical Society, and total urea and P₂O₅ data for China are from Zhang and Zhang (no date). (C) and (D) Correlations between annual duration of blooms (months) and urea use in Changjiang watershed (C) and the urea : P₂O₅ ratio (D).

Microcystis blooms has increased from ~ 1 month yr^{-1} to nearly 10 months yr^{-1} in the past 15 yr (Duan *et al* 2009; figure 3(B)). The Changjiang watershed produces >30% of China's agricultural output (Xing and Zu 2002) and in the Taihu region, N fertilizers from manures and mineral fertilizers have increased eight- to ten-fold since the 1950s (Chen *et al* 2008) and fertilizer N use in Jiangsu Province (2.5 MT N yr^{-1}) is 80% of TN inputs (PBL 2012). The change in HABs in Taihu is strongly related to the increase in urea and in the ratio of urea : P₂O₅ use scaled to the Changjiang watershed (Chen *et al* 2003, Ye *et al* 2007, Duan *et al* 2009; figures 3(B)–(D); $r^2 = 0.85$ and 0.92 , respectively, $p < 0.01$).

These trends in availability of reduced forms of N and in increased N : P ratios in this region are further accelerated by aquaculture development and atmospheric deposition. In 2007, 13% of Chinese inland aquaculture production was in Jiangsu (China Fishery Yearbook 2007), and large quantities of NH_4^+ and urea with high N : P ratio are also discharged from that source to Taihu. It should be noted that waste from aquaculture not only has a high N : P ratio (>20) but is largely in reduced N form with significant amounts of urea (Bouwman *et al* 2013). Also, 80% of the atmospheric deposition in this region has been associated with NH_4^+ mobilization from intense fertilization during the growing period (Chen

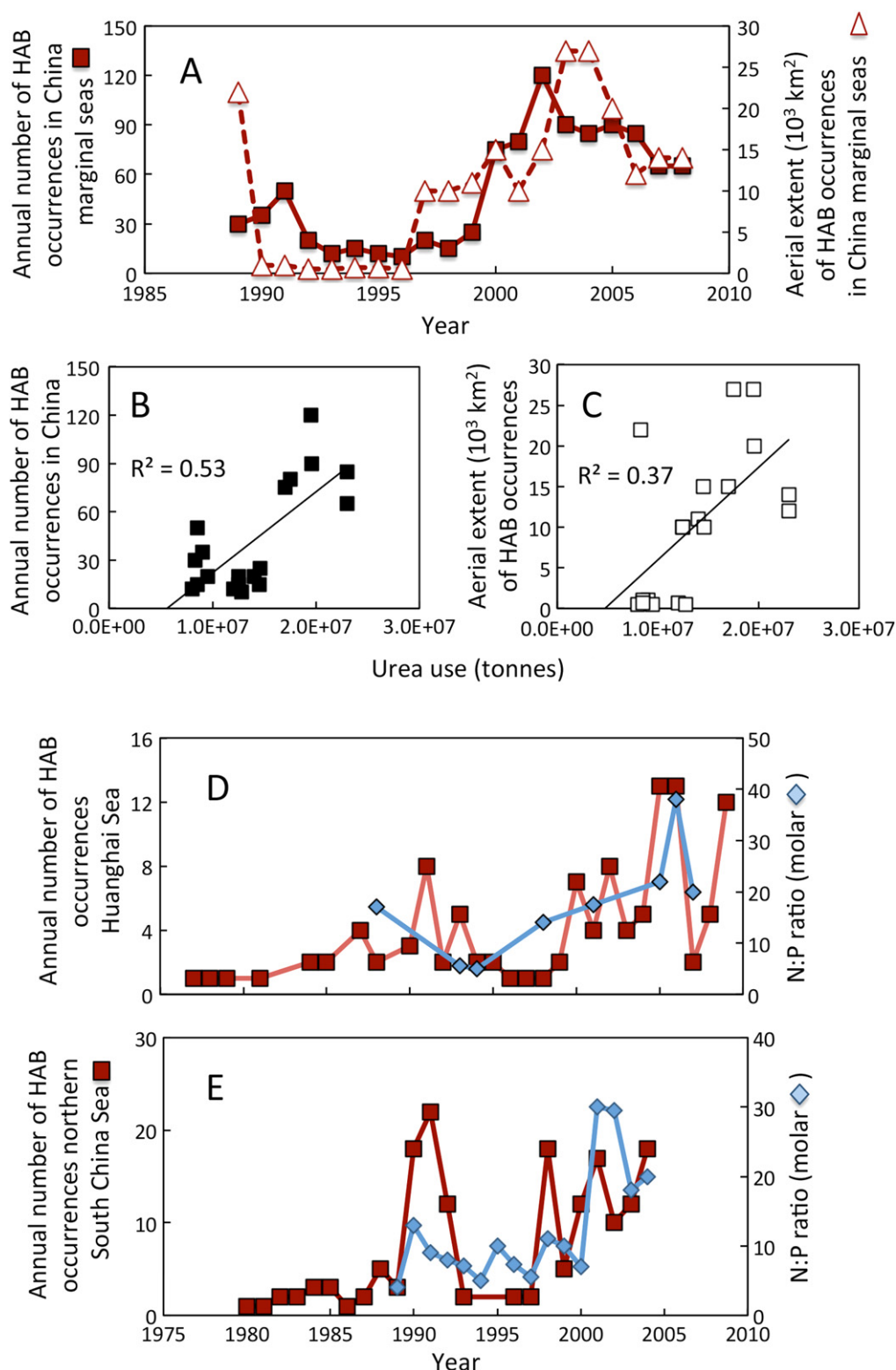


Figure 4. (A) The total number of recorded HAB occurrences (red squares) along the coast of China and their aerial extent (open triangles). Data are from Wang *et al* (2011), originally reported by SOA (2010; reproduced under Creative Commons license). (B) and C Correlations between annual number of HABs or areal extent of HABs in China marginal seas and urea use. (D) The annual number of HAB occurrences in the Huanghai (Yellow) Sea region (red squares) and the molar N : P ratio of southern Huanghai Sea in spring (blue diamonds). Data are from Fu *et al* (2012), with the HAB data originally reported by SOA (data reproduced with the permission of the Chinese Society of Oceanography and Springer-Verlag). (E) The annual number of HAB occurrences in the Northern South China Sea (red squares) and the molar N : P ratio in the water column. Data on HABs are from Wang *et al* (2008) and N : P data are from Ning *et al* (2009; reproduced under creative commons license) and represent the average values for the upper 200 m of the water column.

et al 2008). With intensive agriculture, N deposition onto the lake is a direct N input not accompanied by P.

In Chinese marginal seas there are similar trends of increased HABs over the past several decades (Wang *et al* 2008, 2011; figure 4(A)). When all China's marginal sea bloom occurrences are considered, there are strong relationships between both number of HAB reports and aerial HAB extent and N use as urea (figures 4(B) and (C); $r^2 = 0.53$ and 0.37 , respectively, $p < 0.01$).

In both the Huanghai (Yellow) Sea region and in the Northern South China Sea, the number of reported occurrences of HABs has increased in parallel with the long-term trend in N:P of the water column (figures 4(D) and (E); $r^2 = 0.46$ and 0.29 , respectively, $p = 0.06$). As in the Taihu example, these relationships do not account for nutrient input from coastal aquaculture or from atmospheric NH_4^+ deposition that would enhance these relationships. Coastal N release from Chinese mariculture increased from 2000 to 2010 by 45% on average and up to 63% in some provinces while P increase was only 37% (Bouwman *et al* 2013). In 2004, NH_4^+ and organic N comprised 75% of N in wet atmospheric deposition in Southeast China (Chen *et al* 2011).

At the mouth of the Changjiang River, molar $\text{NO}_3^- : \text{PO}_4^{3-}$ values were ~ 30 – 40 in the 1960s but had risen to >250 by the late 1990s (Shen and Liu 2009; figure 4(D)). Occurrences of HABs in the East China Sea were rare in the 1970s, had increased to a few dozen over the 1980s but had increased to >130 in just the 5 yr from 1992 to 1997 (Shen and Liu 2009) but the scale of the blooms soared in the years since; the spatial scale of the annual blooms increased from 1000s of km^2 in 2000 to $>15\,000\text{ km}^2$ by 2005 with many millions of dollars lost in high value aquaculture products due to associated fish kills (Li *et al* 2009). The dinoflagellates *Prorocentrum donghaiense* and *Karenia mikimotoi* are among the common HABs now reported in East China Sea (e.g., Zhou *et al* 2008, Li *et al* 2009).

In the Huanghai Sea region, inorganic N:P ratios are now about twice Redfield proportions, and about four-fold higher than in the 1990s (figure 4(E)). There has also been nearly a six-fold increase in HAB occurrences and a shift to proportionately more dinoflagellates compared to diatoms (Fu *et al* 2012). In the South China Sea region, water column inorganic N:P ratios increased from ~ 2 in the mid-1980s to >20 in the early 2000s (Ning *et al* 2009). In addition to the increase in number of HABs, a change in species composition to increasing dominance of species such as *Chattonella*, *Gymnodinium breve*, and *Dinophysis* has occurred (Wang *et al* 2008).

The results herein lend support the view that both N and P controls are necessary to reduce eutrophication in both freshwater and marine waters (e.g., Burkholder *et al* 2006, Howarth and Paerl 2008, Conley *et al* 2009, Paerl 2009, Glibert *et al* 2011, 2013). Loss of biodiversity, and effects on ecosystem and human health due to eutrophication are considered major challenges of our current day (e.g., Borja 2014). Given the known inefficiencies in all aspects of N use in both industrialized nations and throughout the world, the benefits of increased emphasis on N reduction, and improved N use

efficiencies at all levels of the production side, would have far reaching benefits to ecosystems and especially to water quality (Houlton *et al* 2013, Sobota *et al* 2013). Calculated damage costs of loss of ecosystem services, eutrophication and human health due to loss of reactive N to the environment are large (Compton *et al* 2011, Sobota *et al* this issue). So too are the economic impacts to aquaculture, increased risks to human health and ecosystems, and losses to fisheries and ecosystem services due to HABs (Hoagland and Scatista 2006). More work is needed to accurately quantify the sources and fluxes of N at all stages of the supply-to-loss pathways, and there is no question that control of N may be more challenging than control of P. Given our increasing knowledge of the physiological response of many HABs to increasing N:P and to increasing ratios of reduced:oxidized forms of N, we can conclude that without more aggressive N control the future outlook in terms of HABs is likely to include more events, more often, and such events may also be more toxic (O'Neil *et al* 2012, Glibert *et al* 2013, 2014b, Paerl and Otten 2013). Indeed, a recent modeling effort in which the physiological responses of HABs to altered N:P ratios and altered N form, even without any further increases in N loading, in conjunction with projected climate change effects, suggest an expansion in area and/or number of months annually conducive to development of several HAB genera along the NW European Shelf-Baltic Sea system and NE Asia by end of the century (Glibert *et al* 2014b). Such projections alone should be cause for advancing our understanding of the relationships between HABs and nutrient loading, and together with the projected global expansion in N loading should be serve to sound the alarm that our existing approaches to nutrient management of sensitive coastal and freshwaters are not sufficient, particularly in the face of climate change and other stressors.

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