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Escalating worldwide use of urea – a global change contributing to coastal eutrophication

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Abstract. While the global increase in the use of nitrogen-based fertilizers has been well recognized, another change in fertilizer usage has simultaneously occurred: a shift toward urea-based products. Worldwide use of urea has increased more than 100-fold in the past 4 decades and now constitutes >50% of global nitrogenous fertilizer usage. Global urea usage extends beyond agricultural applications; urea is also used extensively in animal feeds and in manufacturing processes. This change has occurred to satisfy the world's need for food and more efficient agriculture. Long thought to be retained in soils, new data are suggestive of significant overland transport of urea to sensitive coastal waters. Urea concentrations in coastal and estuarine waters can be substantially elevated and can represent a large fraction of the total dissolved organic nitrogen pool. Urea is used as a nitrogen substrate by many coastal phytoplankton and is increasingly found to be important in the nitrogenous nutrition of some harmful algal bloom (HAB) species. The global increase from 1970 to 2000 in documented incidences of paralytic shellfish poisoning, caused by several HAB species, is similar to the global increase in urea use over the same 3 decades. The trend toward global urea use is expected to continue, with the potential for increasing pollution of sensitive coastal waters around the world.

Introduction

Global increases in total nitrogen fertilizer use in recent decades are well documented (Galloway et al. 1995, 2003; Howarth et al. 2000; Smil 2001; Galloway and Cowling 2002), and there is ample evidence of the detrimental effects of these increases on aquatic and forested ecosystems (Howarth et al. 2002; Nosengo 2003). However, little consideration has been given to the recent and dramatic changes in composition of fertilizer nitrogen that are occurring throughout most of the world. In particular, worldwide use of urea as a nitrogen fertilizer and feed additive has increased more than 100-fold in the past 4 decades, with a doubling in just the past decade alone (Figure 1a). Indeed, the 1990s were hailed as an 'especially joyous time' for urea sales

(International Raw Materials 2000). Global production capability of urea is now approximately 70 million metric tons year^{-1}.

Although urea fertilizer is commonly assumed to be retained in soils, there is growing evidence of urea transport to sensitive coastal waters (e.g. Glibert et al. 2005a). There is also mounting evidence that urea differentially stimulates the growth of some types of phytoplankton in coastal waters and that it may, under some conditions, promote a shift in phytoplankton species to organisms that are more noxious to the ecosystem and to human health (e.g. Berg et al. 1997, 2003; Gobler et al. 2002; Glibert et al. 2001, 2004b, 2005b). Here we show the extent of recent changes in urea consumption and production globally and its contribution to dissolved nitrogen in some coastal waters. We also substantiate the linkage between coastal urea enrichment and compositional changes in microbial communities leading to species that are more deleterious to the environment.

Global production and consumption

Commercial urea production began in the 1920s with the development of the Haber-Bosch process (Smil 2001). Urea is produced by reacting carbon dioxide with anhydrous ammonia under pressure at high temperatures. The molten

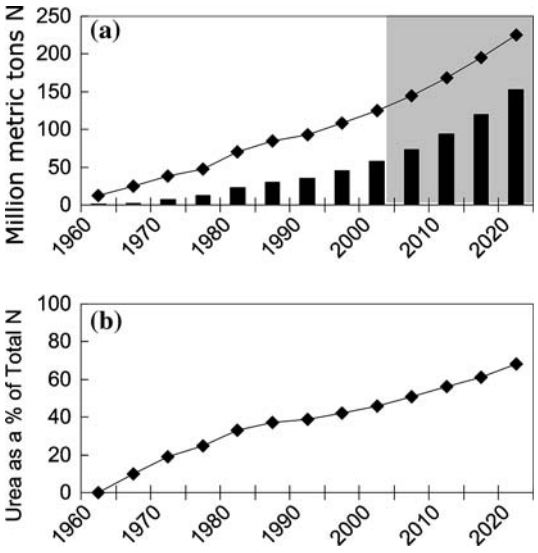

Figure 1. (a) The change in world consumption (million metric tons of N) of total synthetic nitrogen fertilizers (solid line) and urea consumption (solid bars) since 1960. The data through 1990 are from Constant and Sheldrik (1992); data for 1990–2000 are from the Global Fertilizer Industry (FAO 2001) data base; and for 2005–2020 (shown as the shaded region) are calculated assuming an annual increase of 3% in total consumption and 5% in the fraction that is urea. (b) Same data as in panel (a) with the fraction that is urea displayed as a percentage of the total nitrogen fertilizer.

mixture is then further processed into granules or other forms. Urea production is energy intensive. Most commonly, it is produced using natural gas, so the major producing regions are those where natural gas is abundant. Several leading manufacturing countries for urea are Russia, Canada, and Saudi Arabia, but other Middle East producers, including Iran and Iraq are (or were before the Gulf Wars) significant. In the US, urea production facilities are located mainly in the Gulf of Mexico states.

Production of urea has at least doubled every decade since 1980 in the Middle East (Hamdi and Ashkar 1999), increasing from 2 million metric tons $year^{-1}$ in 1980 to 10 million metric tons $year^{-1}$ in 2000. Further expansion of production is anticipated in the coming years in Kuwait, Qatar, Egypt, Oman and Iran (Prud'homme 2002, 2003, 2004). From the mid-1970s to the early 1990s, Russia (USSR) erected at least 40 new ammonia and urea production facilities (Constant and Sheldrick 1992). Production of urea in China tripled from 1989 to 1999 (International Raw Material 2000). Dramatic increases in global production have also occurred in many countries since 2000, with several Latin American countries increasing production by more than 25% (Prud'homme 2002).

As late as the 1960s, urea represented only about 5% of world nitrogen fertilizer use (FAO 2001; Smil 2001; Figure 1b). However, urea usage escalated in the 1980s, such that it represented about 40% of global nitrogen fertilizer by the early 1990s (Smil 2001), and soon thereafter urea surpassed ammonium nitrate as the most common nitrogen fertilizer (Overdahl et al. 1991). It is now estimated that urea represents $> 50\%$ of world nitrogen fertilizer (Figure 1b). Assuming urea consumption continues at 5% $year^{-1}$, as projected for many parts of the world (e.g. http://nation-com.pk/daily/dec-2004/3/bnews5.php and www.the-innovation.group.com/ChemProfiles/Urea.htm), urea consumption may reach 70% of total nitrogen use by the end of the next decade (Figure 1b): this is a dramatic global change in the composition of nitrogen applied to land throughout the globe. Such projections depend on global commodity markets, construction of new plants, and other factors that are difficult to project, but most of this increase is expected to occur in developing countries, particularly in Asia and Latin America (Constant and Sheldrick 1992).

China and India together account for about half of the global consumption (Soh 2001), and have at least doubled their consumption of urea in the past decade (Roy 2001). In India, Bangladesh and Pakistan, urea fertilizer has been heavily subsidized (as much as 50% of the cost of production) leading to its widespread use and over-application (e.g. Ayala 2002). The US and Canada now represent about 20% of the global urea market, with urea constituting about 30% of US synthetic nitrogen fertilizer usage. Consumption is increasing even in regions where land applications of nitrogen have heretofore been low. The rural Canadian provinces of Manitoba, Saskatchewan and Alberta, for example, are now the regions where over 70% of Canada's urea is consumed. Urea is the only form of fertilizer used in British Columbia forests (www.for.gov.bc). In Latin America, consumption of urea has fluctuated more than in Asia during the past decade due to various economic crises and

unstable political environments, leading to fluctuating incentives and subsidies (Matthews and Hammond 1999). This global trend in increased urea consumption represents both a net increase in total nitrogen applied, as well as a shift from the use of nitrate or anhydrous ammonium to urea. These increases parallel the increases in the production of both cereal and meat (associated with increasing human population) that have occurred globally in the past several decades (Matthews and Hammond 1999).

Urea is used in the production of virtually all crops from corn to Christmas trees, sugar cane to sweet potatoes, and vegetables to vineyards. Urea is preferable to nitrate for growing rice in flooded soils (Soh 2001), and thus the Far East and the Mid-East are major consumers of urea. In coated form, urea becomes a slow-release fertilizer and this is one of the most popular forms for applications to lawns, golf courses, and parks, as well as many crops (Overdahl et al. 1991).

The global shift toward the use of urea fertilizer stems from several advantages it has over other fertilizer forms. It is less explosive than ammonium and nitrate when stored, it can be applied as a liquid or solid, and it is more stable and cost effective to transport than other forms of reactive nitrogen. The increasing production of 'granular' urea has contributed to its widespread use, as this is safe and easy to transport. Urea also contains twice the nitrogen of ammonium sulfate, making application rates per unit of fertilizer less costly for individual farmers. With the growth of large, industrial farms, the economics and safety of urea transport and storage are thus major factors in the shift away from ammonium nitrate.

Range of global uses of urea

While more than 75% of manufactured urea is consumed as nitrogen fertilizer (e.g. Rabchevsky 1996), there are other significant uses of urea, which also are increasing globally. These non-fertilizer uses can be categorized according to their potential pollution impact: those that involve direct applications of urea to land and sea, and those that involve the use of urea in manufacturing. The direct applications are of greatest environmental concern. One such use is as a feed additive for ruminants, used to stimulate gut microbial flora. This application represents about 10% of non-fertilizer usage (Constant and Shedrick 1992). Urea can be added directly to feed, such as in urea-treated wheat or rice straw (Noi et al. 2001; Celik et al. 2003), or mixed with molasses ('urea–molasses licks' or 'urea multi-nutrient blocks') for sheep, cattle, water buffalo, and horses (Tiwari et al. 1990; Sansoucy 1995; Salman 1996; Celik et al. 2003). Urea may also be used as a fertilizer of the grasslands on which cattle or sheep may graze.

Another direct application of urea to land is as urea-based herbicides or pesticides (sulfonyl urea pesticides). In this case, urea is chemically synthesized with a poison or inhibitor. Sulfonyl urea is one of the preferred herbicides for broadleaf and grassy weeds. It is also commonly used in non-agricultural

situations, such as to control weeds in railroad and electric utility rights of way (Flogel 1998). Urea-based herbicides potentially have a large impact by both increasing urea inputs and reducing the potential for local uptake.

Urea has long been used as a de-icer. Commercial airports and airfields are the largest consumers of these de-icing materials (Stefl and George 1992), although recommendations are now in place to reduce its usage in the US and elsewhere (Jones 1997) because of its recognized contribution to water pollution (e.g. US EPA 1986). Even with such reductions, it is still the de-icer of choice under some weather conditions. It is also used fairly extensively for domestic ice-melting applications (e.g. roads and sidewalks). Urea may also be spread on agricultural crops to prevent frost when temperatures drop to a level that may cause crop damage, and commercial formulations of urea are available for this purpose.

Urea is also used in some direct applications to seawater. It is used in the growing world aquaculture industry. In intensive shrimp culture, for example, ponds may be fertilized with urea and superphosphate to initiate an algal bloom that eventually serves as food for the commercial resource (Landesman 1994). A significant proportion of such nutrients are subsequently discharged to local waters with pond effluent (Boyd and Musing 1992), as only a small fraction of added nutrients ultimately winds up in marketable product (Burford and Glibert 1999).

Urea may also be spread on coastal oil spills, to stimulate the growth of natural bacteria populations which break down the oil (Prince et al. 2003); it was widely used, for example, during the Exxon Valdez spill (Prince et al. 2003), and has been used in numerous other spills since. For the Exxon Valdez spill, fertilizer applications continued for years following the initial crisis, and this approach was estimated to have enhanced the degradation of the oil by 2–5-fold (Prince et al. 2003). Recommended protocols for future oil spills call for maintenance of 100 μM-N throughout the oil clean-up period (Prince et al. 2003).

In addition to the direct applications of urea to land and sea, urea is used in many other applications, including manufacture of a wide range of common materials such as urea formaldehyde and plastics. This use represents about 50% of the non-fertilizer urea (Constant and Sheldrick 1992). Urea is also an additive in fire retardant paints, tobacco products, and in some wines. In the cosmetics industry, urea is an ingredient in moisturizing creams. There are numerous uses of urea in holistic medicine therapies. One application currently being considered which would greatly expand the global use of urea is as a reductant in catalytic and non-catalytic reduction of combustion products in vehicles (Jackson et al. 2001; Fable et al. 2002).

Urea in sewage and excretory products

In addition to agriculture and the anthropogenic uses described above, there are other pathways by which urea reaches both the land and aquatic environments. An important one is sewage, as urea is the major nitrogen

component of urine. The extent to which this source of nitrogen is released to the environment depends on the state of the sewage treatment plant, the effectiveness of its mineralization and nitrification processes and the degree of nitrogen removal (Maurer et al. 2003). Urea is also one of the major nitrogen excretory products of dairy cattle, sheep and many other large animals (Livingston et al. 1962). Sheep that have been supplemented with urea–molasses licks have a higher excretion rate of urea than those that have not received such supplements (Nuwanyakpa and Butterworth 1986). Therefore, large animal operations located near waterways may be a source of urea to surface waters. Non-ruminants animals are also a source of this nitrogen nutrient. Uric acid is the primary nitrogen form released by poultry, and the first decomposition product of uric acid is urea. The time scale of conversion from uric acid to urea depends on the microbial activity of the poultry litter and its moisture content (Gordillo and Cabrera 1997). Poultry manure is a common fertilizer.

Natural and anthropogenic enrichment of urea in coastal waters

In order to assess urea enrichment of coastal waters, it is necessary to differentiate between *in situ* production and anthropogenic inputs. Within the water column itself, urea is known to be produced *in situ* from zooplankton excretion (Corner and Newell 1967; Mayzaud 1973; Bidigare 1983; Miller and Glibert 1998), fish excretion (McCarthy and Kamykowski 1972; Wright et al. 1995; Wood et al. 1998; Chadwick and Wright 1999; Walsh et al. 2000), bacterial regeneration (Mitamura and Saijo 1980; Cho and Azam 1995; Cho et al. 1996), and from release from sediments (Lomstein et al. 1989; Lund and Blackburn 1989; Therkildsen et al. 1996). While measurements of *in situ* urea production are relatively few for coastal waters, these rates are generally lower than the rates of *in situ* ammonium production, and are also generally too low to sustain the high concentrations of urea found in many coastal waters (Hansell and Goering 1989; Lomas et al. 2002). In Chesapeake Bay, annual average rates of urea regeneration are <1 μM-N h^{-1} (Lomas et al. 2002), and on the western English Channel rates of urea regeneration by plankton have been measured in the range of 0.6–20.6 nM-N h^{-1}(L'Helguen et al. 2005).

Anthropogenic sources of urea can be characterized as those associated with urea production and transport, and those associated with use of the product. During the industrial production process itself, both urea and ammonium may be released to surface waters and to the atmosphere, but such release depends on the age and quality of the manufacturing plant. Although few, there have been catastrophic spills of urea during transport and distribution, including a 12,500 tonne spill of granular urea in Alaska (Fable et al. 2002), and the grounding of a bulk carrier in New Zealand with 9500 tonnes of urea (Maritime Safety Authority of New Zealand 2003).

More generally, anthropogenic urea can reach coastal waters where agriculture or animal operations are located near streams, tributaries, rivers or

estuaries. It has long been assumed that nitrogen in the form of urea applied to soils will be consumed by crops, rapidly oxidized to nitrate, or will volatilize to the atmosphere as ammonia, and thus will not contribute to coastal pollution or eutrophication as urea (Meisinger and Randall 1991). However, relatively few studies have directly measured the fate of urea in agricultural applications (but see Moe et al. 1968; Dunigan et al. 1976; DeDatta et al. 1989). Urea is readily hydrolyzed to ammonium carbonate by the enzyme urease. The rate of hydrolysis to ammonium and loss from volatilization in the form of ammonia depends on the timing of application, weather, soil temperature and pH and other factors (Khakural and Alva 1995; Wali et al. 2003). These losses may exceed 20%, even 40% depending on pH (Figure 2). Urea itself has also been found in atmospheric precipitation, in concentrations that can match those of nitrate (e.g. Timperley et al. 1985). Once urea has been hydrolyzed it can be subsequently nitrified and leached from agricultural soils to surface and ground waters. While these are probably the largest fluxes of fertilizer nitrogen, there are several reasons to suspect direct runoff of urea may be significant in systems with local waterways. First, urease inhibitors are increasingly being added to urea fertilizer to slow the transformation of amide nitrogen to ammonium hydroxide and ammonium (Marking 1995; Kiss and Simihalan 2001). The use of urease inhibitors delays the hydrolysis of urea for up to several weeks, and thus increases the likelihood that runoff or overland transport will contain urea and not its decomposition products (Prakash et al. 1999). In fact, urease inhibitors are being explored for cattle and swine manure, in order to reduce ammonia emissions and odors from feedlots (Hardlin 1998). Second, in many regions, no-till agricultural practices are encouraged to minimize soil erosion. Consequently, surface applied fertilizers are more likely to leave agricultural fields via overland flow than is the case when fertilizers are injected into the soil. In irrigated agriculture, urea is often applied just before irrigation, thus providing a window of time for urea runoff losses, depending on soil type and condition. Lastly, urea is often applied when rainfall is anticipated. This further increases the likelihood that some urea will be carried into local surface waters. While in total quantity, overland and runoff losses of urea may not be large (it is commonly estimated that 3–5% of surface applied urea may be lost via runoff), the contribution may, nevertheless, be significant to a receiving water body.

Urea concentrations and contribution to total organic nitrogen in receiving waters

Urea is not typically measured in either oceanographic surveys or in pollution monitoring. Some older data exist, and a few newer monitoring programs are beginning to incorporate this variable (Table 1). Several examples demonstrate that high concentrations often are coincident with fertilization or other agricultural activities. In Chesapeake Bay, where urea has been monitored in the tributaries for 5 years, concentrations of urea exceeding 10 μM-N have been

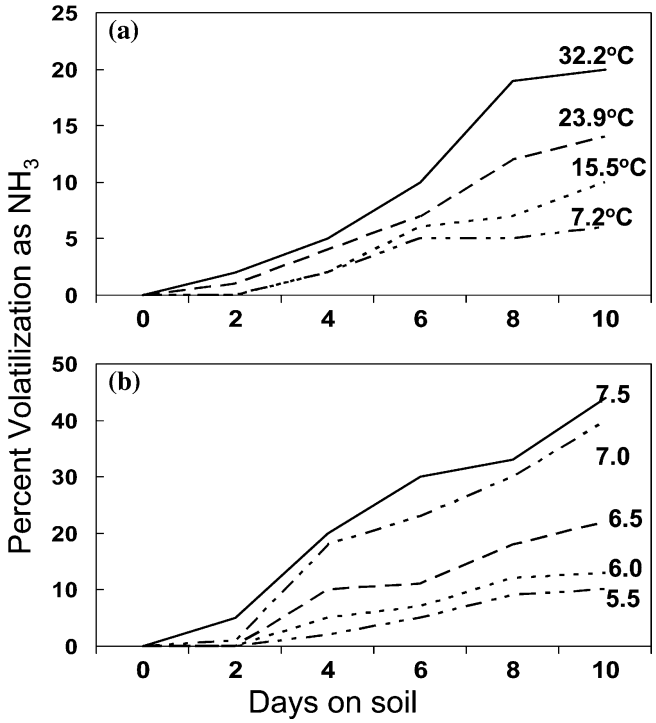

Figure 2. The percent of surface-applied urea fertilizer to soils that volatilizes as ammonia as a function of days on soil. (a) Response pattern with variable soil temperatures; (b) response pattern with variable soil pH. Data derived from North Dakota State University Extension Service (http://www.ag.ndsu.nodak.edu/aginfo/procrop/fer/ureavo05.htm).

observed frequently, generally in late spring when urea or poultry manure is applied to winter wheat and corn (Figure 3a; Glibert et al. 2001, 2005a). These levels are 50-fold higher than average urea concentrations in surface waters of Chesapeake Bay (Lomas et al. 2002). In Mexico's Yaqui Valley, which is intensively fertilizer with urea ($\sim$250 kg N ha^{-1}; Naylor et al. 2001), up to 20–40% of the nitrogen is lost in surface runoff, much of it occurring within a few days of peak irrigation (Beman et al. 2005). Irrigation and fertilization events commonly occur in December, and significantly elevated urea concentrations, from 13 to 43 μM-N, were found in six stations post-fertilization, compared to values < 10 μM-N from the same stations from non-fertilization (March), and pre-fertilization (early November) periods (Figure 3b – from J. Harrison unpub.). In yet another example (Heil and Glibert, unpub. data), urea concentrations were mapped on the Western Florida Shelf during two seasons near the mouths of the Shark and Caloosahatchee Rivers which drain significant agricultural lands in sugarcane production: the first time period was during the low flow, dry season, and the second time was 1 week after the passage of Hurricane Charley through this region in 2004. Concentrations of urea are generally low,

Table 1. Range of concentrations (μM-N) of urea from some coastal and estuarine sites reported in the literature.

Location	Range of concentration	Reference
Savannah R., Georgia	0.59–8.89	Remsen 1971
Ogeechee R., Georgia	1.26–4.89	Remsen 1971
Great South Bay, New York	0.6–9.4	Kaufman et al. 1983
Mankyung and Dongjin River estuary, Korea	0.6–4.3	Cho et al. 1996
Oslofjord, Norway	0.1–10.0	Kristiansen 1983
Chesapeake Bay, mainstem	< 0.01–8.16	Lomas et al. 2002
Florida Bay, Florida	0.36–1.7	Glibert et al. 2004
Coastal Bays, Maryland	< 0.01–14.4	Glibert et al. 2005a
Kings Creek, Chesapeake Bay, Maryland	0.3–24.2	Glibert et al. 2005a
Chicamicomico R., Chesapeake Bay, Maryland	1.0–23.4	Glibert et al. 2005a
Baltic Sea	0.09–6.91	Stepanauskas et al. 2002
Knysna Estuary, South Africa	0.4–5.8	Switzer, unpub data

< 0.5 μM, during the dry season when gated discharge through the Caloosahatchee River and normal flows through the Shark River are both low (Figure 4a). Concentrations were significantly greater over the entire region following hurricane flooding, with elevated urea patches adjacent to the mouths of both the Shark and Caloosahatchee Rivers (Figure 4b). Localized reduced urea concentration near-shore following the hurricane coincide with areas of high chlorophyll *a* concentrations that developed with this nutrient pulse (data not shown). Lastly, in the Krysna Estuary of South Africa, where the catchment is used for cattle farming and also heavily fertilized with urea, concentrations of urea were found to double from winter to summer, and to increase 4-fold following a spring storm event (T. Switzer, unpub. data). These findings show that the sources of urea in these sensitive ecosystems cannot solely be *in situ* microbial regeneration; anthropogenic urea is reaching the water column.

Another indicator of the potential for anthropogenic sources to be significant contributors of urea to local waters is the contribution of urea to total dissolved organic nitrogen (DON). DON is now recognized to be a dynamic component of the nitrogen pool in aquatic systems (Seitzinger et al. 2002a, b; Stepanauskas et al. 2002; Berman and Bronk 2003), but urea has heretofore generally been thought of as a minor constituent. In the few cases where it has been measured, urea can make up a significant portion of the DON pool. Urea concentrations as a percent of total DON have recently been measured over various time scales in several estuaries: Chesapeake Bay, Florida Bay, Moreton Bay, Australia, and the Baltic Sea. These results reveal that urea, while typically representing only ~5% on average of the DON pool, can exceed 40% (Figure 5). In fact, some of the highest percentages of urea in the DON pool come from data from the Chesapeake Bay and demonstrate that even when urea concentrations are low (< 1 μM-N), their relative contributions to the DON pool can be very high, suggesting a high degree of bioavailability of many fractions of DON in this system.

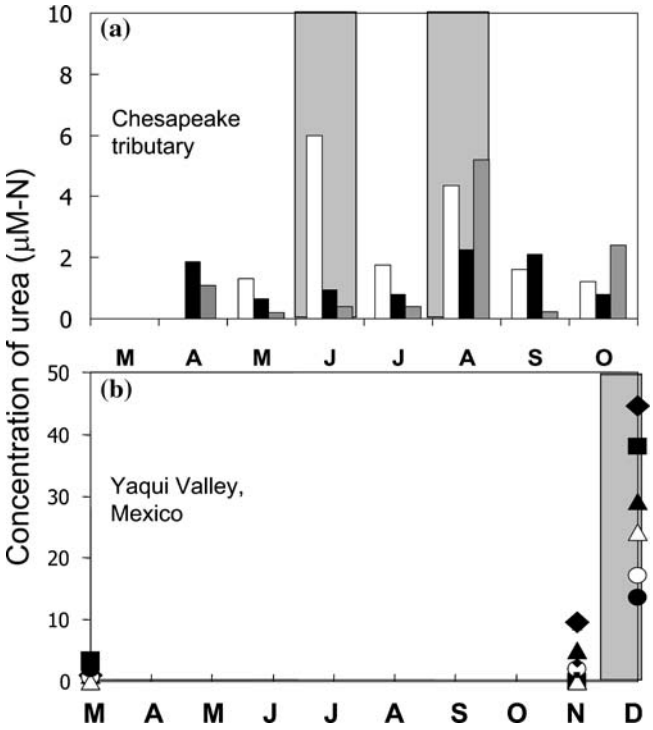

Figure 3. (a) Concentrations of urea (μM-N) in one tributary of Chesapeake Bay (Chicamacomico River) as a function of month of the year for three years (1999–2001); and (b) Concentrations of urea (μM-N) in six stations of the receiving waters of the Yaqui Valley, Mexico, as a function of month of the year for 2001. In both panels the major period of urea fertilization is shown by gray shading.

Urea uptake by phytoplankton

Urea is not environmentally inert in aquatic systems. With concentrations that often exceed 1 μM-N, urea can be a significant nitrogen source for phytoplankton. Phytoplankton groups differ in their requirements for, and in their ability to utilize, both inorganic and organic forms of nitrogen. Within the cell, the enzyme urease breaks urea down into carbon dioxide and ammonium for assimilation into amino acids and proteins (Paul 1983). The extent to which any nutrient form is used, however, depends not only on physiological ability of the cells to use specific substrates, but also on the physiological state (nutrient status, growth rate, temperature and other conditions for growth) of the cells at the time of nutrient supply.

Urea is a significant contributor to the total nitrogen used by phytoplankton in estuarine and coastal waters (McCarthy 1972; Harvey and Caperon 1976; McCarthy et al. 1977; Furnas 1983; Kaufman et al. 1983; Harrison et al. 1985; Glibert et al. 1991). Kudela and Cochlan (2000), in reviewing the range of

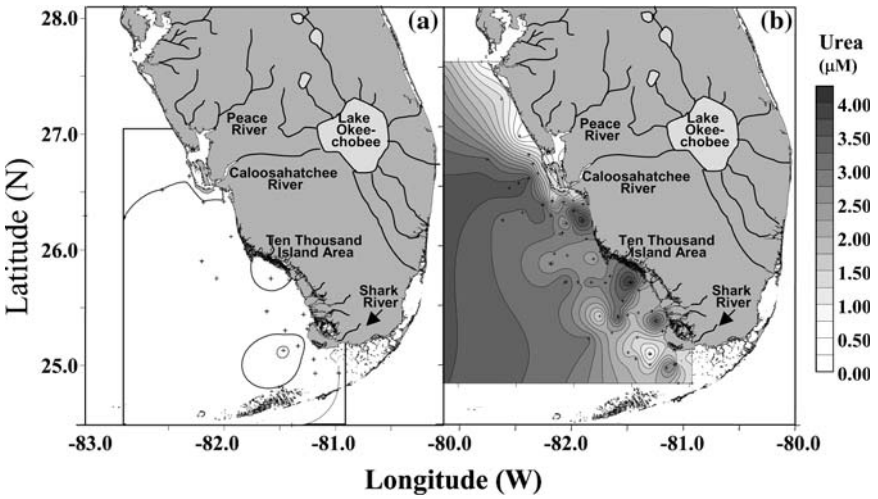

Figure 4. Contour plots of urea concentration on the southwest Florida Shelf during (a) the dry season (May 2003) and (b) one week following Hurricane Charley (August 2004).

literature values for urea uptake as a percentage of total nitrogen uptake, found for that urea can contribute up to 56% of the total nitrogen taken up in ocean regions (e.g. NE Subarctic Pacific; Varela and Harrison 1999), and that it commonly constitutes more than 50% of the total nitrogen taken up in coastal and estuarine regions (e.g. Oslofjord, Norway, Kristiansen 1983; Narragansett Bay, Furnas 1983; Chesapeake Bay, Glibert et al. 1991; Tasman Sea, New Zealand, Chang et al. 1995; and Gulf of Bothnia, Sweden, Cochlan

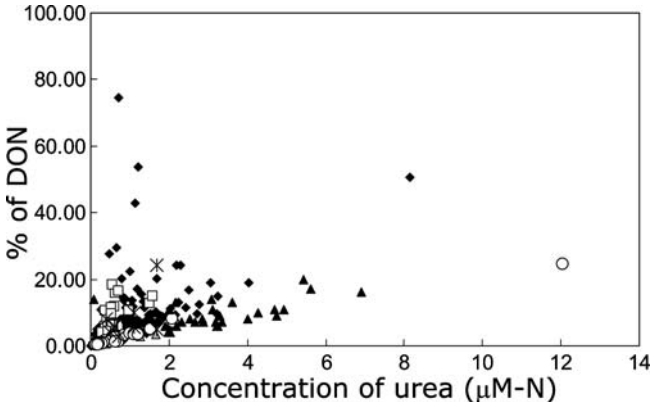

Figure 5. Relationship between total dissolved organic nitrogen as urea and urea concentration for various rivers and tributaries of the world's oceans. Open symbols represent data from Moreton Bay, Australia (squares), and Florida Bay (triangles); closed diamonds are data from Chesapeake Bay and its tributaries (from Glibert et al. 2004a, b), and closed triangles are data from the Baltic Sea (from Stepanauskas et al. 2002). The open circle is data from Maryland Coastal Bays.

and Wikner 1993). Furthermore, in the subartic Pacific, netplankton (1–200 μm) were found to have higher nitrogen-specific uptake rates for urea than nanoplankton (<10 μm; Kokkinakis and Wheeler 1988), a result of higher cell-specific demand by the phytoplankton relative to the bacteria. Further reviews by Bronk (2002) and Berman and Bronk (2003) support this contention. Urea has been shown to serve as the primary source of nitrogen for many phytoplankton species in the field and in the laboratory (Thomas 1968; Carpenter et al. 1972; Antia and Landymore 1975; Bekheet and Syrett 1977; Oliveira and Antia 1986; Gu et al. 1997; Kudela and Cochlan 2000).

Of particular interest is the fact that many regions of the world where both total nitrogen use has increased, and where the urea dominates the agricultural applications of nitrogen, are also regions that have experienced increasing frequency and extent of harmful algal blooms (HABs). HABs are those proliferations of algae that can cause fish and shellfish kills, produce toxins harmful to human health, and develop biomass accumulations that can alter ecosystems in other deleterious ways (Hallegraeff 1993; GEOHAB 2001). The most common HABs are caused by either dinoflagellates or cyanobacteria, although not all dinoflagellates or cyanobacteria are harmful, and not all HABs are made up of these species groups.

Throughout much of the world, the number, intensity, and toxic nature of dinoflagellate algal blooms have increased dramatically in the past few decades (Smayda 1990; Hallegraeff 1993; Anderson et al. 2002) but this is especially pronounced throughout Southeast Asia (GEOHAB 2001; Anderson et al. 2002; Glibert et al. 2005c). China, for example, is experiencing more dinoflagellate blooms of longer duration, and of wider geographic coverage, than a decade ago (Qi et al. 1993; Zhang 1994; Anderson et al. 2002). In the Gulf of California, the coastal waters of Mexico are also experiencing greater numbers and frequencies of algal blooms than a decade ago (Sierra Beltran et al. 2005). Global eutrophication is now recognized to be one of the important factors contributing to habitat change and to the geographical and temporal expansion of these blooms (Smayda 1990; Hallegraeff 1993; Nixon 1995; Anderson et al. 2002; Trainer et al. 2003; Glibert et al. 2005b).

Available data permit a global comparison of the changes in urea consumption and one significant type of harmful dinoflagellate bloom over the past several decades (Figure 6). In this comparison, the change in urea consumption by country over the past 30 years was compared with the change in the number of recorded observations of outbreaks of those species that are responsible for paralytic shellfish poisoning (PSP). PSP is a toxin syndrome associated with the consumption of toxic shellfish exposed to saxitoxin-containing dinoflagellates, including *Pyrodinium bahamense* var. *compressum*, *Alexandrium* spp. and *Gymnodinium catenatum*. This comparison demonstrates that many of the regions of the world that have substantially increased urea consumption are also those regions of the world where increased number of recorded PSP events have

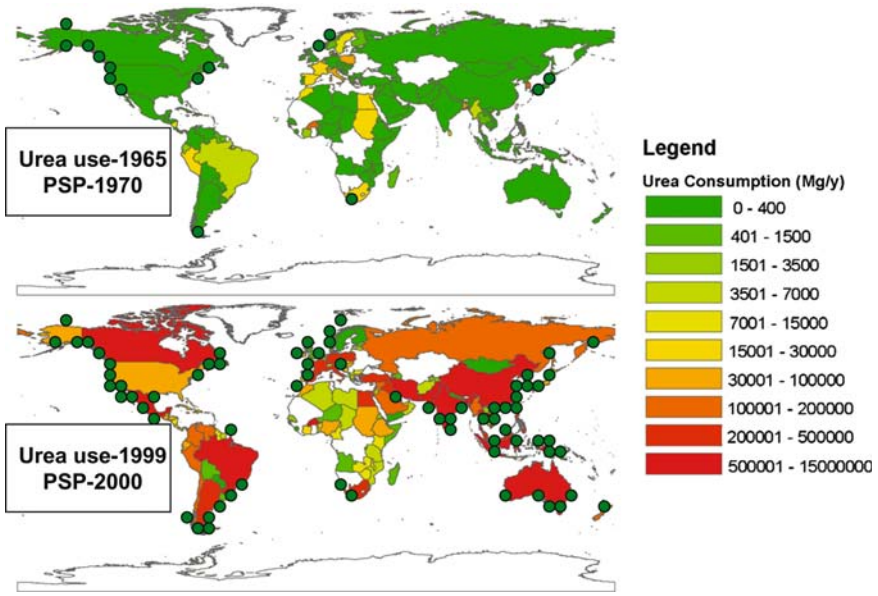

Figure 6. Global distribution of the consumption of urea fertilizer, in metric tons per year by country, in 1960 (upper panel) and in 1999 (lower panel), based on data from the Global Fertilizer Industry data base (FAO 2001), and the global change in recorded observations of dinoflagellates contributing to paralytic shellfish poisoning (PSP) or documented cases of PSP from 1970 (upper panel) to 2000 (lower panel) (modified from GEOHAB 2001). The PSP observations are shown as small circles superimposed on the base map of changes in global urea use by country from the time interval from 1965 (upper panel) to 1999 (lower panel). Note that these estimates of urea consumption do not include uses other than fertilizer.

occurred. The increases are of particular note for Asia, Europe and the US coasts. It should also be recognized that some regions of the world receiving significant applications of urea (e.g. Brazil, and the east African nations) are most likely significantly under-sampled with respect to HABs, and thus the relationship for these regions of the world remains a question. While the distributions of these bloom-forming species may be related to multiple factors, such as physical dynamics, temperature, salinity, total community composition, nutrient availability and composition can and does influence their distribution (Glibert et al. 2005b). The potential for PSP-producing HABs to be related to nutrient loading is underscored by the recent observation of Trainer et al. (2003) who found for Puget Sound that the maximum levels of recorded PSP toxin were strongly correlated with the increase in human population over the past several decades, and they attributed this relationship to increasing eutrophication from sewage. From measurements of activity of the enzyme urease, urea has been suggested to be important in the nutrition of the PSP-associated dinoflagellate *Alexandrium fundyense* (Dyhrman and Anderson 2003).

The correlation of increasing numbers of HABs occurring in regions receiving increasing agricultural urea runoff is supported by the physiological

capability for urea uptake by many HAB species. Several specific examples illustrate that urea may contribute disproportionately to the proliferation of some dinoflagellates and cyanobacteria (Figure 7). In the subtropical waters of Moreton Bay, Australia, the percent contribution of urea to total nitrogen uptake was found to be highly related to the percent of the algal community that was comprised of dinoflagellates when all sampled stations from a western to eastern bay transect of the bay from 3 seasons of the year are compared ($R^2 = 0.76$; Figure 7a; Glibert and Heil unpub. data). Urea uptake in this system was proportionately greatest during austral spring when it represented more than 30% of total nitrogen uptake (Glibert et al. in press). In a large red tide of the dinoflagellate *Lingulodinium polyedrum* off the Baja Peninsula, Mexico, urea was not only used preferentially to the other nitrogen forms, it constituted the major form of nitrogen supporting the bloom (Kudela and Cochlan 2000). Results re-analyzed from that bloom show that the percent contribution of urea to the total nitrogen pool also predicted the concentration of dinoflagellates (based on chlorophyll *c* concentrations) with an R^2 of 0.77, while the percent contribution of nitrate was a poor predictor. Blooms of the dinoflagellate *Prorocentrum minimum* have been observed to follow short term increases in urea in Chesapeake Bay tributaries following a heavy rainfall and fertilizer application (Glibert et al. 2001), and during one *P. minimum* bloom in North Carolina, urea contributed up to 35% of the total nitrogen demand of the bloom (Fan et al. 2003). Urease activity in *P. minimum* has also been found to equal the nitrogen demand of the cells (Fan et al. 2003). Toxic *Pfiesteria piscicida*, the dinoflagellate associated with fish kills along the eastern seaboard of the US, has been shown to use urea even though the bulk of its nutrition is obtained from feeding on other microbes (Lewitus et al. 1999). In Chesapeake Bay, the presence of *P. piscicida* in the sediment has been shown to be directly correlated ($R^2 = 0.94$) with the mean concentration of urea in the water column (Glibert et al. 2004a). For the dinoflagellate *Alexandrium catenella*, the uptake rate of urea has been found to be considerable greater than that of

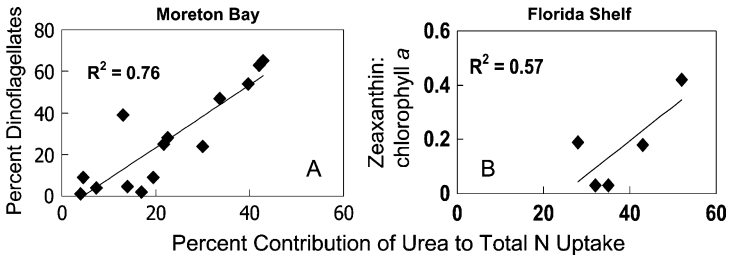

Figure 7. Relationship between the percent contribution of urea to total nitrogen uptake (as measured using stable isotope tracer techniques) and the response of two harmful algal bloom species groups. In panel A is shown the relationship for dinoflagellates in Moreton Bay, Australia (determined by direct enumeration). In panel B is shown the relationship for cyanobacteria on the southwestern Florida Shelf (determined by the ratio of zeaxanthin: chlorophyll *a*).

nitrate at all concentration levels, and to be faster than that of ammonium uptake at concentrations above 10 μg at N l^{-1} (Collos et al. 2004).

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 higher than that of nitrate-grown cells, but not as high as cells grown on ammonium (Leong et al. 2004), and the biosynthesis of toxin when grown on urea appears to differ from that which occurs under nitrate or ammonium growth conditions. For another dinoflagellate, *Karenia brevis*, increases in toxin content, up to 6-fold, under urea growth have also been observed 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 ammonium or nitrate (Armstrong and Kudela 2003; Cochlan et al. 2005; Kudela et al. 2005).

In the case of some recently reported cyanobacterial blooms, similar relationships have been observed. In Florida Bay and on the southwest Florida shelf, the fraction of the algal community composed of cyanobacteria has been shown to be positively correlated with the fraction of nitrogen uptake from urea (R^2 = 0.48 to 0.55; Figure 7b), and negatively correlated with the fraction of nitrogen uptake from nitrate (R^2 = −0.46 to −0.55; Glibert et al. 2004b). Results from the Gulf of Riga, Baltic Sea, also indicate that the percent of urea taken up was a far better predictor of the cyanobacterial contribution to the total plankton assemblage than was nitrate, and that other forms of organic nitrogen also predicted cyanobacterial and dinoflagellate abundance with $R^2 > 0.8$ (Berg et al. 2003). Culture studies have also reported urea to be important in the growth of cyanobacteria. For example, *Aphanizomenon ovalisporum* and *Trichodesmium theibautii* have been shown to grow faster on urea than on other nitrogen sources (Berman and Chava 1999; Mulholland et al. 1999).

Similar patterns are also beginning to emerge from some other classes of algae that are also considered harmful. For the species that causes brown tides off of Long Island, New York, the pelagophyte *Aureococcus anophagefferen*, urea has been shown to be an excellent nitrogen source for growth and a preferred nitrogen source in natural blooms (Lomas et al. 1996; Berg et al. 1997; Gobler et al. 2002). Furthermore, in mesocosm experiments, enrichments with urea stimulated growth of *A. anophagefferns* but inorganic nitrogen enrichments did not (Kana et al. 2004). The fish-killing rhaphidophyte *Chattonella* cf. *verriculosa* grows far better on urea or ammonium compared to nitrate, and natural outbreaks have confirmed higher concentrations of these nitrogen forms compared to nitrate (Tomas 2005).

The frequency of reports that urea is used preferentially by many HAB species, and can result in disproportionate community dominance of some HAB species, has thus grown in recent years. The quality of the nutrient supply has a direct impact on the rate of uptake, and ultimately on the relative composition of the plankton community, but this impact is also dependent on the prevailing environmental conditions, such as temperature, salinity, or

abundance of other nutrients, and plankton composition at the time of nutrient delivery. Our understanding of the potential for urea, or any form of nutrient, to affect phytoplankton abundance, growth, or community composition, requires a fundamental understanding of physiological differences within and between species groups. This understanding is growing, but is still rudimentary, not only for urea but for many other organic substrates as well.

Implications and future trends

Urea now represents a significant anthropogenic nitrogen form, and one which likely will be used at escalating rates for years to come throughout the globe. This review has shown that: (1) global rates of urea fertilizer usage have increased rapidly over the past several decades, so that more urea is now used than any other nitrogen fertilizer; (2) unhydrolyzed urea can be lost to surface runoff; (3) urea concentrations in receiving estuaries and coastal waters can be significantly enhanced by land-based inputs; (4) urea can constitute a significant fraction of the total DON pool in some coastal waters; and (5) urea may contribute disproportionately to nitrogen nutrition of some harmful and nuisance phytoplankton groups. The latter contention is supported by the demonstrated ability of harmful and nuisance algae to use urea and by the emerging correlations between HAB formation and either the ambient urea concentration or the proportion that urea contributes to their nutrition. However, demonstrating a causal link between urea inputs and HABs will require future work. To better understand the connection between urea and its coastal impacts we must begin to understand the significance of the global shift to urea fertilizers in a comprehensive fashion, integrating the study of agricultural soil urea nitrogen transformations with the study of biogeochemical fate of urea–nitrogen in local waters, and the role of urea in the physiological ecology and successional patterns of aquatic microbial communities.

The world's human population is expected to continue to increase by 1–2% $year^{-1}$ (Cohen 2003). Current projections are that cereal and meat production will increase by about 10–20% by the year 2010, but global fertilizer use may increase another 50% in the same decade (Matthews and Hammond 1999). Given the current rate at which urea production facilities are being constructed, the enrichment of the globe with urea will only escalate. Most of these increases are on track to occur in parts of the world that are already saturated with nitrogen and frequently plagued by harmful blooms.

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