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R. Eugene Turner

Nancy N. Rabalais

D. Justic'

Q. Dortch

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Global patterns of dissolved N, P and Si in large rivers

R.E. TURNER[1,*], N.N. RABALAIS[2], D. JUSTIC'[1] and Q. DORTCH[2]
[1]*Coastal Ecology Institute and Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, Louisiana 70803, USA;* [2]*Louisiana Universities Marine Consortium, 8124 Highway 56, Chauvin, Louisiana 70344, USA; *Author for correspondence*

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Abstract. The concentration of dissolved inorganic nitrogen (DIN), dissolved nitrate-N, Total-N (TN), dissolved inorganic phosphate (DIP), total phosphorus (TP), dissolved silicate-Si (DSi) and their ratios in the world's largest rivers are examined using a global data base that includes 37% of the earth's watershed area and half its population. These data were compared to water quality in 42 subbasins of the relatively well-monitored Mississippi River basin (MRB) and of 82 small watersheds of the United States. The average total nitrogen concentration varies over three orders of magnitude among both world river watersheds and the MRB, and is primarily dependent on variations in dissolved nitrate concentration, rather than particulate or dissolved organic matter or ammonium. There is also a direct relationship between the DIN:DIP ratio and nitrate concentration. When nitrate-N exceeds 100 μg-at l^{-1}, the DIN:DIP ratio is generally above the Redfield ratio (16:1), which implies phosphorus limitation of phytoplankton growth. Compared to nitrate, the among river variation in the DSi concentration is relatively small so that the DSi loading (mass/area/time) is largely controlled by runoff volume. The well-documented influence of human activities on dissolved inorganic nitrogen loading thus exceeds the influences arising from the great variability in soil types, climate and geography among these watersheds. The DSi:nitrate-N ratio is controlled primarily by nitrogen loading and is shown to be inversely correlated with an index of landscape development – the "City Lights" nighttime imagery. Increased nitrogen loading is thus driving the world's largest rivers towards a higher DIN:DIP ratio and a lower DSi:DIN ratio. About 7.3 and 21 % of the world's population lives in watersheds with a DSi:nitrate-N ratio near a 1:1 and 2:1 ratio, respectively. The empirical evidence is that this percentage will increase with further economic development. When the DSi:nitrate-N atomic ratio is near 1:1, aquatic food webs leading from diatoms (which require silicate) to fish may be compromised and the frequency or size of harmful or noxious algal blooms may increase. Used together, the DSi:nitrate-N ratio and nitrate-N concentration are useful and robust comparative indicators of eutrophication in large rivers. Finally, we estimate the riverine loading to the ocean for nitrate-N, TN, DIP, TP and DSi to be 16.2, 21, 2.6, 3.7 to 5.6, and 194 Tg yr^{-1}, respectively.

Introduction

The intensified use of the world's water resources in the last 100 years has been hastened by technical developments, expansion of energy capture systems and the subtle and direct consequences of population growth at a scale unprecedented in human history. These developments occur amidst the natural variability in soil types, river drainage networks, and climate among the world's watersheds. How the variability in the earth's natural geo-physio-climatic framework amends or exaggerates the effect of these changes on water quality is somewhat unclear, but deserves the increasing attention as water quality management becomes more complex, if not more uncertain. Among the important constituents of aquatic systems is the dissolved concentration and loading of nitrogen, phosphorus and silica. This paper is concerned with the concentration and ratios of these three constituents in the world's largest rivers that arise or are subdued under the influence of anthropogenic change.

Factors affecting N, P and Si loading

The factors controlling the loading rates of N, P and Si into large rivers are dissimilar. Nitrate and phosphorus loading is dependent on landuse, fertilizer application, and population density (Howarth et al. 1996; Caraco and Cole 1999). Indeed, the global nitrogen cycle has been altered by the widespread use of nitrogen-fixing crops, fertilizer production and use, habitat change, and burning of fossil fuels to the point where the terrestrial nitrogen budget has doubled in the past five decades and continues to increase (Vitousek et al. 1997). Nitrogen easily leaks from agricultural and urban landscapes as the very mobile inorganic nitrate ion. These robust human influences are strong enough to satisfactorily model the multi-year average nitrogen fluxes using simple land-use characteristics and knowledge of population size, e.g., (1) Caraco and Cole (1999) described 89% of the variability in the annual nitrate and TP export from 35 large rivers using rather simple variables describing population density and land use, and (2) Howarth et al. (1996) constructed statistically-robust annual nitrogen budgets for the major watersheds entering the North Atlantic Ocean using similar variables.

In contrast to nitrogen, DSi appears in surface waters as a result of the weathering of sedimentary and crystalline rocks. About 26% of the earth is silica, so there is much source material, whose dissolution rate is, in part, temperature dependent (Wollast and Mackenzie 1986). The dissolved silicate flushed out of the soil ecosystem enters waters both above- and below-ground. The DSi may not flow to the sea, however, and for several reasons, including: (1) Diatoms, a major component of phytoplankton, absorb significant amounts of dissolved silicate during growth to build a distinctive and durable external structure called a frustule. Lakes and ponds are potential burial sites for these siliceous remnants. (2) The increased water residence times of new water bodies (e.g., reservoirs, farm ponds and beaver ponds) allows sediments to settle, light penetration to increase, and more diatom production to occur, which is also followed by Si burial. DSi concentrations were reduced to less than half their pre-dam construction values in the Danube and Nile River (Humborg et al. 2000). Presumably the de-construction of dams and small ponds would have the opposite effect. (3) Eutrophication may stimulate additional diatom production, and result in even higher Si retention in freshwater bodies. The resulting higher accumulation of phytoplankton biomass and subsequent DSi retention leads to reduced DSi export from waterbodies. Indirect relationships between DSi and P-fertilizer use may be expected, therefore, if the phytoplankton production is

P limited (Schindler 1976; Whaby and Bishara 1980; Schelske et al. 1983; Turner and Rabalais 1991). Additional, less well-known reasons for silica to be lower as the landscape is altered by human influences may be involved; there may be some non-biological mechanisms of trapping silicate in large reservoirs, perhaps through an organic complex, and, agricultural cropping practices may sequester silicate in the soil system if the native plant vegetation is replaced with a commercial crop of higher Si content and different decomposition rate.

The above changes in N, P and Si loading affect the relative proportion of elements available for plant growth and plant consumers. Redfield ratios (Redfield et al. 1963) are the elemental ratios that aquatic organisms tend to require for sustained growth, e.g., a 16:1 DIN:DIP for phytoplankton, and 1:1 DSi:DIN for diatoms (DIN = dissolved inorganic nitrogen; DIP = dissolved inorganic phosphorus, or ortho-phosphate). Significant deviation from these ratios indicates a growth-limiting deficiency of one element. Schelske et al. (1983) and Turner et al. (1998) described how freshwater and marine ecosystems, respectively, can undergo fundamental aquatic food web changes as diatom growth is compromised when the DSi:DIN ratio falls below 1:1. Justic' et al. (1995) proposed that phytoplankton production became less dependent on one growth-limiting nutrient, more 'balanced' and increasingly higher for the same amount of nitrogen loading as the N:P, P:DSi and N:DSi ratios simultaneously approached their respective Redfield ratio. Increased nutrient loading, therefore, affects not only the total quantity of plant production, but also its quality.

Objectives

We address whether the variability in natural bio-geo-physical and climatic factors are subsumed under the influence of human intervention on the nutrient cycling of N, P and Si. In particular we investigate the stoichiometric relationships between DIN and DSi, and between DIN and DIP in the major rivers of the world as nitrogen loading increases, and how close they become to the 'Redfield ratios.'

Methods

The data used are from six sources, all of which represent substantial data quality control and standardization efforts: (1) A United Nations global environmental monitoring program, (2) A literature review by Meybeck (1982), (2) Three US government agency reports, and (3) A non-governmental program report on watershed characteristics. The five water quality data sets are for annual averages, and do not represent variability in river flow within seasons or from year-to-year and the same kinds of data are not reported in all data sets, e.g., total nitrogen (TN) and total phosphorus (TP). The majority of the data on large rivers are from the United Nations Environment Programme (UNEP), Global Environment Monitoring System, Freshwater Quality Programme (Global Environmental Monitoring System

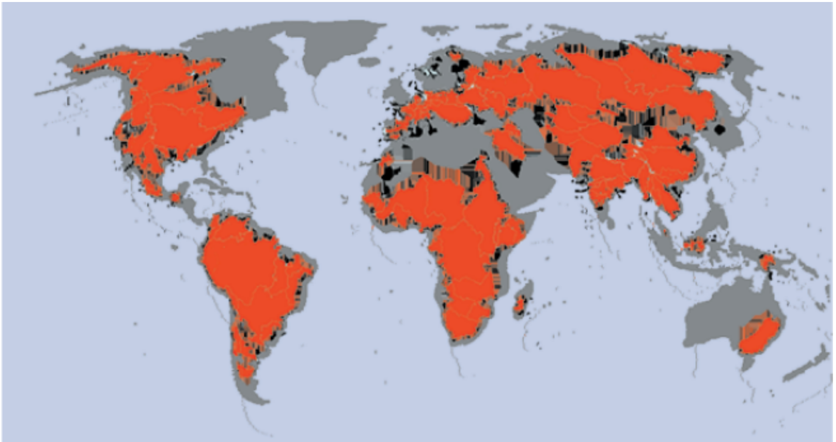

Figure 1. The large river watersheds included in the data analysis.

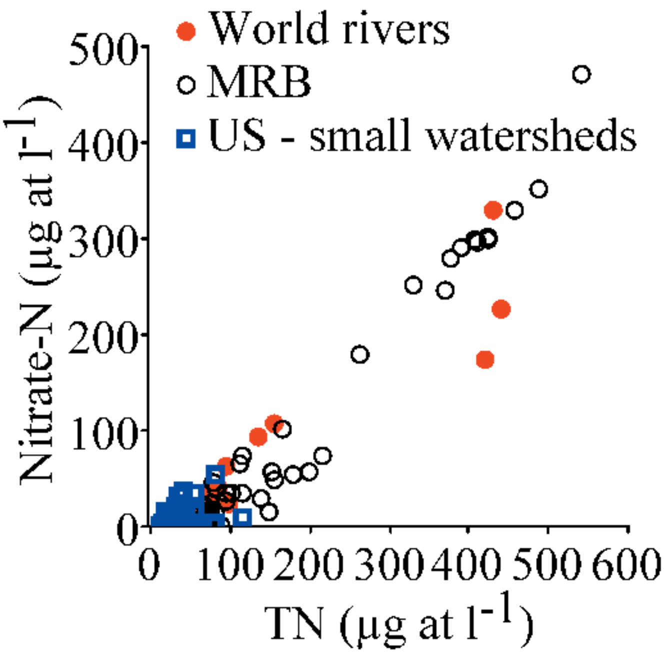

Figure 2. Average nitrate and total nitrogen concentration in large world rivers, large subbasins of the Mississippi River and small relatively undisturbed watersheds of the United States, including some that drain into the Mississippi River. Data are from (Meybeck 1982; Goolsby et al. 1999; Clark et al. 2000).

2000). These data are available from the UNEP/GEMS Collaborating Centre for Freshwater Quality Monitoring and Assessment at the National Water Research Institute of Environment Canada, Ontario, Canada (and on the internet @ http://www.cciw.ca/gems/intro.html). The data from 66 countries were collected between

Table 1. DSi: nitrate N ratios for the analyzed GEMS data set. Population estimates are for 1994.

A. Area included		Cumulative Population (10^6 persons)	Area (10^6 km^2)	Average Population Density (persons km^{-2})
A.1 Earth minus Antarctica		5,500	136	40.4
A.2 within the 72 watersheds of the whole data set		2,276	60.2	37.8
A.3 within the 45 watersheds with DSi: nitrate-N data		1,869	50.1	37.3
B. Data coverage		**Cumulative Population (= % A.2)**	**Area (=% A.2) Area (=% A.2)**	**Average Population Density (persons km^{-2})**
B.1 with DSi: nitrate-N data		34%	37%	24.2
B.2 with DIN: DIP data		29.5%	29.7%	40.3
C. DSi: nitrate-N Ratio	**Rivers included**	**Cumulative Population in Watersheds (10^6 persons)**	**Area (10^6 km^2)**	**Average Population Density (persons km^{-2})**
> 3	30	1,007	41.1	25
⩽ 3	16	850	8.73	97
⩽ 2	11	210	5.4	39
⩽ 1	6	72.5	0.61	119
⩽ 0.5	4	46.3	0.42	110

1976 to 1995, with some station data representing monitoring of only two years. The total area of the world river watershed data used here (n = 82; Figure 1) drains 44% (60.2×10^6 km^2) of the world's land area (135.8×10^6 km^2; excludes 6×10^6 km^2 of the Antarctic land mass; Table 1). The total discharge of these rivers is 20,295 km^3 yr^{-1}.

Additional data on the total nitrogen and dissolved nitrate in the world's larger rivers are from a seminal review by Meybeck (1982) whose data were collected much earlier than almost all the data in the GEMS data set.

Data on water quality in the Mississippi River watershed are assembled by the United States Geological Survey (USGS) and are generally available in the both printed and electronic medium through annual reports of the state and federal agencies collecting these data. The water quality data for 42 sub-watershed basins have been summarized by Goolsby et al. (1999) and Lurry and Dunn (1997). These data, besides being a substantial addition to the data base, also served as an independent reference point for data quality in the GEMS data set. Additional data for flow-weighted concentrations from 85 relatively undeveloped basins in 41 of the 48 conterminous US states are from Clark et al. (2000). These data were used to compare water quality in smaller river watersheds with that in the large subbasins of the Mississippi River. The size of these smaller basins ranged from 0.1 to 22 km^2.

These river data are for water samples that may have been collected above the actual mouth of the river. The USGS, for example, samples at the 'fall-line', below which the elevation gradient is so slight that tidal influences may be important. The watershed nutrient loading rates and population densities used in this analysis were based on the size of the entire watershed, and were not corrected for changes in nutrient concentrations occurring between the sampling site and the river mouth. Thus some statistical uncertainty is included in these data sets.

Because silica dissolution is temperature-dependent, we also examined latitudinal differences in silica export. The range in latitude among subbasins of the Mississippi River watershed is 23°. For other world rivers, latitude was estimated for where the river entered the sea, and before the river bifurcated into deltaic distributaries, and ranged from 34° S to 73° N.

The water quality data are reported as μg-at l^{-1} concentration of dissolved nitrate+nitrite-N, ammonium-N, total nitrogen (TN), dissolved phosphate P (orthophosphate; DIP), Total-P (TP) and dissolved silica as silicate (DSi). The load is the amount of constituent delivered per unit time and is normalized per unit land area. Not all data sets included estimates for all nutrient concentrations. For example, the GEMS data set does not include information on TN or TP, and only Goolsby et al. (1999) and the GEMS data set has information on silicate concentrations.

Estimates of population density for each watershed in 1994 are from Revenga et al. (1998). A relative index of land "development" is from Revenga et al. (1998) who used a "City Lights" data set of 1 km × 1 km maps of nighttime imagery from the Defense Meteorological Satellite Program Operational Linescan System. The category "percent development" is the percentage of the watershed that the satellite system detects as illuminated. The index is not corrected for clouds for African watersheds and there were data only from the equator to 54° N. The estimate of population density in a watershed and this development index are weakly correlated (R^2 = 0.09; p = 0.04), and so this index is seen as a less-than-perfect, but still useful, cumulative indicator of the intensity of socio-economic development, and not just of agricultural land use or urbanization.

Some water quality data were excluded for the following reasons. The average nitrate concentration value for the Rhone River in the GEMS data set is 0.71 μg-at l^{-1}, compared to 35.7 μg-at l^{-1} in Meybeck (1982), which described the river as "contaminated." The Colorado, Murray Darling and Rio Grande watersheds had extremely low rainfall (1, 7, and 5 mm yr^{-1}, respectively) and were excluded. The Neva River had a very low DSi: nitrate-N ratio (0.16), because the DSi concentration reported was very low 3.3 μg-at l^{-1} compared to all others (minimum = 8.3 μg-at l^{-1}; n = 69), but is included and identified where it is an outlier.

Results

Nitrogen

Figure 2 includes the relationship between the total nitrogen and nitrate-N concentration for the world's rivers (from Meybeck (1982); n = 22) and the Mississippi River subbasins (from Goolsby et al. (1999); n = 42) and small United States watersheds (from Clark et al. (2000)). The range of nitrate concentration spans three orders of magnitude across these rivers, and there is no outstanding difference between the range of nitrate-N and total nitrogen values for the Mississippi River subbasins and the other large rivers. Nitrate-N, not ammonium, particulate or dissolved organic nitrogen, is the major constituent to the additional total nitrogen pool above a minimal threshold TN concentration of about 75 μg-at l^{-1}. A linear regression analysis indicates that nitrate-N is 59% and 86% of TN for these two data sets (Meybeck (1982) and Goolsby et al. (1999), respectively), and 77% when combined (p = 0.0001 for all three analyses). In relatively undeveloped small watersheds, increases in dissolved nitrogen do not appear as ammonium, but as nitrate+nitrite (Figure 3). Dissolved nitrite, which is not often measured, is a relatively small component of the dissolved nitrogen in rivers (i.e., almost always it is less than 1% of the TN concentration). Thus the major constituent of change in Figures 2 and 3 is the nitrate ion, and not nitrite, ammonium, organic nitrogen or particulate nitrogen.

A linear regression analysis of nitrate yield (Y; kg N ha^{-1} yr^{-1}) and population density (X; individual km^{-2}) resulted in the following statistics: for all rivers the Nitrate-N yield = 24.1 + 2.12X (n = 49; R^2 = 0.39; p = 0.0001); for only North America and European rivers the Nitrate-N yield = −55.4 + 4.3X (n = 24; R^2 = 0.82; p = 0.001. The mean value for all data (n = 50) was 191.4 ± 41.6 (± 1 S.E.) kg nitrate-N ha yr^{-1}.

If the Nitrate-N yields for the rivers with data (35% of the land mass) were prorated for the earth's surface (exclusive of Antarctica; 136×10^6 km^2), then the yield equals 16.6 Tg nitrate-N yr^{-1}. If the nitrate-N yield is 77% of the TN yield, then the TN yield for the Earth's surface is 21 Tg TN yr^{-1}.

Phosphorus

The concentration of dissolved phosphate is about 46% of the total phosphorus concentration in the Mississippi River watershed subbasins, but 70% in the small United States watersheds (Figure 4). This one-third reduction of the percentage in suggests that the TP in larger rivers is more refractory, compared to the P in the relatively smaller rivers, perhaps because there is a higher suspended sediment concentration in larger rivers (because of turbulence).

A linear regression analysis of phosphate yield (Y; kg P ha^{-1} yr^{-1}) and population density (X; individual km^{-2}) resulted in the following statistics: for all rivers the Phosphate-P yield = 14.7 + 0.22X (n = 40; R^2 = 0.15; p = 0.007); for only North America and European rivers the Phosphate-P yield = 10.3 + 0.44X (n = 22;

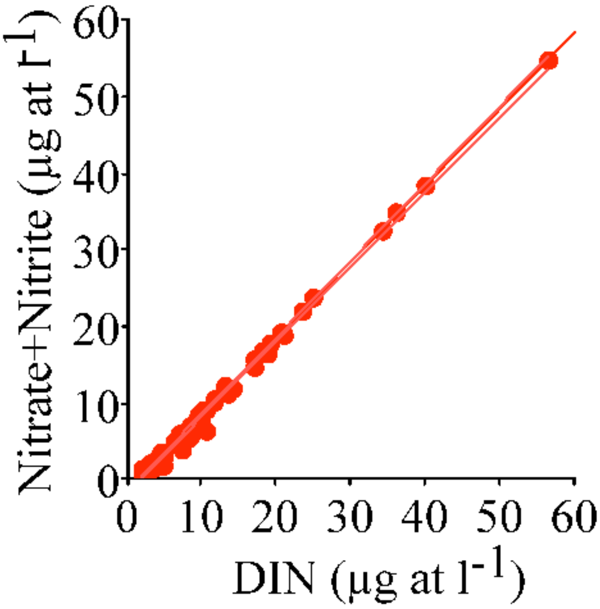

Figure 3. The relationship between the nitrate+nitrite N concentration and total dissolved inorganic nitrogen concentration in small basins of the Mississippi River (data are from Clark et al. (2000)). A linear regression of the data with a 95% confidence interval for the true value of Y is shown. ($Y = 1.003X - 1.684$; $R^2 = 0.996$).

$R^2 = 0.37$; $p = 0.002$). The mean value for all data (n = 43) was 34.87 ± 8.3 (± 1 S.E.) kg phosphate-P ha^{-1} yr^{-1}.

If the TP yields for the rivers with data (32% of the land mass) were prorated for the earth's surface (exclusive of Antarctica), then the annual yield equals 2.6 Tg phosphate-P yr^{-1}. If the phosphate-P yield is between 46% to 70% of the TP yield, then the TP yield for the Earth's surface ranges from 3.7 to 5.6 Tg P yr^{-1}, respectively.

Silicate

Data on the yield of DSi (mass per area) versus runoff for the world rivers and for the subbasins of the Mississippi river are in Figure 5. The DSi yield rises steadily over the thousand-fold increase in runoff. The data for silicate yield (mass per area) are similar for the Mississippi River subbasins and for the large river data set, and there is no apparent difference in DSi yield within three latitude groupings (0–30, 31–60 and > 60 degrees). There is no apparent change in the slope of the linear regression of DSi yield vs. runoff in watersheds with the highest runoff to indicate a major effect of dilution on concentration, but this might be masked by the log transformation of the data and the relatively greater effect of runoff (see discussion below). The graph illustrates the low variance in silicate concentration over the

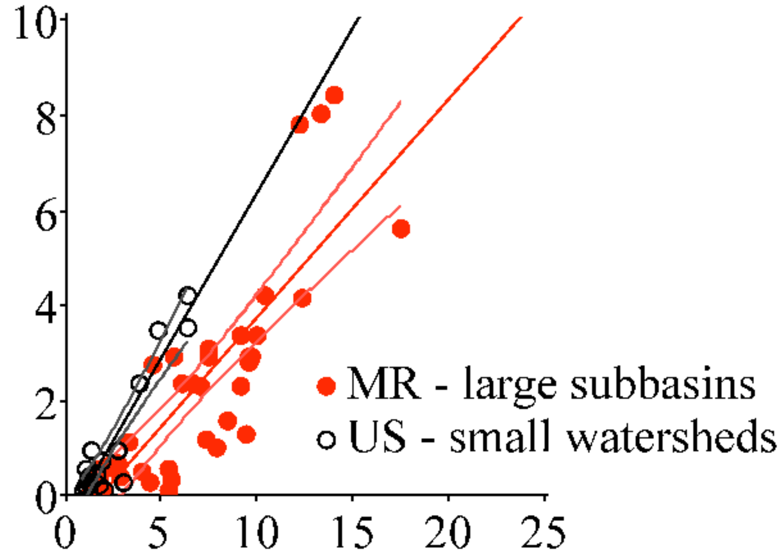

Figure 4. The relationship between the dissolved ortho-phosphate and total phosphorus concentration large subbasins of the Mississippi River and small, relatively undisturbed watersheds of the United States, including some that drain into the Mississippi River. Data are from Goolsby et al. (1999) and Clark et al. (2000). Linear regressions with 95% Confidence Limits for the true value of Y for the two data sets are shown. The slopes of the two regression analyses are significantly different from each other ($p = 0.001$)

wide range in runoff (on an average whole-basin basis). The bottom panel of Figure 5 reveals how the annual average concentration of DSi is higher near the equator (average = 163 μg-at l^{-1} [n = 10; 1 S.E. = 24.5] between latitude 0 to 10 degrees latitude [north or south] compared to 74.7 μg-at l^{-1} [n = 9; 1 S.E. = 18.0 [between latitude 60 and 70). There is a significant linear relationship between latitude and DSi concentration ($R^2 = 0.28$; $p = 0.001$; $n = 67$). The lowest DSi concentration is at sites with high runoff (defined as runoff > 500 mm yr^{-1}) (Figure 5, bottom), which supports the hypothesis that dilution occurs in high discharge watersheds. This dilution effect, however, appears to be a lesser influence on Si yield than does the absolute amount of runoff.

There was no statistically-significant relationship between DSi yield and population density among all rivers or for individual continents. The mean value for all data (n = 63) was 14.3 ± 2.4 (± 1 S.E.) kg DSi ha yr^{-1}.

If the DSi yields for the rivers with data (38% of the land mass) were prorated for the earth's surface (exclusive of Antarctica), then the annual yield equals 194 Tg DSi yr^{-1}.

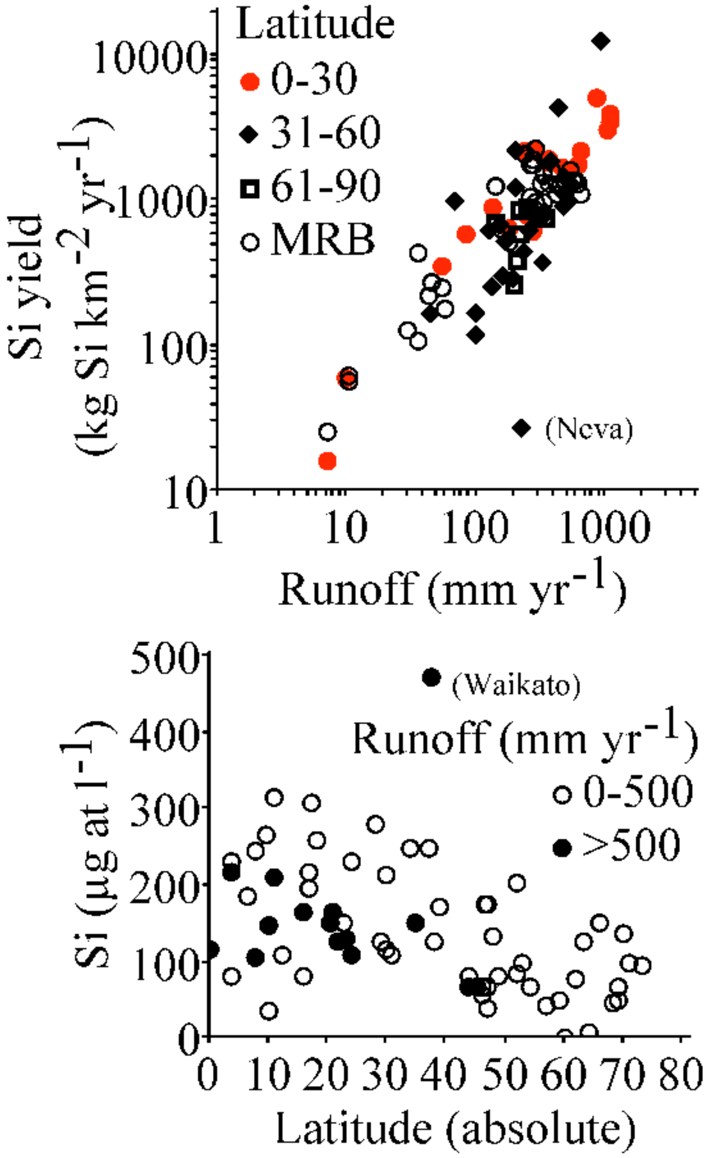

Figure 5. Upper panel: Dissolved silicate yield (mass per unit area) versus runoff for large world rivers and for the subbasins of the Mississippi river basin (MRB), grouped by latitude. The data are from Global Environmental Monitoring System (2000) and Goolsby et al. (1999). Note the logarithmic scale. The outlier data point is for the Neva River. Lower panel: Dissolved silicate-silica concentrations and latitude for large rivers. The data are from Global Environmental Monitoring System (2000). A linear regression of all data shown in the lower panel (exclusive of the Waikato River) has an $R^2 = 0.28$ and $p = 0.0001$ ($n = 67$).

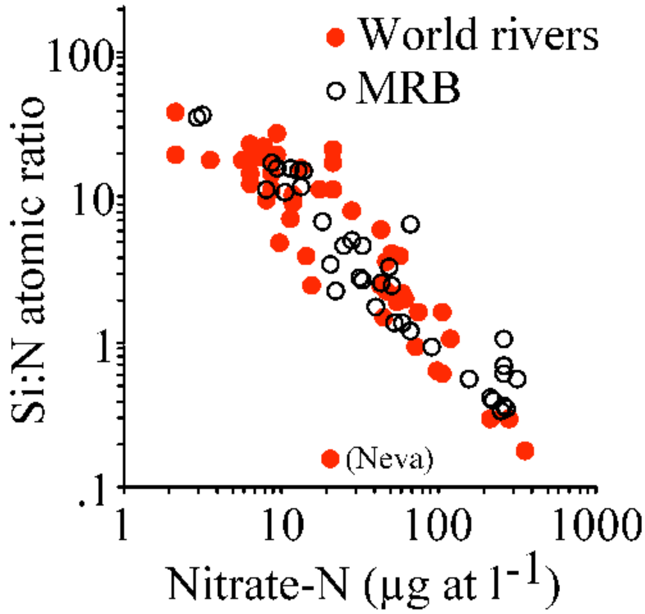

Figure 6. Dissolved nitrate-N concentration (μg-at l^{-1}) for large world rivers and for subbasins of the Mississippi River (MRB) versus dissolved silicate (μg-at l^{-1}):nitrate-N ratio (DSi:nitrate. The data are from Global Environmental Monitoring System (2000) and Goolsby et al. (1999). The outlier is the Neva River.

N:P and N:DSi ratios

The Coefficient of Variation for the widely varying nitrate concentration (Figure 2) and for the relatively constant DSi yield per runoff (Figure 5) is 142% and 56%, respectively, for 46 paired samples. There is a dramatic lowering of the ratio of DSi:DIN as the nitrate-N concentration increases (Figure 6). The DSi:nitrate-N ratio is below the 'Redfield ratio' of 1:1 in eight rivers (all in Europe or North America) at a concentration of about 100 μg-at nitrate-N l^{-1}. A linear regression analysis of the relationship between the DSi:nitrate-N ratio and the concentration of nitrate concentration yielded a similar coefficient of determination (R^2) for data from both large world rivers and the subbasins of the Mississippi River ($R^2 = 0.72$ and 0.90, respectively, and the $p = 0.001$ for both; $n = 45$ and 47, respectively). The slopes were not significantly different from each other ($p = 0.01$).

The population in these watersheds that have an average DSi:nitrate-N ratio below 2:1, 1:1 and 0.5:1 is 21%, 7.3% and 4.6%, respectively, of the total data set with suitable data (Table 1). These ratios are based on annual averages, and so there will be times when a watershed whose annual average DSi:nitrate ratio is 2:1 will be closer to 1:1.

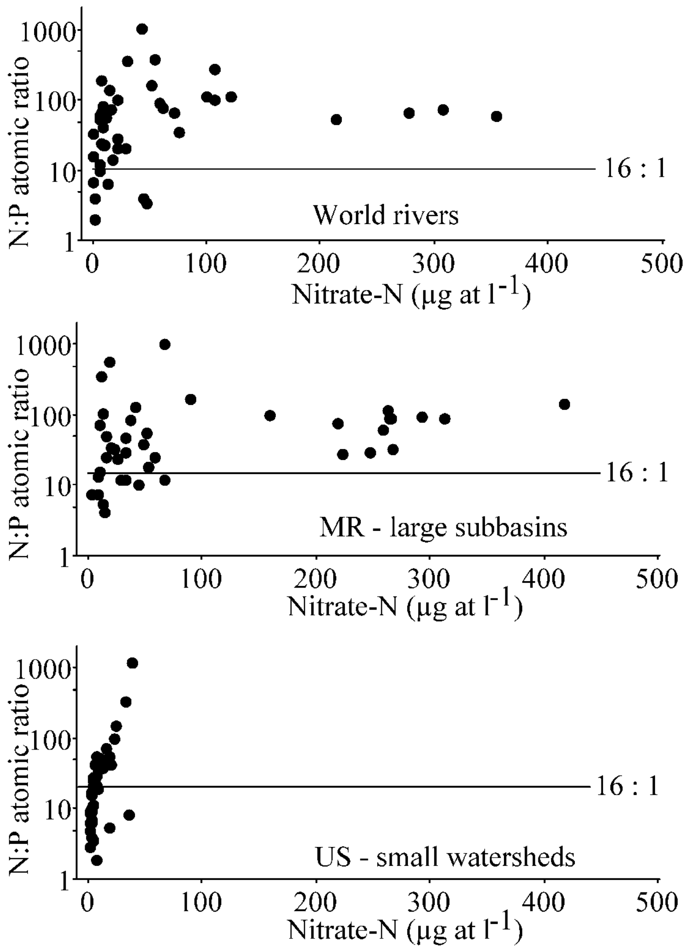

Figure 7. The relationship between nitrate concentration and the atomic ratio of DIN:DIP in large world rivers, large subbasins of the Mississippi River and small relatively undisturbed watersheds of the United States, including some that drain into the Mississippi River. The data are from Global Environmental Monitoring System (2000) and Goolsby et al. (1999), Clark et al. (2000), respectively.

The average DIN:DIP ratio also increases as the nitrate concentration increases from 0 to 50 μg at l^{-1} for large and small rivers (Figure 7). There is a peak in the DIN:DIP ratio at about 50 to 80 μg at l^{-1}, and the ratio remains above 20:1 for watersheds with a nitrate concentration > 100 μg at l^{-1}. The DIN:DIP ratio exceeds the 'Redfield ratio' of 16:1 in 35 of 45 large rivers, suggesting phosphorus limitation of phytoplankton growth in the river (assuming no light limitation occurs) and in the receiving waters.

The DSi:nitrate-N ratio drops rapidly as the development index increases (Figure 8).

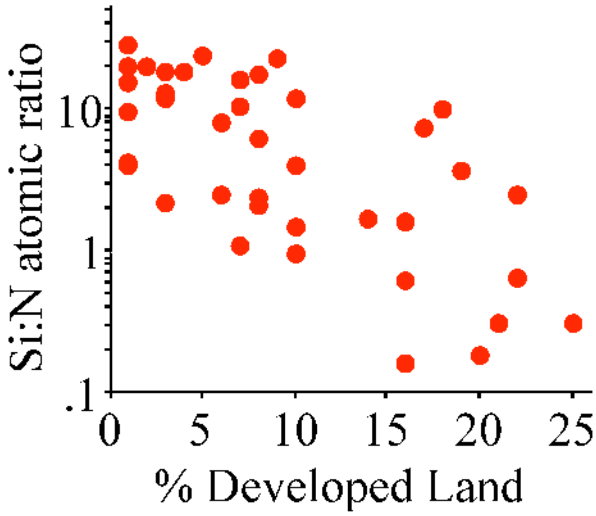

Figure 8. The relationship between the DSi:nitrate-N ratio (from the GEMS data set) and the percent of the watershed that is developed (from Revenga et al. (1998)). A linear regression of the % developed land and the $\log_{10}$ transformed Si:DIN ratio yields an R^2 of 0.46 ($p = 0.0001$; $n = 40$).

Relationships between discharge and constituents

Except for that shown in Figure 5 for Si yield, there were no statistically-significant linear relationships found between discharge and the following $\log_{10}$ transformed or untransformed variables: (A) the concentration of nitrate-N, DIP, or DSi, (B) the DSi:nitrate-N and DIN:DIP ratios, (C) the City-Lights Index, and (D) the DIP-yield, and the nitrate-yield.

Discussion

The consistency observed among the data sets provides considerable assurance that the patterns are real, and are not the artifact of differing methods, equipment or protocols. The relationships between nitrate and TN, DSi, and both runoff and latitude, and also with DSi:nitrate-N vs. nitrate-N match up well among data from the well-regarded USGS water sampling program and the data from other countries.

Nitrogen loading to the world's rivers increased in the last century and altered the balance of DIN, DIP and DSi concentrations (Conley et al. 1993; Justic' et al. 1995; Howarth et al. 1996; Cloern 2001). With increased loading, the nitrate ion becomes the dominant form of dissolved nitrogen and represents the vast majority of nitrogen loading to streams. The entry point for this nitrogen loading is small streams, whose ability to process, to retain and to denitrify the increased N load eventually becomes overwhelmed and inorganic nitrogen is transported further and further downstream and in higher amounts as nitrogen loading increases (Alexander et al. 2000; Peterson et al. 2001). As the TN concentration increases among the world's rivers, almost all of this increase is in the form of nitrate (Figure 2). There appears to be a disproportionately larger increase in nitrate compared to phosphate as nitrogen loading increases, as evidence by the higher DIN:DIP ratio as nitrate concentration increases (Figure 7). The increase in DIN:DIP ratio with higher N loading is consistent with the results arising from some long-term monitoring programs. Conley (2000), for example, reviewed data on riverine nutrient loading into the Baltic Sea, Chesapeake Bay, Narragansett Bay and the Phison River/Eden Bight (a model study) and concluded that the present N load is 1.5 to 4.5 times above that around 1900 and that the P load is 2 to 6 times higher. Conley's estimates were calculated on a weight basis, not an atomic basis. When converted to a molar basis, the equivalent increase in N is 66% higher than for P, i.e., an increase in the N:P atomic ratio occurred in the loading waters.

There are varying sources of nitrogen and phosphorus available throughout watersheds that are continually being added and often in large quantities as point and non-point sources. This is in great contrast to factors controlling DSi loading. Compared to TN and TP, there is little additional DSi entering downstream, and DSi losses from large dam construction (up to 50%; Humborg et al. (2000)) are not compensated for as river water flows to the sea. Thus, the maximum silicate concentration in large rivers (average annual value) within a broad geographic range is less than three times the minimum average annual value, whereas the nitrate concentration varies almost 1000-fold (Figure 2).

The yield of DSi among the world's rivers appears to be much more dependent on watershed water yield than factors which co-vary with latitude (e.g., temperature) (Figure 5). Thus the changes in DSi:DIN ratio are heavily controlled by the nitrate concentration and indirectly through human intervention in the earth's nitrogen cycle. The influence of the great global variability in soil types, climate and geomorphic setting on the DSi:nitrate-N ratio is important, but less influential, it seems, than the effects of land use and other human influences.

The estimates of the annual N, P and Si loading from rivers are comparable to other estimates for the dissolved constituents (Table 2). Our estimates were based on a calculation that prorated the yield per area for land without water quality data. Although the data set we used included more rivers than these other studies, the missing area was still equal to, or larger than, the area with data. Previous studies have compensated for missing data with various extrapolations (e.g., multiplying an average concentration of all data by global discharge) or different years. These results have unsampled areas, too, and remain unquantified. Our values for the TN and TP loading are quite different from these previous studies, however. These differences are the result of using various conversion factors to extrapolate the total loading on the basis of carbon loading, the dissolved:total ratio, or from suspended sediment data collected independently from the dissolved constituent samplings. Furthermore, there are significant climatic factors operating on decadenal scales that may affect the concentration of solutes. We tried to reduce these uncertainties by using nitrate-N:TN and DIP:TP ratios from a wide range of rivers to extrapolate to

Table 2. Estimates of the annual global flux of nitrogen, phosphorus and dissolved silica carried from rivers to the ocean. All estimates are in Tg element yr^{-1}. Tg = 10^{12} g.

Annual Load	Tg element yr^{-1}	Source
nitrate-N	16.2	this study
	21	Seitzinger and Kroeze (1998)
	12	Meybeck (1982)
TN	21	this study
	41	Galloway et al. (1995)
	43	Meybeck (1982)
	7	van Bennekome and Solomons (1981)
DIP	2.6	this study
	0.8	Meybeck (1982)
TP	3.7 – 5.6	this study
	21	Meybeck (1982)
DSi	194	this study
	171	Tréguer et al. (1995)
	181	Meybeck (1979)

the TN and TP loadings. We are confident that significant uncertainties remain, however, if only because of the large area of unsampled discharges.

Aquatic food webs are affected by the quantity of nutrients loaded into water bodies (Nixon et al. 1986; Vollenweider 1976; National Research Council [NRC Committee on the Causes and Management of Coastal Eutrophication, Ocean Studies Board and Water Science and Technology Board] 2000), but also by the *relative* supply of different kinds of nutrients (Elser et al. 2000; Turner et al. 1998). Diatoms, the algae that dominate the algae-zooplankton-fish food webs of productive marine ecosystems, have an intracellular dissolved silicate:dissolved nitrogen atomic ratio (DSi:DIN) of 1:1, and the regeneration of DSi and DIN is also 1:1. Redfield and others (Redfield et al. 1963; Elser et al. 1996) postulated that there were stoichiometric and physiological limits to phytoplankton community composition and food web structure. Results from field and laboratory studies suggest that the lack of dissolved silicate relative to nitrogen can control phytoplankton community composition and production by reducing the abundance of diatoms relative to other algae (Egge and Aksnes 1992; Rabalais et al. (1996, 1999); Egge and Jacobsen 1997; Dugdale and Wilkerson 1998). Schelske et al. (1983), for example, described how the diatom production in Lake Michigan was reduced as the DSi-:DIN ratio dropped below 1:1, and Elser et al. (1996) have shown how these ratios constrain ecological organization at the cellular, organism, and community level.

The DSi:DIN atomic ratios of riverine water entering coastal waters, and within coastal waters, has been declining in many areas of the world and approaching the

Table 3. Table 3. Examples of nutrient concentrations *in situ* or in the waters entering coastal ecosystems where the DSi:DIN ratio (atomic) has been declining to near or below 1:1.

DSi:DIN concentration *in situ* < 1:1	Observation; source
Irish Sea	declined since 1959 (Allen et al. 1998)
Bothnian Sea	declining during winter (Rahm et al. 1996)
Bay of Brest	(Le Pape et al. 1996)
DSi:DIN loading concentration < 1:1	Source
Bay of Brest rivers	(del Almo et al. 1997)
Bothnian Sea watershed	(Rahm et al. 1996)
Baltic proper rivers	(Rahm et al. 1996)
Mississippi River	(Turner and Rabalais (1991, 1994))
Morlaaix River (English channel)	(Wafar et al. 1983)
Po River, Italy	(Justic' et al. 1995)
Susquehanna (Chesapeake Bay)	(Fisher et al. 1988; Correll et al. 2000)
Danube River	(Humborg et al. 2000)

critical ratio of 1:1 (Table 3). Officer and Ryther (1980) hypothesized that if the minimal DSi:DIN proportion of 1:1 for diatoms was not met, then an alternate phytoplankton community composed of non-diatoms might be competitively enabled. They proposed that this alternate community would be more likely to be dominated by flagellated algae, especially dinoflagellates, including noxious bloom-forming algal communities. Smayda (1990) reviewed the global increase of harmful marine algae blooms and came to the same conclusion. Officer and Ryther (1980) further argued that as the DSi:DIN ratio fell below 1:1, the fisheries food web would become composed of less desirable species, which turns out to be a correct prediction for the Louisiana shelf near the Mississippi River delta. There the percent of copepods in the mesozooplankton, the fecal pellet production, carbon flux to the bottom and respiration rate of carbon in bottom waters were all sensitive to the DSi:DIN "pivot point" of 1:1 (Turner et al. 1998). Thus, important food web dynamics leading to fisheries harvests could be affected by the relative quantities of nutrients being loaded into the receiving waters.

The DSi:nitrate-N ratio is thus a sensitive indicator of aquatic food web health. Based on this analysis, the DSi:nitrate-N ratio and the nitrate concentration, when used together, could be applied as a comparative indicator of eutrophication that is robust across the broad landscapes represented by large river systems.

A final conclusion is that the influence of anthropogenic factors on the concentrations and yields of nitrate and phosphorus in the worlds largest rivers are more important than is the natural background variability resulting from climate, discharge, soil and geomorphology. These influences are large enough to influence the growth and composition of aquatic food webs, to the point that freshwater and marine food webs are grossly affected. Vörösmarty et al. (2000) recently examined the current and future adequacy of the world's freshwater resources, and concluded that the present shortage of water for large areas will only be exacerbated by population growth and economic development, whose influence is grossly superior to that of the predicted global climate changes of the next 25 years. Tilman et al. (2001) estimate that nitrogen and phosphorus fertilizer use will increase by 2.4 and 2.7 times, respectively, the application rate in 2000. The qualitative impact of these human influences will push the DSi:nitrate-N ratio lower, and the N:P ratio higher. It is easily seen that the consequences of these developments, if they follow the empirical patterns discussed herein, will result in further shifts from desirable to undesirable fisheries food webs and also increases in the frequency and severity of noxious algal blooms.

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Appendix 1

Table A1. The watersheds included in the GEMS data set.

Africa
Chari
Niger
Nile
Orange
Semega
Zaire
Zambezi
Asia
Amu Daria
Amur
Brahmaputra
Cauveri
Chang Jiang
Chao Phrya
Ganges
Godavaria
Hong He
Huang He
Indgirka
Indus
Irrawady

Table A1. Continued.

Kolyma
Krishna
Lena
Mahanadi
Mekong
Narmada
Ob
Salween
Shatt El Arab
Syr Daria
Tapiti
Xi
Yennissei
Europe
Dalaven
Danube
Dnepr
Don
Ebro
Elbe
Garnone
Glama
Guadalquivir
Kemijoki
Loire
Neva
Pechora
Po
Rhine
*Rhone
Seine
Tagus
Thames
Volga
North America
Balsas
Churchill
Columbia
*Colorado
Fraser
Hudson
Mackenzie
Mississippi
Nelson
*Rio Grande

Table A1. Continued.

St. Lawrence
Thelon/Kazan
Yukon
Oceania
Burdekin
Flinder
Fly
*Murray Darling
Sepik
Waikato

*some data for these rivers were excluded for reasons explained in the text

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