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Importance of Suspended Particulates in Riverine Delivery of Bioavailable Nitrogen to Coastal Zones

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Importance of suspended particulates in riverine delivery of bioavailable nitrogen to coastal zones

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Abstract. Total nitrogen (TN) loadings in riverine sediments and their coastal depocenters were compared for 11 river systems worldwide to assess the potential impact of riverine particulates on coastal nitrogen budgets. Strong relationships between sediment specific surface area and TN allow these impacts to be estimated without the intense sampling normally required to achieve such budgets. About half of the systems showed higher nitrogen loadings in the riverine sediments than those from the coastal depocenter. In spite of uncertainties, these comparisons indicate that large, turbid rivers, such as the Amazon, Huanghe, and the Mississippi, deliver sediments that in turn release significant or major fractions of the total riverine nitrogen delivery. Riverine particulates must therefore be considered an essential factor in watershed nutrient loading to coastal ecosystems and may affect delivered nutrient ratios as well as total nutrient loading. The relative importance of particulate versus dissolved delivery has decreased over recent decades in the Mississippi as a result of damming and fertilizer use in the watershed.

1. Introduction

Several lines of evidence imply that terrigenous organic matter delivered to coastal regions by rivers undergoes significant decomposition but is only partially replaced by marine carbon deposition [e.g., *Berner*, 1982; *Showers and Angle*, 1987; *Smith and Hollibaugh*, 1993; *Aller et al.*, 1996]. These inferences have derived primarily from organic carbon (OC) budgets, with riverine delivery exceeding that observed to be buried in the shelf depocenter. Such budgets are difficult to construct, because extensive sampling is needed to assess shelf sedimentation and carbon burial rates.

We have recently demonstrated that estimates of the loss of terrigenous carbon can be assessed by taking advantage of grain size relationships present in both the material delivered by rivers and that deposited on shelves [*Keil et al.*, 1997]. Briefly, a proportionality between organic carbon concentrations and sediment surface area allows organic carbon loading to be expressed as a ratio between these two parameters. Thus while organic carbon concentrations and burial rates vary throughout a shelf region, because of geographically varying grain size and sedimentation rate, the organic carbon:surface area ratio is a more conservative parameter. Carbon budgets assessed by this method agreed well with other means of reaching these budgets in the Amazon river-shelf system [*Showers and Angle*, 1987; *Aller et al.*, 1996].

The net regeneration of organic carbon on shelves has led to the inference that the nitrogenous components of organic matter are likewise regenerated and may provide important nutrient subsidies to the coastal zone [*Smith and Mackenzie*, 1987; *Smith and Hollibaugh*, 1993]. Quantitative estimates of this riverine particulate subsidy to coastal nitrogen available for processes such as primary production or bacterial nitrification/denitrification have been difficult, for the same reasons as for organic carbon. Accurate estimation of nitrogen inputs to coastal ecosystems is critical to issues such as fisheries production and eutrophication, especially in the context of increases in nitrogen loading to coastal zones [*Nixon*, 1995; *Howarth et al.*, 1996]. The potential importance of riverine particulates to coastal ecosystem productivity has long been inferred from the history of fishery and planktonic population declines following damming of the Nile River [*Elster and Gorgy*, 1959; *Halim*, 1991].

In this paper we provide an improved quantitation of this effect. We use differences in surface area-normalized nitrogen loadings between river and depocenter sediments to show that nitrogen undergoes net release at the land-ocean interface in some but not all coastal areas. We then compare the observed releases to estimates of dissolved inorganic nitrogen delivery by the rivers, the parameter most commonly used to assess terrigenous nitrogen loading to these ecosystems.

2. Methods and Materials

Sediment samples were collected from rivers and their coastal depocenters. The river-shelf couples sampled for this study include (1) Fly River and its adjacent shelf (Papua-New Guinea): Riverine-deposited sediments were collected from lower reaches of the river, just above its opening to the sea, at stations with no

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measurable seawater influence; shelf sediments derived from subtidal sites ranged out to 350 km from the river mouth; (2) Tomales Bay (California): The river endmember included suspended and deposited sediment from its two main inputs, Walker and Lagunitas Creeks, collected December 1994 to January 1995; depocenter sediment was derived from intertidal and subtidal sites along the length of the bay; (3) Sacramento River, San Francisco Bay (California): Riverine-suspended sediment was collected (April 1994 and January 1995) from the Sacramento River at Rio Vista, just above the bay, and deposited riverine sediment was collected at several sites in the lower Sacramento River delta; intertidal and subtidal estuarine sediments were collected throughout the northern bay; (4) Eel River and its adjacent shelf (California): Riverine-suspended and deposited sediments were collected in the lower reaches of the Eel River (near Ferndale and Scotia) during high flow conditions in February 1995; shelf sediments outside the mouth of the river, over a region of several tens of kilometers, were collected from 30 to 100 m depth; (5) Trinity River and Galveston Bay (Texas): Riverine-suspended sediment was collected in April 1997; estuarine sediments were collected from northeastern Galveston Bay; (6) Amazon River and its adjacent shelf (Brazil): Riverine-suspended sediments were collected from Obidos, Marchantaria, and Vargem Grande; shelf sediments are those reported by *Mayer* [1994]; (7) Huanghe River and its adjacent shelf (China): Riverine-suspended sediments were collected in April 1994 and July 1996, near Jinan (Shandong Province); shelf subtidal sediments were collected just off the mouth of the Huanghe in water depths <28 m; (8) Changjiang River and its adjacent shelf (China): Riverine-suspended sediment was collected in Nanjing (JiangSu Province) in June 1996; shelf samples are those proximal to the river mouth reported by *Aller et al.* [1985]; (9) MacKenzie River and its adjacent shelf (Canada): Riverine-suspended sediments were collected in the lower reaches of the river; subtidal shelf sediments were collected off the river mouth out to water depths of 200 m, as reported by *Ruttenberg and Goñi* [1997]; (10) Mississippi River and its adjacent shelf (United States): Suspended sediment was collected at Baton Rouge in April 1994 and March 1997; shelf subtidal sediments from west of the river mouth were collected from water depths of 6-61m; (11) Susquehanna River and Chesapeake Bay (Maryland): Riverine-suspended sediments were collected just below Conowingo Dam throughout the period 12/95-11/96; estuarine subtidal sediments were collected from several locations in northern Chesapeake Bay, which represents the principal depocenter of the Susquehanna.

Riverine samples were collected either as suspended or as bed sediments. In the case of suspended samples, river water was collected, centrifuged (sometimes after a period of gravitational settling to concentrate particulates), and the centrifuged pellet frozen until analysis. In the case of the Mississippi, Eel, Huanghe, Changjiang, Tomales Bay, and on one occasion the Susquehanna, riverine-suspended sediment was obtained during high-water stage in order to sample material most likely to dominate sediment in the depocenter. In some rivers we obtained samples of bed sediment in addition to or instead of suspended sediment; these included the Fly, Tomales, and Eel systems. Shelf sediments were collected by various grabs and corers, and all samples reported here represent material from within a few centimeters of the sediment-water interface.

Subsamples of riverine-suspended sediment for the Amazon and Huanghe were separated into grain size fractions using split-flow-lateral-transport-thin separation (SPLITT) [*Giddings*, 1985], as described by *Keil et al.* [1994]. Separates were frozen until analysis for organic matter and surface area.

The total nitrogen content of samples was determined by CHN analyzer (either Perkin-Elmer 2400 or Carbo Erba 1106), after vapor phase HCl pretreatment to remove carbonate phases for simultaneous organic carbon analysis [*Hedges and Stern*, 1984]. Precision was better than $\pm$ 5%.

The specific surface area of samples was determined after H_2O_2 treatment [*Mayer*, 1994] or 350°C oven oxidation [*Keil et al.*, 1997] to remove organic matter, by N_2 adsorption and BET analysis (*Brunauer et al.*, 1938). Both one-point and multipoint adsorption isotherms were used, and the two approaches showed excellent agreement with one another.

Stable carbon and nitrogen isotope analysis was performed on a VG Micromass Prism mass spectrometer, following acidification to remove carbonates, sealed quartz tube combustion, and cryogenic separation of gases. The $\delta^{13}C$ and $\delta^{15}N$ values are reported in standard delta notation relative to PeeDee Belemnite (PDB) and atmospheric nitrogen, respectively.

3. Results

The concentrations of total nitrogen (TN) in shelf sediments generally show strong correlation with sediment specific surface area values within regions (Figures 1, 2), as has been noted

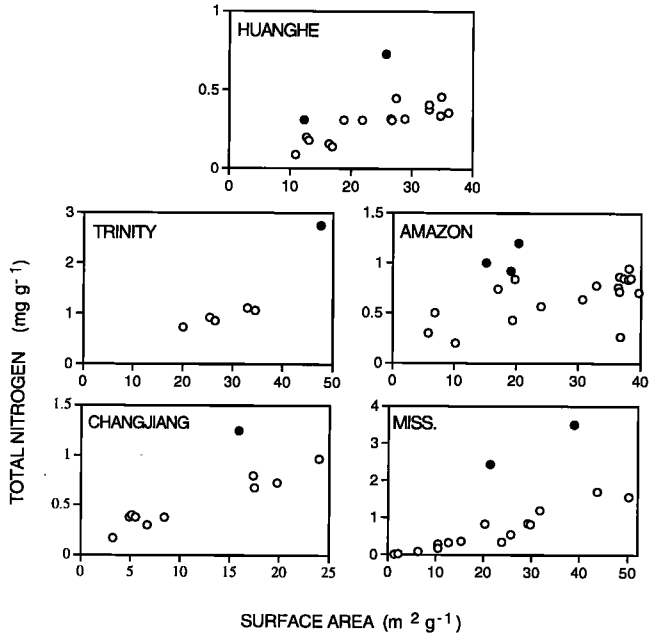

Figure 1. Total nitrogen (mg g^{-1}) versus sediment specific surface area (m^2 g^{-1}) for river-depocenter pairs in which an excess of nitrogen loading is evident in the riverine sediments relative to those from the depocenter. Solid circles represent riverine-suspended particulates, and open circles represent depocenter bed sediments. All systems are denoted by the name of the river (Miss. is Mississippi). Correlations between nitrogen and surface area are significant ($p < 0.05$) for every system.

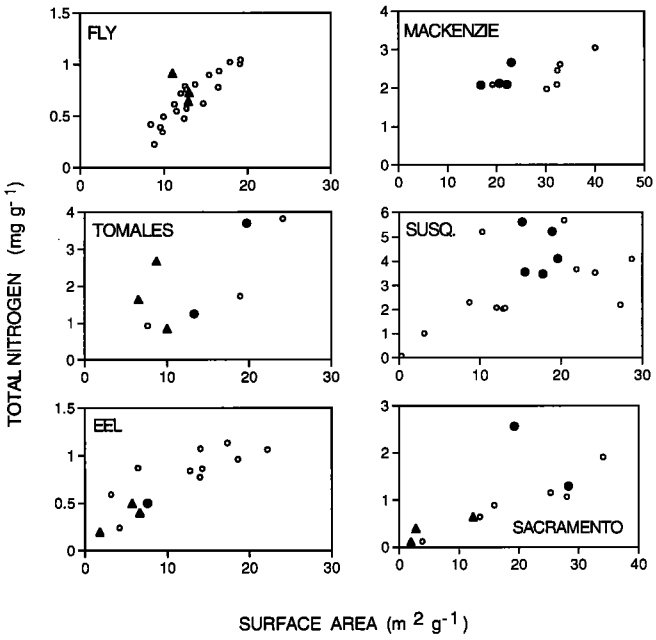

Figure 2. Total nitrogen (mg g^{-1}) versus sediment specific surface area (m^2 g^{-1}) for river-depocenter pairs in which no difference in nitrogen loading can be discerned. Solid circles represent riverine-suspended particulates, solid triangles represent riverine bed sediments, and open circles represent depocenter bed sediments. All systems are denoted by the name of the river except for Tomales Bay (Susq. is Susquehanna). Correlations between nitrogen and surface area are significant ($p < 0.05$) for every system except Tomales Bay.

before [e.g., *Mayer et al.*, 1988]. Size fractionations (SPLITT) supported this correlation for Amazon shelf sediments (Figure 3). These relationships usually have significant non-zero intercepts, obviating the use of TN:surface area ratios to characterize the nitrogen loadings. Nevertheless, it is clear that TN loadings, after accounting for the surface area dependence, vary widely among the sites examined. For example, at a surface area value of 20 m^2 g^{-1}, TN values range over an order of magnitude, from 0.2 mg g^{-1} in the Huanghe to 4-5 mg g^{-1} in the Chesapeake. These relationships are for sediment-water interface samples, which for organic carbon generally show less tight relationships with surface area than downcore samples [*Mayer*, 1994].

This surface area dependence is not so evident for bulk riverine-suspended material, because of (1) the small numbers of samples and (2) the small spread in surface area values for suspended material compared to the better sorted and hence wider variations in surface area values among coastal depocenter sediments. However, grain size separations of Amazon and Huanghe riverine suspended sediments (Figure 3) show a clear grain size dependence for nitrogen, similar to that observed for riverine organic carbon [*Keil et al.*, 1997].

For the Amazon, Huanghe, Chiangjiang, Trinity, and Mississippi riverine samples, the surface area-normalized TN loading is higher than that found for the sediment-water interface samples in the adjoining coastal sediments (Figures 1, 3). This inequality was inferred if the majority of riverine data had values higher than the 95% confidence intervals for the data points of

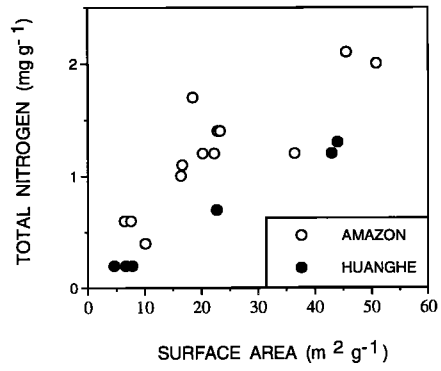

Figure 3. Total nitrogen (mg g^{-1}) versus sediment specific surface area (m^2 g^{-1}) for grain size separates (SPLITTs) of riverine-suspended particulates from the Amazon (solid circles) and Huanghe (crosses) rivers, and Amazon shelf sediments (open circles).

the shelf samples. In contrast, the Eel, McKenzie, Sacramento, Susquehanna, Fly, and Tomales Bay systems show statistically similar TN-surface area relationships in riverine and coastal sediments (Figure 2).

Stable isotope analysis shows that the transition from riverine to coastal sediments is generally accompanied by a shift in $\delta^{13}C$ values from terrigenous toward marine values (Figure 4), though "marine" values may also be due in part to the influence of terrestrial C4 plant detritus [*Ruttenberg and Goñi*, 1997; *Goñi et al.*, 1997]. However, the corresponding $\delta^{15}N$ values for bulk samples show little systematic shift from terrigenous to marine values. Although covarying shifts in $\delta^{13}C$ and $\delta^{15}N$ values have occasionally been reported for the terrigenous-marine transition [*Peters et al.*, 1978; *Mayer et al.*, 1988], this agreement is also missing in many systems [e.g., *Gearing*, 1988; *Thornton and McManus*, 1994], as $\delta^{15}N$ values are subject to relatively intense alteration during diagenetic processes [*Cifuentes et al.*, 1988].

Size separations show some grain size effect on stable isotope compositions (Table 1). The finer silt-size fractions have higher $\delta^{15}N$ values than the medium silt fraction (15-38 μm), although there is little size variation in $\delta^{13}C$ values. These trends may

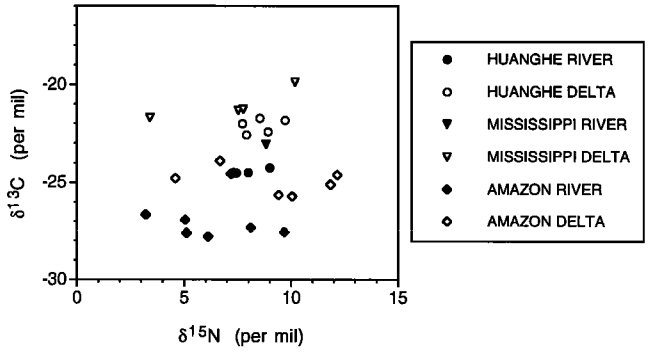

Figure 4. The $\delta^{13}C$ and $\delta^{15}N$ values for riverine (solid symbols) and depocenter (open symbols) sediments from the Huanghe (circles), Mississippi (triangles) and Amazon (diamonds) systems. SPLITTs and whole sediments are included.

Table 1. Values of $\delta^{13}C$ and $\delta^{15}N$ in Size Fractions of Amazon and Huanghe River-Suspended Particulates and Amazon Shelf Sediment

	Amazon River				Amazon Shelf					
	Marchantaria		Vargem Grande		Station 4351		Station 4315		Huanghe River	
	$\delta^{13}C$	$\delta^{15}N$	$\delta^{13}C$	$\delta^{15}N$	$\delta^{13}C$	$\delta^{15}N$	$\delta^{13}C$	$\delta^{15}N$	$\delta^{13}C$	$\delta^{15}N$
3-8 μm	-27.6	5.1	-27.6	9.7	-24.5	7.3	-25.1	11.8	-24.5	8.0
8-15 μm	-27.8	6.1	-27.3	8.1	-24.6	7.2	-24.6	12.2	-24.3	9.0
15-38 μm	-26.7	3.2	-26.9	5.1	-24.8	4.6	-25.6	9.4	-24.5	7.5

reflect relatively large amounts of vascular plant debris, which tends to have low $\delta^{15}N$ values, in the coarser fractions and relatively high concentration of microbially reworked material with higher values of $\delta^{15}N$ in the finer fractions [*Tiessen et al.*, 1984; *Mayer et al.*, 1993]. These separations suggest that whole sediment nitrogen isotope compositions may be affected by size sorting during depositional processes. Shifts in $\delta^{15}N$ at the terrigenous-marine transition certainly warrant greater attention, but for this study, we cannot infer the extent of replacement of riverine nitrogen by marine-derived nitrogen.

4. Discussion

Impact of N-regeneration on Coastal Nutrient Delivery by Rivers

The minerals in the depocenters of each of the systems studied derive primarily from delivery by the major river. Because detrital mineral phases generally do not show significant diagenetic changes upon sedimentation, their specific surface area can be expected to remain constant in the land-ocean transition. Thus the surface area-normalized nitrogen loading should be affected primarily by changes in nitrogen and reflect changes in the nitrogen loading in the system. The good correlations between TN and specific surface area among shelf sediments (Figures 1, 2) indicate that this surface area-normalized loading is consistent throughout the basin. Changes in the nitrogen loading between river and depocenter, multiplied by the sediment flux, can then be used to quantify nitrogen releases associated with the particulate phase. These releases can be compared to fluxes due to dissolved inorganic nitrogen, for which data are generally available. Other sources of nitrogen to the system, such as riverine-dissolved organic nitrogen or upwelled nitrogen from offshore, cannot be considered in this comparison because of lack of data.

The excess TN in riverine-suspended sediments relative to sediment-water interface values in some coastal, deposited sediments indicates that nitrogen is released from the riverine particulates before burial. This nitrogen may then be converted into dissolved inorganic forms which can provide nutrients to the coastal water column or fuel heterotrophic reactions such as nitrification/denitrification [*Smith and Mackenzie*, 1987; *Smith and Hollibaugh*, 1993].

To some degree, this conversion may occur in the estuarine water column. Evidence for such a reaction is the frequent observation of positive, nonconservative mixing profiles between dissolved inorganic nitrogen and salinity, especially in muddy systems such as the Amazon [*Edmond et al.*, 1981], Changjiang, and Huanghe [*Zhang*, 1996]. Whether this reaction is dominated by biological regeneration of riverine organic nitrogen or an abiotic displacement of ammonium [*Zhang*, 1996], each followed by nitrification in turbid low-salinity regimes [*Owens*, 1986], is unclear. We did not examine the chemical nature of the terrestrial TN in this study, but previous work has shown it to consist of varying mixtures of organic and inorganic forms [*Bremner*, 1967; *Ittekot and Zhang*, 1989], which could be regenerated by various pathways.

The magnitudes of some estuarine nutrient regeneration reactions are consistent with the difference in surface area-normalized nitrogen loading observed in this study. For example, positive nonconservative mixing plots of nitrate in the Amazon indicate regeneration of the order of 2-5 μM nitrate, normalized to the river water endmember [*Edmond et al.*, 1981]. This value is about 20-50% of the nitrogen release found here from riverine sediment (Figure 1), if also normalized to riverine water volume (see calculations below). Regeneration from riverine sediments could thus be an alternative explanation to the nutrient trap hypothesis, in which regeneration operates on estuarine phytoplankton detritus, suggested by *Edmond et al.* [1981]. In the Huanghe, excess nitrate observed in estuarine mixing profiles, of ~25-90 μM [*Zhang*, 1996], is a much smaller fraction of the N released from sediments - 762 μmol N per liter of river water.

Alternatively, this regeneration may occur after deposition, again perhaps because of either biotic or abiotic reactions. In either case, the released nitrogen supplements riverine-dissolved inorganic nitrogen (DIN) delivered to coastal areas and available for primary production.

The quantitative importance of riverine, particulate nitrogen released from sediments can be compared to delivery in the form of DIN for several systems (Table 2). We performed this comparison by assessing nitrogen released from riverine sediment delivered to the coastal zone, normalizing this release to average riverine water flow, and comparing this "concentration" to the average concentration of riverine DIN. To perform these calculations, long-term sediment delivery estimates were divided by long-term water delivery rates to obtain a time-averaged, suspended sediment concentration. This flow-weighted, average-suspended load was then multiplied by the difference in nitrogen concentrations between the riverine suspended particulate matter and the coastal sediment values. This difference was determined at the average surface area value of the coastal sediments sampled in this study, which is presumed to represent the average

Table 2. Estimates of Contribution of Particulate Nitrogen (PN) Lost From Riverine Particulates (SPM) to Total of This Loss Plus Dissolved Inorganic Nitrogen (DIN) Delivered by Rivers

	Ave. SPM ($mg\ L^{-1}$)	Ave. DIN (μM)	Mean SFA ($m^2\ g^{-1}$)	ΔPN ($mg\ g\text{-}sed^{-1}$)	Labile PN in SPM (μM in River Water)	% of Total Riv. N-Loading from PN (Labile-PN/(DIN+Labile-PN))
Huanghe	26800	122	23.3	0.398	762	86.2
Mississippi						
1950-1952	1049	69	20.9	1.28	95.9	58.2
1953-1972	491	45	20.9	1.28	44.9	49.9
1973-1982	558	77	20.9	1.28	51.0	39.9
Amazon	217	16.7[1]	28.2	0.739	10.1	40.7
	217	6.2[2]	28.2	0.739	10.1	64.9
	217	3[3]	28.2	0.739	10.1	79.2
Trinity	86.1	34.4	29.8	0.753	4.6	11.9
Changjiang	540	48.1	14.5	1.05	40.5	45.7

These estimates, explained in text, rely on determining the difference in nitrogen loading (ΔPN) between riverine and depocenter sediments at an average surface area (mean SFA), and then normalizing this loss to water delivery rate (labile PN in SPM).

Data sources (a, SPM; b, DIN): Huanghe: a. *Zhang* ([1996]; b. *Zhang* [1996]; Mississippi: a, *Meade and Parker* [1985, Figure 27 (Baton Rouge)]; b, *Turner and Rabalais* [1991, Fig. 2]; Amazon: a, *Meade et al.* [1985, for sediment], *Edmond et al.* [1981, for water]; b, (1) *DeMaster and Pope* [1996], (2) *Edmond et al.* [1981], (3) *Meybeck* [1982]; Trinity: a, *Brock et al.* [1996]; b, *Joye and An* [1998]; Changjiang: a, *Zhang* [1996] ; b, *Zhang* [1996].

value delivered by the river over long time periods. The weight-normalized nitrogen concentration for sediment at this average surface area was determined from regression equations of the data in Figure 1, except for the Amazon and Huanghe which were determined from the SPLITT data of Figure 2. Subtracting the shelf nitrogen concentrations at their respective, average surface area values led to the released nitrogen normalized to weight of sediment. This value was in turn converted to a concentration per liter of river water delivered, which was then compared to the average DIN. The results show that several rivers deliver significant amounts of nitrogen to coastal zones in particulate form, relative to that delivered as DIN (Table 2). However, these results need to have several caveats considered.

Nitrogen flux to the water column from deposited riverine sediment will be tempered to some degree by denitrification, as released ammonia is nitrified and then subjected to denitrification reactions before release at the sediment-water interface. The importance of denitrification to release flux varies among systems but is typically of the order of several tens of percent of the regenerated nitrogen [*Seitzinger*, 1988]. Among systems reported here, denitrification in Amazon shelf sediments has been estimated to convert about half of regenerated nitrogen [*Aller et al.*, 1996] to N_2 gas. *Aller et al.* [1985] reported 37% for the Changjiang. The sediments of the Mississippi River plume denitrify ~42% of regenerated N [*Rowe et al.*, 1992], while Tomales Bay and the Trinity Bay system denitrify ~33% and 45%, respectively [*S.B. Joye*, unpublished data, 1997]. The importance of N regenerated from riverine particulates to coastal primary production should therefore be reduced by these percentages if all regeneration occurs after deposition. However, to the extent that unloading of nitrogen occurs in the water column during estuarine mixing, this correction will not apply. Because we do not know the relative percentages of regeneration occurring before and after deposition, it is impossible to correct the results of Table 2 for denitrification.

Other uncertainties render these calculations only rough estimates. There are significant uncertainties in the amount and average surface area of delivered sediment. There are small numbers of data points that define the TN-surface area relationship for many of the riverine endmembers, though the SPLITT data (Figure 3) increase confidence in the probability of surface area dependence for riverine-suspended particulate N concentrations. Because our samples are all from the sediment-water interface, the calculations do not take into account that further burial leads to greater downcore regeneration of nitrogen, which would bias sedimentary regeneration in the opposite direction as denitrification (i.e., offset losses due to denitrification). Last, we are not considering the potential role of dissolved organic nitrogen (DON), either delivered by rivers or released from depocenter sediments. For example, DON delivered by rivers may become available to coastal phytoplankton, decreasing the relative importance of particulate delivery. Alternatively, release of particulate nitrogen after deposition may be in the form of DON that is not made available to coastal phytoplankton communities, also reducing the relative importance of particulate delivery.

Nevertheless, the results shown in Table 2 make it clear that turbid rivers can deliver significant or major fractions of their bioavailable nitrogen to coastal ecosystems via regenerated nitrogen from riverine particulates. In the Huanghe, virtually all of the bioavailable nitrogen is delivered in particulate form. The Amazon calculations are dependent on the various reported measurements of DIN delivery, but particulates probably contribute at least as much nitrogen as DIN. The modern Mississippi and Changjiang Rivers deliver about 40-45% of their nitrogen via particulates. The Trinity calculation indicates only 12% from particulates, but this figure is probably a strong underestimate because the suspended sediment concentrations do not include high-sediment delivery events.

These releases are net and not gross releases from riverine

particulates. Nitrogen buried in the depocenter sediments also receives inputs from water column autotrophy that incorporates riverine-dissolved nitrogen and locally upwelled nitrogen from offshore. Gross release of N from riverine sediments will therefore be higher than the estimates calculated here.

Calculations were not carried out for systems showing indistinct excess nitrogen loading in the riverine versus depocenter sediments. The Eel River particulates do not appear to be important, in spite of high riverine sediment delivery, because the nitrogen loading changes little between river and shelf sediments. Particulates are probably not very important in the Susquehanna-Chesapeake system, accounting for no more than a few percent of DIN delivery even if significant nitrogen release is assumed, because of low sediment delivery rates.

Low-latitude shelf systems might be particularly affected by particulate delivery, because they tend to receive more sediment delivery due to higher rainfall in the watersheds [*Nittrouer et al.*, 1994]. The low-latitude coastal sediments also tend to have lower loadings of nitrogen per unit sediment surface area (Figures 1, 2).

Damming of rivers can change the importance of particulate delivery [*Halim*, 1991; *Vörösmarty et al.*, 1997]. Such changes are evident for the Mississippi (Table 2), the only river in our data set for which adequate historical data are available. Over the last several decades, sediment delivery has decreased due to dam construction, while DIN concentrations have increased due to fertilizer use in the watershed [*Meade and Parker*, 1985; *Turner and Rabalais*, 1991]. The resultant contribution of particulate nitrogen thus decreased from 58% to 40% from 1950 to 1982. The increase in DIN from fertilizer over this period, an important concern in eutrophication of coastal waters, has been thus somewhat compensated by decreases in particulate-borne nutrient inputs. Alternatively, accelerated erosion resulting from deforestation and cultivation may enhance the importance of this form of nutrient delivery in many watersheds.

Release from riverine particulates may influence coastal productivity through changed timing of nutrient flux, in addition to its enhancement of gross flux. Riverine dissolved nutrients can be expected to have maximum impact during the time of maximum dissolved flux, for example, during spring runoff. However, release from particulates may be delayed until some time after delivery and deposition if the responsible release process is governed by a parameter such as sediment temperature, which can be the master variable in sediment metabolic rates [*Rudnick and Oviatt*, 1986].

Nutrient ratios have consequences for phytoplankton speciation. There is increasing evidence that riverine influences on coastal nutrient ratios may have profound effects on shelf phytoplankton populations [e.g., *Dortch and Whitledge*, 1992; *Humborg et al.*, 1997]. However, other nutrients besides nitrogen are probably released from riverine particulates [*Chambers et al.*, 1995; *Berner and Rao*, 1994; *Conley*, 1997], so that the net impacts on nutrient ratios are not yet clear.

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