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Annual fluxes of sediment-associated trace/major elements, carbon, nutrients and sulfur from US coastal rivers

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Abstract About 260–270 Mt of suspended sediment are discharged annually from the conterminous USA; approximately 69% derives from Gulf rivers (n = 36), 24% from Pacific rivers (n = 42), and 7% from Atlantic rivers (n = 54). Elevated sediment-associated chemical concentrations relative to baseline levels occur in the reverse order of sediment discharges: Atlantic rivers (49%) > Pacific rivers (40%) > Gulf rivers (23%). Elevated trace element concentrations (e.g. Cu, Zn) tend to occur in association with present/former industrial areas and/or urban centres, particularly along the northeast Atlantic coast. Elevated nutrient concentrations occur along both the Atlantic and Gulf coasts, but are dominated by rivers in the urban northeast and by southeastern and Gulf coast "blackwater" streams. Elevated Ca, Mg, K and Na levels appear to reflect local petrology whereas elevated Ti, S, Fe, and Al concentrations are ubiquitous, possibly because they have both natural and anthropogenic sources. Almost all the elevated sediment-associated chemical concentrations/fluxes are lower than worldwide averages.
Key words fluvial sediment-associated constituents; annual fluxes; conterminous USA

INTRODUCTION

About 80% of all coastal/marine water quality degradation is associated with various land-based human activities (UNEP [OCA], 1995). Rivers account for about 95% of the sediment, as well as a substantial portion of the sediment-associated natural and anthropogenic chemical constituents discharged to the world's coastal zones (CZ) and oceans (Förstner & Wittmann, 1981; Meybeck, 1994; Syvitski *et al*., 2005; Walling, 2006; Viers *et al*., 2009; Milliman & Farnsworth, 2011).

Based on in-stream measurements, as well as various modelling exercises, marked changes have been noted in the annual suspended sediment fluxes of numerous river systems over the past 100 years (e.g. Milliman *et al*., 1995; Syvitski *et al*., 2005; Walling, 2006, 2008). Many of these changes have resulted from anthropogenic activities that have directly or indirectly altered existing discharge and/or erosion patterns (e.g. Syvitski *et al*., 2005; Walling, 2006, 2008). In most but not all cases, particularly as a result of dam construction, these anthropogenic activities have led to substantial declines in annual suspended sediment fluxes. Global climate change (particularly changing temperature and precipitation patterns), whether the result of natural weather cycles or through the emission of anthropogenically-generated greenhouse gases, also may alter patterns of weathering and erosion with concomitant changes in the annual fluxes of sediment and sediment-associated chemical constituents (e.g. Syvitski & Kettner, 2007; Walling, 2008; Viers *et al*., 2009). These alterations in annual sediment and sediment-associated chemical fluxes have generated numerous downstream hydrological, ecological, socio-economic and engineering issues.

The current consensus estimate for worldwide annual fluvial suspended sediment fluxes is ~12–15 Gt (e.g. Syvitski *et al*., 2005; Walling, 2006; Milliman & Farnsworth, 2011). These flux estimates are substantially below those postulated for natural and/or pre-anthropogenic levels and probably represent a balance between increasing erosion due to land clearance for agriculture, logging, mining and urbanization juxtaposed against the introduction of soil conservation measures and, particularly, sediment trapping behind dams and/or in reservoirs (e.g. Syvitski *et al*., 2005; Walling, 2006). River runoff from the conterminous USA to the CZ (~1.2×10^3 km^3 year^{-1}) accounts for about 3% of the annual global discharge budget of 38–40×10^3 km^3 year^{-1} (van der Leeden *et al*., 1990; Syvitski *et al*., 2005, Milliman & Farnsworth, 2011). The same geographical area accounts for about 350 Mt of the annual worldwide fluxes of fluvial suspended sediment

(12–14 Gt), also about 3% of the annual worldwide load (e.g. Milliman & Meade, 1983; Osterkamp *et al*., 1998; Syvitski *et al*., 2005; Milliman & Farnsworth, 2011). The Mississippi River Basin (the Mississippi and Atchafalaya rivers) alone accounts for about 60%, of conterminous USA sediment discharges, whereas the remaining approximately 40% derives from a number of medium- and large-sized rivers such as the Eel, Klamath, Brazos, Rogue, Santa Clara and Columbia (e.g. Milliman & Farnsworth, 2011). Although on a global scale the effect of the discharge volumes and suspended sediment masses from the conterminous USA appear relatively small, *viz-a-viz* global sediment fluxes and water quality, this is likely offset, at least to some extent, by the high degree of industrialization, urbanization, and intensive agricultural practices extant in the USA (e.g. Osterkamp *et al*., 1998). Certainly there is little question that industrial and agricultural activity, in conjunction with elevated population densities within the conterminous USA, have a substantial effect on coastal water quality (e.g. US NOAA, 1990; US EPA, 1997; Osterkamp *et al*., 1998; ACWI, 2006).

As a result of the physical (e.g. coastal losses, harbour silting), and water quality (e.g. eutrophication, toxicity) effects of suspended sediment and sediment-associated constituents on the CZ, combined with the fact that climate change may cause substantial alterations in suspended sediment and sediment-associated chemical levels and fluxes in coastal rivers, the US Geological Survey (USGS) has attempted to establish current baseline levels for these constituents for the conterminous USA. This study entailed a year-long sampling and subsequent chemical analysis programme at 132 coastal river sites that generated current baseline estimates against which future changes in the concentrations/annual fluxes of a variety of sediment-associated chemicals could be evaluated.

METHODOLOGY

The determination of the annual fluxes of suspended sediment-associated chemical constituents (mass in Mt) requires a measure of the annual suspended sediment fluxes (t) from selected coastal rivers, as well as a measure of the mean chemical composition of that material (g t^{-1} = mg kg^{-1} = µg g^{-1}) and can be determined using the following equation:

Annual Sediment-Associated Chemical Flux (Mt) =
    [Annual Suspended Sediment Flux (t)] [Chemical Concentration (g t^{-1})]/(10^{-6})   (1)

Equation (1) was used to estimate annual fluxes of sediment-associated chemical constituents determined herein. Due to uncertainties associated with estimating mean annual suspended sediment discharges for USA coastal rivers, fluxes only are reported to two significant figures (e.g. Milliman & Meade, 1983; Milliman & Farnsworth, 2011) and may represent only the correct order of magnitude.

The estimation of the fluxes of suspended sediment-associated chemical constituents to the CZ requires measures of the mean annual suspended sediment flux for each river (equation (1)). Two sources are available: (1) published long-term averages where measurements are available (e.g. Horowitz *et al*., 2001, Gellis *et al*., 2004, 2008; Horowitz, 2010; Meade & Moody, 2010; Milliman & Farnsworth, 2011), and (2) various model-derived estimates (e.g. Syvitski *et al*., 2005; Syvitski & Kettner, 2007). The final list originally contained 130 coastal sites, but ultimately was increased to 132 (Fig. 1). One site was added due to the logistics associated with sampling the York River (Virginia); the original site was replaced by sites on the two major tributaries (Pamunkey and Mattaponi rivers) that join to form the river and its estuary. The other extra sample came from the Atchafalaya River (Louisiana) because it has two distributary outlets, one at Morgan City and the other at Wax Lake outlet (Fig. 1).

Ideally, suspended sediment should have been collected and subsequently analysed to determine the current range of suspended sediment-associated chemical variability at each coastal river mouth. That would have required the existence of a national coastal monitoring network that, whilst proposed, does not currently exist (e.g. Osterkamp *et al*., 1998; ACWI, 2006). As a result,

Explanation
Site Number/River Name

1 St. Lawrence	23 Delaware		62 Aucila	73 Pearl	86 Brazos	101 Pajaro
2 St. Croix	24 Schuykill		63 St. Marks	74 Mississippi	87 Colorado (Texas)	102 Salinas
3 Sheepscot	25 Patuxent		64 Ochlockonee	75 Atchafalaya	88 Nueces	103 Carmel
4 Penobscot	26 Susquehanna	44 Cooper	65 Apalachicola	76 Amite	89 Rio Grande (US)	104 San Lorenzo
5 Narraguagus	27 Tuckahoe	45 Consawatchie	66 Chocktawatchee	77 Ticktaw	90 Colorado (Arizona)	105 San Joaquin
6 Denny's	28 Choptank	46 Edisto	67 Conecuh-Escambia	78 Tangipahoa	91 San Diego	106 Russian
7 Kennebec	29 Potomac	47 Savannah	68 Yellow	79 Bayou LaFourche	92 San Dieguito	107 Sacramento
8 Androscoggin	30 Pocomoke	48 Altamaha	69 Perdido	80 Calcasieu	93 San Luis Rey	108 Mad
9 Presumpscot	31 Nanticoke	49 Ogeechee	70 Blackwater	81 Mermentau	94 San Juan	109 Eel
10 Saco	32 Rappahanock	50 Satilla	71 Mobile	82 Sabine	95 Los Argeles	110 Klamath
11 Ipswich	33 York-Pamunkey	51 St. Marys	72 Pascagoula	83 Neches	96 Santa Anna	111 Coos
12 Merrimack	34 York-Mattaponi	52 St John's		84 Trinity	97 Santa Clara	112 Coquille
13 Charles	35 Appomattox	53 St Lucie		85 Guadelupe/San Antonio	98 Ventura	113 Siuslaw
14 Neponset	36 James	54 Miami			99 SantaYnez	114 Alsea
15 Connecticut	37 Chowan	55 Myakka			100 Santa Maria	115 Siletz
16 Housatonic	38 Roanoke	56 Peace				116 Nehalem
17 Shetucket	39 Tar-Pamlico	57 Caloosahatchee				117 Trask
18 Hudson	40 Neuse	58 Suwanee				118 Columbia
19 Peconic	41 Cape Fear	59 Hillsborough				119 Chehalis
20 Toms River	42 Yadkin-Pee Dee	60 Withlacoochee				120 Nisqually
21 Raritan	43 Santee	61 Econfina				121 Rogue
22 Passaic						122 Umpqua
						123 Puyallup
						124 Green-Duwamish
						125 Queets
						126 Hoh
						127 Skokomish
						128 Snohomish
						129 Stillaguamish
						130 Skagit
						131 Nooksack

Kilometers
0 125 250   500   750   1,000

Fig. 1 Map of the sampling sites used in this study.

in lieu of collecting a series of representative suspended sediment samples for chemical analysis, the <63-µm fractions of near-surface (upper 1 cm) composite bed sediment samples, collected as far downstream as practicable, were used as a surrogate for suspended sediment.

Prior to chemical analysis, each sample was thoroughly homogenized using pre-cleaned glass and/or Teflon[®] rods. About 10% of the sample was wet-sieved through a 63-µm polyester mesh in a plastic frame using deionized water, and dried at 105°C. All the dried samples were analysed for a suite of trace/major elements (Al, Sb, As, Ba, Be, Cd, Ca, Ce, Cr, Co, Cu, Fe, La, Pb, Li, Mg, Mn, Hg, Mo, Ni, K, Se, Ag, Na, Sr, Sn, V, Zn and Ti), as well as total phosphorus (TP), total carbon (TC), total organic carbon (TOC), total nitrogen (TN), and total sulfur (TS) (Horowitz *et al*., 1989, 2001). For all the trace/major elements other than As, Sb, Se, Hg, C and N, 500-mg aliquots were digested with a combination of HF/HClO$_4$/*aqua regia* in Teflon[®] beakers at 200°C. Ag, Cd, and Pb were determined by flame atomic absorption spectrometry (AAS). Most of the remaining constituents were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Aliquots from the same digestion were pre-treated to quantitate As, Sb and Se by hydride generation-ICP-AES. Hg was analysed using separate 500-mg aliquots digested with LeFort *aqua regia* at 140°C; quantification was by cold vapour employing an AAS as the detector. TC and TN were determined on the combustion products of separate 250- to 500-mg sample aliquots using a gas chromatograph with a thermal conductivity detector in a C/N/S analyser. TOC was also determined by combustion, but in a C/S analyser that quantified evolved CO$_2$ with an infrared detector after pretreatment with 10% v/v HCl to remove inorganic carbonates. Typically,

precision was better than ±10%; no bias was detected; however, when concentrations neared the reporting limits, precision could be as poor as ±100%.


RESULTS AND DISCUSSION

Annual suspended sediment fluxes

The annual pattern of sediment discharged from the conterminous USA to the CZ has not substantially changed since the early 1900s (Fig. 2). About 69% of the total annual discharge comes from the Gulf coast (dominated by the Mississippi River Basin); 24% comes from the Pacific coast, and the remaining 7% comes from the Atlantic coast (e.g. Curtis *et al*., 1973; Milliman & Meade, 1983; Osterkamp *et al*., 1998; Milliman & Farnsworth, 2011). However, there has been a significant decline in the estimated mass of annual sediment discharge. In 1909, Dole & Stabler estimated the annual mass at about 510 Mt; in 1973 Curtis *et al*. revised that number downward to about 490 Mt. Osterkamp *et al*. (1998) further revised the Curtis *et al*. figure down to about 450 Mt, whereas Milliman & Farnsworth (2011) estimate it at ~350 Mt. The current compilation generates an estimate of 260–270 Mt. By far, the most significant change in the annual fluxes of suspended sediment is the major decline in the estimated suspended sediment discharged from the Mississippi River Basin from about 240 to 160 Mt; substantial declines also have been noted in the Rio Grande and Colorado river basins (e.g. Dole & Stabler 1909; Curtis *et al*., 1973; Milliman & Meade, 1983; Horowitz *et al*., 2001; Meade & Moody, 2010; Horowitz, 2010; Milliman & Farnsworth, 2011).

The long-term decline in annual suspended sediment fluxes from the conterminous USA results from a number of factors. Some of that trend reflects improved sampling equipment and procedures (e.g. Edwards & Glysson, 1999). However, the majority of the estimated declines almost certainly can be ascribed to the construction of numerous dams and other engineering structures, particularly in major USA river basins (e.g. the Colorado, Missouri, Ohio, Arkansas, Rio Grande and Columbia rivers), in conjunction with the introduction of markedly improved best management practices (BMPs) intended to reduce soil erosion and loss (e.g. Milliman & Meade, 1983; Osterkamp *et al*., 1998; Syvitski, *et al*., 2005; Walling, 2006, 2008; Milliman & Farnsworth, 2011). Concomitantly, the substantial decline in sediment discharge has been matched with a similar decline in estimated specific yields. With few exceptions (e.g. especially along the Pacific coast, such as the Mad, Eel, and Hoh rivers), most coastal rivers in the conterminous USA have specific yields well below 100 t km^{-2}. The Atlantic coast has the lowest sediment discharges and specific yields; this has been ascribed to the relatively low gradients in many Atlantic coast rivers combined with sufficient vegetation (adequate rainfall) to limit the movement of eroded material off the landscape and into the rivers, as well as to dams (e.g. Curtis *et al*., 1973; Milliman & Meade, 1983; Gellis, *et al*., 2008). Declines along the other coasts mostly are attributable to the construction of dams, reservoirs, and other engineering structures emplaced during the last century (e.g. Syvitski *et al*., 2005; Walling, 2006).

Chemical concentrations and annual sediment-associated chemical fluxes

The basic premise of this study is that the chemical analyses of the <63-µm fraction of the upper 1 cm of riverbed sediment can serve as a surrogate for the average chemical composition of recent suspended sediment transiting the site. To evaluate the validity of that premise, minimum, maximum, and median suspended sediment-associated chemical concentrations measured between 1994 and 2006, as part of the revised NASQAN Program, determined from separated suspended sediment and analysed utilizing the same procedures as in this study (Horowitz *et al*., 2001), were compared with the chemical concentrations generated from the <63-µm fraction of collected coastal river bed sediment. Based on that comparison, it appears that the premise is quite valid for the majority of the trace/major elements reported herein. On the other hand, the data for TC, TIC (total inorganic carbon), TOC, TN, and TP are more ambiguous. The bed sediment values for these constituents tend to fall either just below or just within the minimum levels for suspended
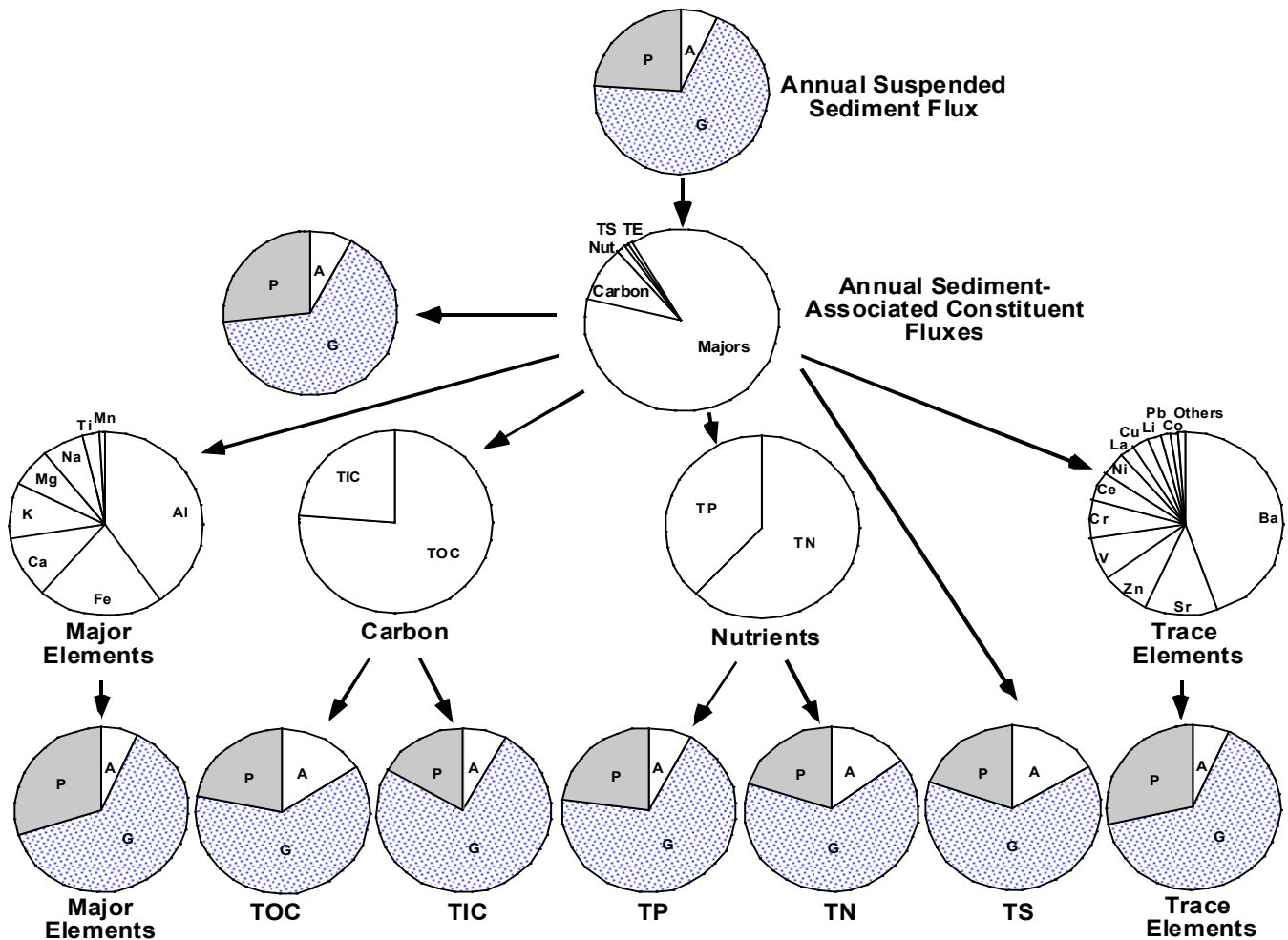
Fig. 2 Nested pie charts showing the distributions and sources of suspended sediment and sediment-associated chemical constituents discharged from the conterminous USA The coastal distribution pie charts use 'A'. 'G', and 'P' for the Atlantic, Gulf, and Pacific coasts, respectively. In the trace element distribution pie chart the term 'others' includes, in descending order of their percentage contribution to the annual fluxes of sediment-associated trace elements: As (0.7%), Sn (0.2%), Be (0.1%), Mo (0.08%), Sb (0.06%), Cd (0.04%), Se (0.04%), Ag (0.02%), and Hg (0.02%).

sediment. This difference may reflect the relatively small number of samples available for the comparison (especially for TN, and the Mississippi River Basin sites which were changed in 2007). However, the difference may also be the result of chemical/biological post-depositional processes that could reduce bed sediment-associated C and nutrient concentrations. Hence, regardless of the cause, the C and nutrient concentrations/annual fluxes determined from the <63-μm fraction of the bed sediments should be viewed as minimums.

The number of sites displaying elevated sediment-associated chemical concentrations/annual fluxes, relative to maximum baseline levels, detected during this study is substantial. This holds regardless of whether the compilation is based on the number of sites where elevated concentrations occur, or on the sum of the rankings for each constituent for each coast; albeit, the relative order is slightly different depending on the selected yardstick (Fig. 3). Based on the first criteria, the order of occurrence [expressed as a percentage of all sampling sites, (n = 132)] for constituents displaying elevated levels is: Ti(80%) > Cr(65%) = TS(65%) > Hg(59%) > Na(57%) > Al(55%) = Cu (55%) > Fe(54%) = V(54%) > Zn(53%) > Ni(49%) > Pb(47%) > Mo(42%) = TP(42%) > Ce(41%) > Co(40%) = Li(40%) > TOC(38%) > As(37%) > La(35%) > Mg(30%) > Sr(29%) > TC(27%) = Cd(27%) > Ca (23%) = Ag (23%) > Se(22%) = Sn(22%) > Mn(20%) = Ba(20%) > K(17%) > Be(16%) > Sb(11%).
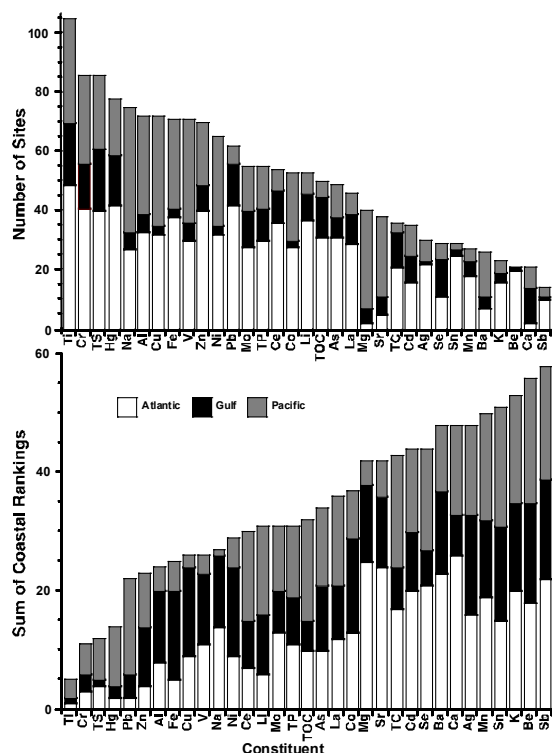
Fig. 3 Stacked bar graphs displaying the frequency of sediment-associated chemical exceedences determined during the study. The upper graph is based on the percentage of sites (n = 132) where the exceedences occurred. The lower graph is based on the sum of the relative rankings for each constituent for each coast, the lower the number, the greater the number of exceedences. An exceedence is defined as a concentration above the maximum baseline level.

The sediment-associated chemical concentrations/annual fluxes determined from the bed sediment samples display some clear geographic/demographic patterns relative to current national baseline levels (Horowitz & Stephens, 2008). Elevated concentrations occur in the reverse order of sediment discharges, with the greatest number occurring along the Atlantic coast (49%), followed by the Pacific coast (40%), and trailed by the Gulf coast (23%). In many cases, the exceedences also occur relative to chemical levels associated with national soil profiles (Shacklette & Boerngen, 1984; Gustavsson *et al.*, 2001). Not surprisingly, there are markedly fewer exceedences when the bed sediment concentrations are compared with localized soil values (e.g. Gustavsson *et al.*, 2001). Even so, almost all the elevated bed sediment-associated chemical levels fall below those reported for mean global suspended sediment-associated levels (Viers *et al.*, 2009). This tends to indicate that current water pollution/discharge regulations in the USA are having a positive effect.

The conterminous USA discharges about 48 Mt of sediment-associated chemical constituents annually: 65% from Gulf of Mexico, 27% from Pacific, and 8% from Atlantic coast rivers (Fig. 2). This represents only about 0.5 Mt more than would be supplied solely as the result of median baseline concentrations. Note that the Atlantic and Pacific rivers tend to be oversuppliers, and the Gulf rivers tend to be undersuppliers, relative to the discharge of suspended sediment (Fig. 2). This almost certainly results from the Mississippi River Basin that supplies the majority of the suspended sediment discharged from both the Gulf coast and the conterminous USA, and drains a major proportion of the latter; however, since this drainage area, in comparison with Atlantic and Pacific drainages is relatively low in population density and urbanization, the sediment-associated chemical levels/annual fluxes are also lower. Of the 48 Mt, 87% is due to major elements [Al (40%), Fe (21%), Ca (11%), K (10%), Mg (7%), Na (7%), Ti (3%), Mn (1%)], 10% is due to TC [TOC (76%); TIC (24%)], 1.3% is due to nutrients [TN (62%); TP (38%)], 0.7% is due to TS, and 0.7% is due to trace elements [Ba (44%), Sr (12%), Zn (8%), V (8%), Cr (7%), Ce (5%), Ni (4%),

La (3%), Li (3%), Cu (2%), Pb (2%), Co (1%), and others (1%, including As, Sn, Be, Mo, Sb, Cd, Se, Ag, and Hg)] (Fig. 2).

Most of the annual suspended sediment-associated chemical fluxes determined from the bed sediment samples are not proportional [Gulf (69):Pacific (24):Atlantic (7)] to the annual sediment discharges from the three coasts (Fig. 2). There are significant departures for TOC, TN and TS, with the percentage of Atlantic fluxes being nearly double those for suspended sediment. These increases are primarily at the expense of Pacific coast rivers, but also represent a lower than expected contribution from Gulf rivers. On that same basis, Pacific rivers are major contributors of Mg and Na (reflecting local petrology), whereas Gulf rivers contribute a disproportionate amount of Mn relative to Atlantic and Pacific rivers. Among the trace elements, Atlantic rivers deliver a disproportionate amount of Cu, Pb, Zn, Be, Hg and Ag, Gulf rivers deliver a disproportionate amount of As, La, Cd, Mo, Se and Sn, and Pacific rivers deliver a disproportionate amount of Cr, Cu, Ni and Hg (Fig. 2).

The proportional differences between the coastal distributions of annual suspended sediment and sediment-associated chemical fluxes are the result of the various bed sediment chemical concentrations. However, large numbers of chemical exceedences may not necessarily engender substantial increases in the annual fluxes of sediment-associated chemical constituents. For example, the greatest number of exceedences occurs along the Atlantic coast, but only produced a relatively small increase in annual sediment-associated chemical fluxes relative to annual suspended sediment fluxes (Fig. 2). This accrues because many of the elevated chemical levels occur in rivers with relatively low annual suspended sediment discharges. Hence, the overall increase in individual coastal sediment-associated chemical fluxes, despite large numbers of concentration exceedences, is small.

Elevated sediment-associated chemical concentrations/annual fluxes tend to fall into one of two categories: (1) those resulting from soil/petrologic anomalies, or (2) those from anthropogenic inputs. The current data set provides a number of examples of the effect of local petrologic/soil anomalies. For example, elevated concentrations of Cr and Ni in northern California (e.g. the San Joaquin, Sacramento, Russian, Eel and Mad rivers; Fig. 1) and southern Oregon (Klamath, Rogue and Coquille rivers; Fig. 1) appear to be due to the presence of mafic and ultramafic rocks in the foothills of the Sierra Nevada as well as in the northern Coast Ranges (e.g. Goldhaber *et al.*, 2009). These deposits may have also affected the concentrations of V, Co, Cu and Mg in the same area/samples. The elevated Hg concentration in the Russian River (Fig. 1) may well reflect the presence of upstream Hg mines. Both cases would indicate that at least some upstream material is getting through/past downstream engineering structures/reservoirs and eventually does reach the CZ. The substantial concentrations/fluxes of TOC and TN associated with southeast Atlantic and west coast Florida rivers (e.g. Edisto, Ogeechee, St Marys, St Johns, St Lucie, Myakka, Peace, Econfina, Aucilla and St Marks; Fig. 1) probably reflect the presence of numerous "blackwater"' (organic-rich) streams that originate in and/or drain local swamps and marshes. The presence of elevated quantities of organic matter may also explain the somewhat elevated Hg levels in many of these relatively rural rivers (e.g. Skyllberg *et al.*, 2000). Finally, the significant differences between TOC and TC displayed in many Florida rivers can probably be ascribed to the presence of inorganic carbonates originating from local limestone bedrock and biogenic $CaCO_3$ (e.g. Windom *et al.*, 1989).

As noted in many prior studies, elevated concentrations/fluxes associated with anthropogenic inputs typically occur in and around large urban centres either as a result of high population densities and/or urbanization, or in and around co-located industrial centres (e.g. Wong *et al.*, 2006; Horowitz & Stephens, 2008). Hence, it is not surprising that a great number of elevated concentrations occur along the northeast Atlantic coast, an area that supports numerous industrial/chemical/petrochemical plants and which also could be viewed as a 'megacity' that extends from Boston to Washington, DC [e.g. elevated concentrations of As, Cu, Pb, Hg and Zn, in the Ipswich, Charles and Neponset rivers (Boston Metropolitan area), the Housatonic, Shetucket-Thames, Hudson, Passaic and Toms rivers (New York/New Jersey Metropolitan area), and the Delaware River (Philadelphia)] (Fig. 1). The Hg level in Toms River (4.3 mg kg^{-1}) was checked multiple

times, is the highest determined during this study, and is more than 2 orders of magnitude higher than baseline. Even the Peconic River (Fig. 1) at the eastern end of Long Island (a predominantly suburban/rural area of New York), displays elevated concentrations of As, Pb, Hg and Zn. Elevated trace element levels also were found in the Miami and Los Angeles Rivers, and in Seattle/Tacoma (Green-Duwamish River); samples for these locations were collected at in-town sites (Fig. 1). Several of these same rivers also display markedly elevated concentrations of TOC, TC, TS and TN that probably result from high population densities and the associated discharge of treated solid waste/wastewater in conjunction with fertilizer applications on lawns and golf courses. Lastly, substantial industrial activity was noted, for example, around the sampling sites on the Schuylkill (Cr, Cu, Pb, Hg, Sn, and Zn), Green-Duwamish (As, Cr, Hg, Mo, Sn and Zn), and Passaic (Sb, Cr, Cu, Pb, Hg, Ag, Sn and Zn) rivers (Fig. 1).

The concentrations/distributions/annual fluxes of several sediment-associated major elements (e.g. Ca, K, Mg, Na) appear to result from local petrologic/soil levels, and generally are not elevated (e.g. Shacklette & Boerngen, 1984; Gustavsson *et al.*, 2001). Na is an exception, but most elevated concentrations occur in Pacific and northeast Atlantic rivers and probably reflect local petrology in conjunction with an underestimated baseline level since both areas were under-represented in the samples used to establish these values (Horowitz & Stephens, 2008). On the other hand, Ti, TS, Al and Fe tend to display numerous and ubiquitous exceedences. In fact, all four are among the top ten constituents displaying elevated concentrations in coastal rivers. This may accrue because all four have both natural as well as anthropogenic sources. Ti is used extensively as a paint pigment and in numerous Fe/Al alloys. It also occurs naturally as rutile and ilmenite, heavy minerals that may naturally concentrate in fluvial depositional zones. TS is associated with urban centres and elevated population densities, probably as a result of the discharge of treated solid waste/wastewater and also has major associations with elevated concentrations of TOC in many blackwater streams. Besides major industrial applications, both Fe and Al are known to form authigenic minerals in freshwater systems, particularly oxides/hydroxides, (e.g. Stumm & Morgan, 1996). Fe in particular has substantial inputs from anoxic groundwater, and almost immediately precipitates as an oxide upon contact with oxygenated surface water; occurrences are readily identifiable as red streaks along exposed river banks.

SUMMARY

1. Currently, between 260 and 270 Mt of suspended sediment are discharged annually from the conterminous USA; this amounts to approximately 2% of global levels and represents a substantial decline relative to historical values.
2. Approximately 69% of the sediment discharge comes from Gulf rivers, 24% comes from Pacific rivers, and 7% comes from Atlantic rivers.
3. With very few exceptions, specific yields from all coastal rivers are below 100 t km^{-2}; this is almost certainly the result of sediment trapping in upstream dams/reservoirs.
4. The <63-µm fraction of near-surface (upper 1 cm) bed sediments does appear to serve as a useful surrogate for the estimation of suspended sediment-associated chemical concentrations; this is particularly true for trace/major elements, but less so for nutrients and carbon.
5. Annually, the conterminous USA discharges about 48 Mt of sediment-associated chemical constituents: 64% comes from Gulf, 28% comes from Pacific, and 8% comes from Atlantic rivers.
6. Elevated sediment-associated chemical concentrations relative to current baseline levels occur in the reverse order of sediment discharges: Atlantic rivers (49%), followed by Pacific rivers (40%), and trailed by Gulf rivers (23%).
7. Almost all the elevated bed sediment-associated chemical levels detected during this study fall below those reported for average worldwide suspended sediment-associated concentrations; this may indicate that current water pollution/discharge regulations in the USA, associated with, for example, the Clean Water Act of 1972, are having a positive effect.

8. *In lieu* of an active coastal monitoring network, it still may be possible to determine trends in at least sediment-associated chemical concentrations using the approach described herein if it is repeated every 5 to 10 years.

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