Ecosystems (2014) 17: 96–111
DOI: 10.1007/s10021-013-9709-5

ECOSYSTEMS

Watershed Deforestation and Down-Estuary Transformations Alter Sources, Transport, and Export of Suspended Particles in Panamanian Mangrove Estuaries

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Abstract

We identified eight Panamanian watersheds in which conversion from wet tropical forest to pastures differed and assessed the effects of degree of deforestation, and down-estuary transformations, on the suspended particulate matter discharged from the watersheds, entering, traversing through mangrove estuaries, and emerging into coastal waters. Deforested watersheds discharged larger concentrations of suspended particulate matter, with lower % C and N, higher mineral content, and heavier isotopic signatures into fresh reaches of estuaries. Down-estuary, sediment entrainment increased non-organic content of particulates, and watershed-derived imprints of deforestation on composition of particulate matter were mostly erased by within-estuary transformations. Isotopic signatures of C, N, and S in particulate matter demonstrated strong land-sea couplings, and indicated that the direction of the coupling was asymmetrical, with terrestrial and estuarine sources delivering particulate materials to coastal waters and sediments. Mangrove estuaries therefore both act as powerful modulators of human activities on land, while also exporting particulate materials to sea.

Key words: land–sea coupling; mangrove forests; stable isotopes; coastal sediment; carbon; nitrogen; sulfur; tropical wet forest.

Received 26 June 2013; accepted 29 July 2013;
published online 5 September 2013

Electronic supplementary material: The online version of this article (doi:10.1007/s10021-013-9709-5) contains supplementary material, which is available to authorized users.

Author Contribution: IV and AG conceived the work, obtained the funding, drafted the paper, and guided all the field and analytic work; MB worked on statistical analyses and graphics; JT, CH, PM, and LC were involved in the field work and chemical analyses; MO did the mass spectrometry and elemental analysis; TS was responsible for the remote sensing work; all authors reviewed and edited the many versions of the text.

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Introduction

The widely reported deforestation of tropical watersheds (Wassenaer and others 2007; Scanlon and others 2007; Downing and others 1999) is a major agent of ecosystem change in tropical latitudes, with regional- and global-scale effects on climate (Gash and others 1996; IPCC 2007; Davin and Noblet-Ducoudre 2010), regional precipitation and water supply (Bosch and Hewlett 1982;

Vorosmarty and others 2000; Sun and others 2006; Scanlon and others 2007) and carbon sequestration (Wolf and others 2011).

Deforestation may alter discharges of water and nutrients from watersheds. Where plant biomass is lower, there is less transpiration, and lower surface area for evaporative loss (Lewis and others 1999; Lewis 2002), which favor greater water discharge. Lower biomass may also have varied effects on interception, sequestering, and transport of sediments and nutrients down hydrological gradients to receiving waters (Williams and Melack 1997; Williams and others 1997; Cleveland and others 1999; Neill and others 2001; Zhang and others 2001; Bruijnzeel 2004; Nosetto and others 2005; Li and others 2007; Bahn and others 2010).

Discharges of materials from deforested watersheds could have further consequences because tropical streams in most circumstances grade into mangrove-lined estuaries, and these ecosystems could themselves be affected. The notion of wetlands, including mangrove estuaries, as components of coastal landscapes essential in the coupling of land and sea, whereby energy-rich exports of terrestrial and estuarine materials support marine food webs has been widely argued, with diverse results from mass balance and stable isotope studies (Jennerjahn and Ittekkot 2002; Dittmar and others 2006; Kristensen and others 2008). If indeed there are mechanisms that couple terrestrial watersheds to streams and estuaries, and to coastal waters, deforestation of tropical forests could have consequences for the receiving down-gradient ecosystems.

To understand land–sea couplings and possible effects of deforestation of tropical watersheds on down-gradient mangrove estuaries and adjacent coastal waters, we investigated the fate of materials transported and transformed as they coursed through coupled land–estuary–coastal ecosystems in the Pacific coast of Panama. By initial surveys, we followed the lead of earlier papers (Martinelli and others 1999; Ralison and others 2008), and identified eight watershed-mangrove estuaries whose watersheds were subject to different degrees of land use, in our case, conversion from forest to pastures (Figure 1) by targeted artisanal-level burning, and where pastures were maintained by machete-based

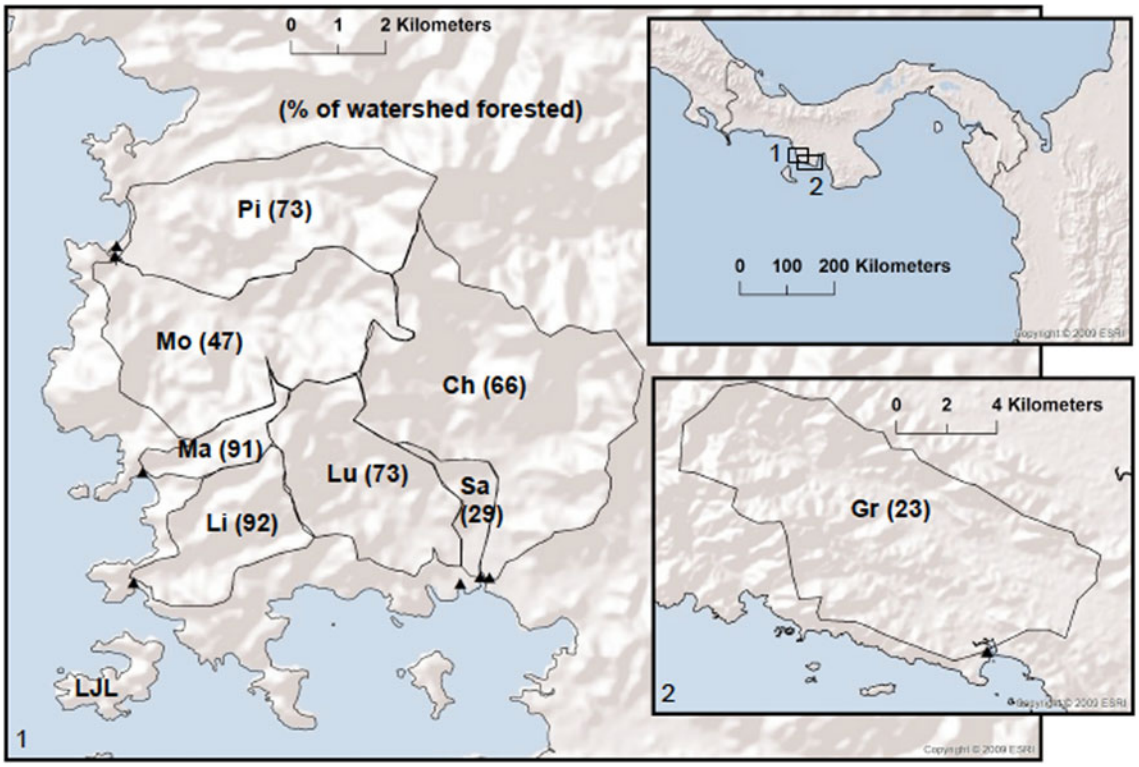


Figure 1. Distribution of the watersheds included in this study [Pi: Rio Pixvae, Mo: Rio de la Mona, Ma: Rio Manglarito, Li: Rio Limon, Lu: Rio Luis, Sa: Rio Salmonete, and Ch: Rio Chamuscado, all in *panel 1*, and Gr: Rio Grande, in *panel 2*]. The *numbers* in parentheses indicate the % of the watershed area in each watershed that was forested. Location of the study areas in the broader Panama region is shown in the inset on *top right*.

Table 1. Selected Properties of the Watershed–Stream–Estuary Systems (Rios) Included in This Study

Rio	Area (ha)	Maximum elevation (m)	Maximum length (m)	Maximum slope (%)	Mean angle (°)	% Forest cover
Pixvae	1,429	629	6,410	9.8	5.6	73
de la Mona	1,575	462	6,468	7.1	4.1	47
Manglarito	239	340	3,626	9.4	5.4	91
Limon	665	382	4,220	9.1	5.2	92
Luis	1,007	382	5,109	7.5	4.3	73
Salmonete	197	330	3,814	8.7	4.9	29
Chamuscado	2,229	599	8,229	7.3	4.2	66
Grande	9,639	662	15,109	4.4	2.5	23

Data obtained from Aster Satellite imagery acquired February 7, 2006 for Rio Grande, and from Quickbird imagery acquired April 5, 2003 for the rest of the Rios. Data on area and % forest cover, plus additional data on land covers, appeared in Valiela and others (2012, 2013). Tide range in all these rios averages 4 m, and owing to the steep topography, freshwater residence times within the rios is about a day; depths within the rios vary with location and tide state, over a range of less than 1 to less than 10 m., and depth increases sharply seaward of the estuary mouth.

removal of invasive or re-growing woody plants. These eight watershed–estuary systems constituted a landscape-level experimental setting in which we could assess consequences of different degrees of terrestrial watershed deforestation on land–sea coupling. Further details of land covers and deforestation were included in Valiela and others (2012, 2013, and in press) and additional features of the watersheds are added in Table 1.

Previous studies on the Pacific coast of Panama revealed that inter-annual increases in rainfall associated with La Niña severely altered salinity regimes (Valiela and others 2012), and altered fate and transport of dissolved nutrients. Nutrient retention within-watersheds was high, and forested watersheds discharged larger concentrations of dissolved inorganic nitrogen to streams than pasture-dominated watersheds. The imprint conferred by degree of deforestation on export of dissolved materials exported was detectable in fresh reaches of the streams, but was erased by active down-estuary biogeochemical transformations (Valiela and others 2013). In spite of the substantial transformations, and net interception within watersheds and estuaries, the export of dissolved nutrients to adjacent coastal sea from mangrove estuaries was still significant because of the extremely nutrient depauperate condition of the coastal waters of the region.

In this paper, we focus on particulate materials in transit from the watersheds to the streams and down the estuarine gradient to sea. The fate of particulates is of interest because deforestation of some watersheds increased downstream transport of suspended particulate matter (Martinelli and others 1999; Houser and others 2006) by erosion of soils, stream banks, stream beds, and transport of plant matter, and hence could increase consequent transport of particles out of watersheds and out to sea (Maréchal and others 2009). To evaluate effects of deforestation, we compared measurements taken from the eight Panamanian stream–estuary systems whose watersheds suffered different degrees of deforestation. We report concentrations, fates, and export of particulates in water, and assess sources and transformations by measuring concentration, % nitrogen, % carbon, and stable isotopic signatures of suspended material. To document down-estuary changes we sampled the water column of each stream–estuary along the entire range from fresh to seawater within estuaries and beyond the mouth of the estuaries. To capture possible inter-annual or seasonal variation, we repeated the sampling at the end of the dry and wet seasons, during 2009–2012.

Methods

Study Sites

The watershed-estuaries included in this study (Figure 1) are located in the Veraguas Province of Panama, and discharge into the Pacific Ocean. We selected the eight coupled watershed–estuary systems (*rios*) because they offered a range of conversions from forest to pasture land covers, with forest cover ranging from 23 to 92%. Terrain on the watersheds was generally steep, and largely first order streams carried mostly baseline freshwater discharge (with surface runoff after large rainfall events) down-gradient through mangrove estuaries, and eventually to the Pacific. Details of geological setting, precipitation, and other information were provided in Valiela and others (2012, 2013). Some of that information, plus added details, is summarized in Table 1.

Water Sampling

To determine concentrations of suspended particulate matter (SPM) in water that just exited watersheds and entered freshwater streams, moved through estuaries and out to sea, we sampled water during ebbing tides at six stations spaced between the fresh reaches and the mouth of each of the eight estuaries. This set of stations captured the fresh to seawater salinity gradient within each estuary (Valiela and others 2012). During each sampling trip, location of stations 1–6 was adjusted to make sure the sampling captured the changing gradient from freshwater to full salinity and nutrients. The gradient shifted location owing to differences in tidal state and stream flows from one sampling trip to the next. Locations of the many sampling stations in each of the *rios* are indicated in Figures SI2–SI9 in supplementary information.

Within-estuary sampling was done at one depth because during ebb tides water columns were mostly shallow (<1.5 m) and well mixed vertically. Some vertical stratification was present, but was spatially highly variable because of un-even bathymetry, fast down-gradient flow, and a large tidal excursion (well over 4 m for most tides). To assess what happened to the SPM once estuarine water emerged off the estuaries, we followed the ebb plume in each estuary and sampled at three distances away from the estuary discharge (stations 7–9), which, very roughly, were located about 50, 100, and 300 m off each estuary mouth.

The within- and outside-estuary sampling in stations 1–9 was repeated during periods of 3 weeks each during March 2009, December 2009, March 2010, December 2010, April 2011, and January 2012. This sampling schedule insured data were collected during the end of dry season (generally January–April) and the end of the wet season (generally May–December), across a span of 4 years.

Water Quality and SPM Measurements

Methods and results regarding nutrient concentrations in the samples collected were discussed in Valiela and others (2013). Salinity, oxygen, and temperature were measured in all stations with an YSI 85-10 unit. Water samples to measure SPM and chlorophyll were collected in 20 l carboys and kept cool during transportation to the lab. Water was first passed through a 210-μm mesh to remove zooplankton that would have compromised stable isotope measurements of SPM. SPM samples were then obtained by filtering 0.5–1.5 L of water through pre-ashed and pre-weighed 0.7 mm GF/F filters. Filters were rinsed, dried in a drying oven for 2 days at 60°C and then reweighed. SPM concentrations (in mg l^{-1}) were calculated as (final filter weight-original filter weight)/volume of water filtered. What we refer to as suspended particulate matter or SPM here can also be thought of as seston of less than 210 μm in diameter.

To measure chlorophyll *a* we filtered water through a 47-mm GF/F filter until clogged using a vacuum pump. The volumes varied between 0.8 and 3 l. The filters were then frozen until we were ready for analysis. In our Woods Hole laboratories, the filters were thawed and sonicated in 90% buffered acetone to lyse the cells, and chlorophyll was measured after 12 h of incubation, on a Turner Designs 10AU fluorometer for fluorescence before and after acidification. Chlorophyll *a* concentrations were calculated as

$$\text{chl}a = F_i(r/(r-1))(R_{\text{b-sam}} - R_{\text{a-sam}})\left(V_{\text{acetone}}/V_{\text{sample}}\right),$$

where F_i is the slope of the calibration curve, $R_{\text{b-sam}}$ is the reading of the sample before being acidified, $R_{\text{a-sam}}$ is the reading of the sample after being acidified, r is the ratio of the fluorescence values of a pure chl *a* solution/acidified pure chl *a* solution, V_{acetone} is the volume of the extract (ml), V_{sample} is the volume of water filtered (ml).

Isotopic and Elemental Analysis

N, C, and S stable isotope and elemental analyses of SPM were performed by mass spectrometry at The Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA. Solid samples were analyzed for δ^{15}N, δ^{13}C, and δ^{34}S using an Europa 20-20 continuous-flow isotope ratio mass spectrometer interfaced with an Europa ANCA-SL elemental analyzer. The analytical precision, based on replicate analyses of isotopically homogeneous NIST Standard reference materials, was ± 0.1 ‰ for δ^{15}N and δ^{13}C measurements, ±0.3‰ for δ^{34}S, and about ±1% for %N, %C, and %S measurements. Stable isotope ratios were reported as per mil (‰) using delta notation determined as

$$\delta^{15}\text{N},\ \delta^{13}\text{C, or } \delta^{34}\text{S } (‰) = \left[\left(R_{\text{sample}} - R_{\text{standard}}\right)/R_{\text{standard}}\right] \times 10^3,$$

where R was ^{15}N/^{14}N, ^{13}C/^{12}C, or ^{34}S/^{32}S. To aid interpretation of sources, composition, and transport of SPM, we determined N, C, and S contents of SPM samples analyzed for isotopic signatures. To constrain costs of isotopic and elemental analysis

for sulfur, a subset of samples of SPM, collected during 2009 and 2010, were selected for analysis. These were randomly chosen from the larger set of samples of SPM, from estuaries within the entire range of % forest cover on their watershed.

To compare the isotopic signatures of SPM to those of the various potential sources of suspended materials, we first collected surface sediments within each estuary by taking 1-cm deep, 5-cm diameter cores in the stations down-estuary, and measured stable isotope and elemental contents as in the case of SPM samples. Second, we also sampled large particulate organic matter (POM) being transported down-estuary by installing a 30-cm diameter plankton net near the mouth of estuaries during ebbing tide. Third, to compare SPM values to those of mangrove trees, we used stable isotopic ratios and elemental values in mangrove tree leaves sampled within the same estuaries, reported in Valiela and others (in press). Fourth, we also reviewed published data on tropical terrestrial trees, soils, and coastal sediments as additional comparisons.

Statistical Analyses

SPM concentrations measured during our samplings varied substantially. In this paper we highlight effects of degree of watershed deforestation and down-estuary gradients, and what took place within the mangrove estuaries, and outside the estuaries. We acknowledge that variation in amount and quality of SPM can be influenced by inter-annual, seasonal, tidal elevation, meteorological differences, as well as watershed differences in topography, soils, and vegetation. We did not try to partition and evaluate all sources of variation, but instead focused on assessing whether the effects of watershed deforestation and estuarine gradient—scaled by salinity—were robust enough to emerge through the large variation in SPM concentrations in samples collected within estuaries or outside estuaries.

Comparisons of the eight different estuaries, sampled on five different dates, and with nine stations located from the fresh to marine salinity ranges proved rather cumbersome. To make comparisons practical and more accessible, we stratified the eight watershed–estuaries into three groups, representing high (91–92%, Limon and Manglarito, Figure 1), intermediate (47–76%, Chamuscado, Luis, de la Mona, and Pixvae, Figure 1), and low (23–29%, Grande and Salmonete, Figure 1) forest cover on the surface of contributing watersheds (see also Table 1).

We applied two types of analysis. To first document the link of SPM to both forest cover and salinity down-estuary, while simultaneously showing the entire data sets, we regressed SPM variables versus salinity for each of the three forest cover groups, and then compared the regressions among the forest groups, by either ANCOVA or, where slopes differed, by an equivalent procedure involving t tests of intercepts and slopes among regression equations. These analyses were separately applied to measurements taken within estuaries, and outside estuaries. Second, to then partition the effects of forest cover, salinity, and sampling trip (which included seasonal and inter-annual variation), and test their significance versus the residual from remaining sources of variation, we used a random factor three-way ANOVA with unequal replication. We used a random factors model because initial examination showed that high residual variation made effects of nested structure of sampling and repeated measures undetectable. Statistical analyses were run in R software.

Below we first document the down-estuary course of SPM concentrations and assess the effect of watershed deforestation. Then, we sort out some of the components that made up the SPM that we measured, and end with a consideration of the sources, connections, and transport of particulate materials in these coupled adjoined watershed–stream–mangrove estuary–coastal water ecosystems.

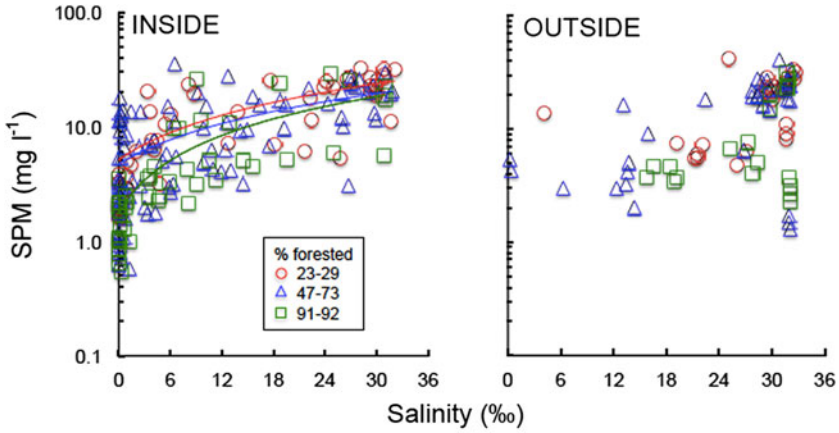
Results and Discussion

Effects of Deforestation and Down-Estuary Gradients on Amount of SPM

Within-Estuary Effects

In spite of substantial variability in concentration of SPM measured within estuaries, water emerging from deforested watersheds contained significantly larger concentrations of SPM compared to water derived from watersheds with greater forest cover (Figure 2). The contrasts were evident in regressions of SPM and down-estuary salinity, which revealed three significant features (Figure 2 left):

(1) water emerging from deforested watersheds had higher concentrations of particles to fresh reaches of receiving estuaries: concentrations of SPM delivered to fresh reaches of the estuaries (evaluated as the intercept of the regressions, where salinity = 0) were three times larger in watersheds with greater conversion to



% forested	x̄±se	equation	F
23-29	14.9±1.4	y=0.609x+5.335	66**a
47-73	9.2±0.8	y=0.497x+4.577	67**a
91-92	6.2±1.1	y=0.549x+1.767	50**b

% forested	x̄±se
23-29	18±2.2
47-73	16.3±1.7
91-92	10.5±1.9

Figure 2. Concentrations of suspended particulate matter in water samples collected inside and outside estuaries draining watersheds shown in Figure 1, plotted versus the salinity of the water. Data from the estuaries pooled into groups with 23–29, 47–73, and 91–92% forest cover on contributing watersheds. *Box* below left panel shows statistics for samples collected within estuaries; **: highly significant regressions; regressions followed by different letter (**a** or **b**) differed significantly from each other. *Box* below right panel shows mean ± S.E. only; there were no significant regressions in samples collected outside estuaries.

pastures (5.3 mg l^{-1}) than in more forested watersheds (1.8 mg l^{-1});

(2) there was net entrainment of particles as water moved down-estuary: SPM concentrations increased downstream, from fresh reaches to estuary mouth, by more than one order of magnitude (Figure 2 left); and

(3) larger concentrations of SPM were present and transported within estuaries with deforested watersheds: mean concentrations of SPM within estuaries with deforested watersheds were more than twice the amount found in estuaries draining well-forested watersheds (Figure 2 left).

Partition of sources of variation by ANOVA confirmed the above results: watershed forest cover, salinity, and ''sampling time'' (a variable that included seasonal and inter-annual variation) all significantly influenced SPM (Table 2). Sampling time interacted significantly with both forest cover and salinity (Table 2). Slopes of forest cover group versus salinity relationships (Figure 2 left) did not differ, justifying application of ANCOVA to that analysis. The significant ''sampling time'' effect points to major seasonal and inter-annual contrasts. We have reported on rainfall effects (Valiela and others 2012), but initial examination of per sampling time effects on SPM did not reveal discernible patterns readily assignable to specific weather or seasonal conditions, so here we simply concluded that variation across time was notable but was, for present purposes, separable from the effects of forest cover and salinity, the focus of this analysis.

The amounts of SPM we report from samples taken within the Panama estuaries fell within a lower range compared to reports from other tropical coastal environments (Table 3) and compared to European temperate latitude estuaries [1–1,000 mg SPM l^{-1}, from Middelburg and Herman (2007)]. SPM in tropical estuaries seems to be extremely variable (Table 3). In general, water transparency in the Panama estuaries we studied was high, and the estuary floor was almost always visible during the occasions we sampled. We note, however, that our sampling did not extend through the entire rain season, so we probably missed short-term higher discharge events, when turbidity was likely much higher.

Outside-Estuary Effects

Samples of SPM from water collected in stations off the mouth of the estuaries were also variable (Figure 2 top right). Mean SPM concentrations sampled outside estuaries were similar to the bulk of the data obtained in within-estuary samples of high salinity (Figure 2 left). In spite of the variation, the mean SPM for samples outside the estu-

Table 2. Three-way, Random Factor Analysis of Variance with Unequal Replication, for Within-estuary SPM Data of Figure 1 (left), Done with R

Source of variation	Degrees of freedom	Mean squares	*F*
For weight of SPM			
Sampling time	4	2666.5	120.3***
Forest cover	2	925.9	41.8***
Salinity	2	2409.0	108.7***
Sampling time × forest cover	8	147.8	6.7***
Sampling time × salinity	8	220.8	10.0***
Forest cover × salinity	4	31.5	1.4 ns
Sampling time × forest cover × salinity	13	31.4	1.4 ns
Residual	229	22.2	
For % carbon			
Forest cover	2	46.70	4.708*
Salinity	2	39.00	3.932*
Sampling time	1	0.29	0.030 ns
Forest cover × Salinity	4	9.40	0.947 ns
Forest cover × Sampling time	2	3.41	0.343 ns
Salinity × Sampling time	1	0.00	0.000 ns
Residual	19	9.92	
For % nitrogen			
Forest cover	2	0.6281	4.252*
Salinity	2	0.4515	3.057 ns
Sampling time	1	0.0017	0.011 ns
Forest cover × Salinity	4	0.1178	0.798 ns
Forest cover × Sampling time	2	0.0135	0.091 ns
Salinity × Sampling time	1	0.0001	0.001 ns
Residual	19	0.1477	
For chlorophyll *a*			
Forest cover	2	3.659	10.541***
Salinity	2	18.691	53.847***
Sampling time	4	5.133	14.787***
Forest cover × salinity	4	0.649	1.870 ns
Forest cover × sampling time	8	0.651	1.876 ns
Salinity × sampling time	7	1.026	2.955**
Forest cover × salinity × sampling time	10	0.482	1.387 ns
Residual	153	0.347	

*''Sampling time'' variable included sampling trips during 2009–2011, and wet and dry seasons. ''Forest cover'' refers to land covers on contributing watersheds (Table 1; Figure 1). ''Salinity'' is a proxy for down-estuary gradient. Comparisons of P level at, or < 0.001 are shown as ***, at, or <0.01 are shown as **, and at, or <0.05 are shown as *, not significant shown as n.s*

aries still retained a trace of effect of watershed deforestation, with larger SPM values associated with discharges from estuaries with deforested watersheds (Figure 2 right). Most samples of SPM collected outside the estuaries resembled values recorded at high salinities inside the estuaries, with some notable exceptions. Samples with salinity lower than 22 were from a December 2010 sampling that followed unusually high wet season rainfall that substantially freshened and diluted concentrations (Valiela and others 2012). Some samples collected outside the estuaries showed lower SPM, probably a measure of particle sinking toward the sea floor after the water mass emerged from the estuaries. Below, we will return to this likely directional flux from estuaries to coastal sediments. SPM measured outside the Panama estuaries fell within the lower range of values measured elsewhere in the tropics (Table 3).

Effects on composition of SPM

To evaluate the effect of deforestation and down-estuary transport on organic and inorganic composition of SPM, we plotted carbon, nitrogen, mineral content, and chlorophyll of SPM versus the % of the watershed that was deforested, for samples collected within salinity ranges of less than 5, 5–25, and greater than 25 inside the estuaries (Figure 3).

Table 3. Comparison of Suspended Particulate Matter (SPM) Measured Within and Outside Different Tropical Estuaries

Locality	SPM (mg l^{-1})		Source
	Within estuaries	Outside estuaries	
Papua-New Guinea	23–775	6–42	Robertson and others (1993)
Mexico	60–260	–	Rivera-Monroy and others (1995)
Ecuador	42–696	50–100	Cifuentes and others (1996)
Kenya	24.5–3,179	3–1,512	Kitheka and others (2005)
Australia	12.3–97.7	–	Smith and others (2012)
Panama	0.5–40	1–50	This study

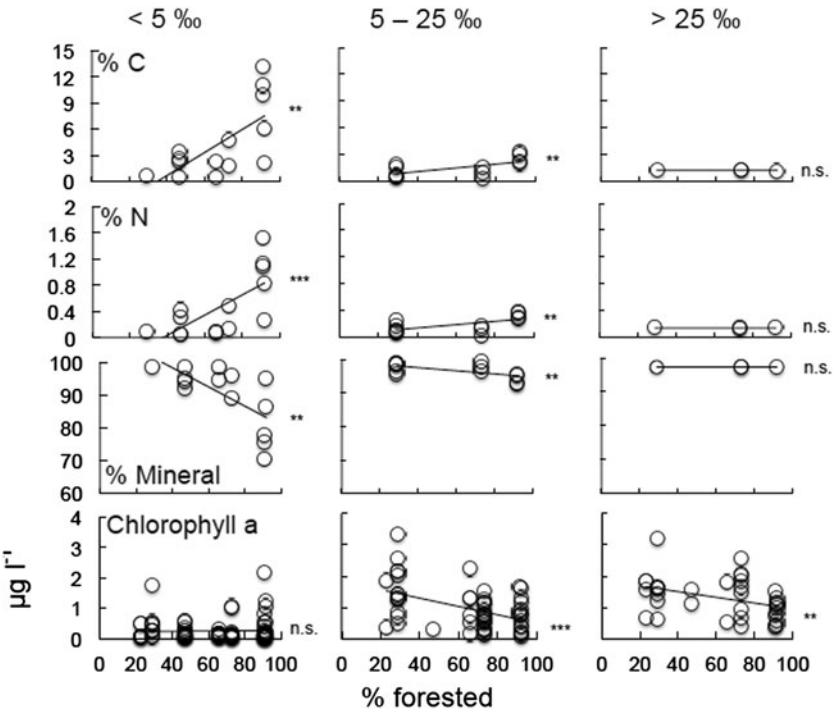


Figure 3. Rows: % carbon, nitrogen, and mineral content, and chlorophyll concentrations in suspended particulate matter in water samples collected inside estuaries. All variables plotted versus the % of the watershed area covered by forests. *Columns* data for each row variable, stratified into salinity groups (<5, 5–25, and >25‰) to show down-estuary transitions.

Carbon Content of SPM

Deforestation on the contributing watersheds significantly lowered the carbon content of SPM derived from watersheds (Figure 3, top panels; Table 1). % C in SPM discharged from watersheds with 91–92% forest cover into fresh reaches of receiving estuaries was more than seven times larger than in SPM discharged from watersheds with forest covers of 23–29% (Figure 3; and regression intercepts in Table 2).

The forest cover imprint on % C diminished down-estuary (Figure 3; Table 2, compare slopes of the regressions). By the time salinity in the estuary water column exceeded 25, %C in SPM in all estuaries converged to about 1% C, regardless of the forest cover on the contributing watershed (Figure 3).

These results suggest that, first, the lability of organic matter in SPM, as well as the amounts of SPM, likely diminished with deforestation. Second, the watershed imprints conveyed by degree of forest cover were erased during down-estuary transit of the particulate materials.

Nitrogen Content and C/N of SPM

The %N in SPM collected within fresh reaches depended on forest cover on the contributing watershed (Table 1). %N was significantly higher in SPM released into fresh reaches from the most forested watersheds (Figure 3, second row of panels, and note >6-fold difference in intercepts in Table 2). The imprint of forest cover, however, was soon erased during transit down-estuary, and %N

in SPM converged toward lower values characteristic of the most deforested watersheds.

C/N values within SPM were relatively unchanging in these estuaries, remaining near about 10 throughout the salinity gradient to sea. A ratio of 10 is fairly N-rich, compared to the 17 most suitable to support heterotrophic animal activity (Valiela 1995, p. 208) so that, whatever the amount of SPM exported from the estuaries, these exports were likely to subsidize consumers in receiving coastal food webs. The range of C/N values we recorded in Panama SPM are within those reported for inside and emerging from other tropical estuaries [3.3–22, Robertson and others (1993); 7.3–9.3, Gonneea and others (2004); 13–14.2, Prasad and Ramanathan (2009)]

Mineral Content of SPM

SPM emerging from deforested watersheds held much larger fractions of mineral matter than SPM from forested watersheds. To assess mineral content of SPM, we used our measurements of the % carbon data of SPM, assumed that, on average, carbon made up 45% of organic matter, and calculated the % organic content for each sample of SPM, and then, by difference, obtained the % mineral content as the remainder of SPM weights. Seventy to 99% of SPM was mineral matter, with the lower values only found in fresh reaches of streams receiving inputs from well-forested watersheds (Figure 3; Table 2, note 12-fold difference in intercepts with zero salinity).

Mineral content of SPM increased during down-estuary transit, from 70 to 98% in fresh reaches, to 94–98% at intermediate salinities, to 98–99% mineral content at full salinity (Figure 3). This trend may be the joint effect of degradation of labile organic matter derived from forested watersheds plus entrainment of sediment during transit down-estuary.

Chlorophyll in SPM

Chlorophyll concentrations were low in the fresher reaches of the estuaries, most likely because groundwater seeping into streams obviously lacks chlorophyll, and these fast-flowing streams allowed too short a time for much cell division (Figure 3 bottom row of panels). Concentrations increased somewhat down-estuary, with an indication that there was more growth of cells within water columns of estuaries with less-forested watersheds (Figure 3, note significant slopes in saltier reaches of the estuaries). This response may be a result of greater light availability in streams where the riparian forest canopy is less dense. The response does not seem related to nutrient supply, because in waters with salinity greater than 5, available N/P in water varied, but averaged around 16:1, the critical Redfield ratio (Valiela and others 2013). Deegan and others (2011) argued that light may play a similar role affecting algal nitrogen uptake and use in Amazonian streams surrounded by pasture dominated vegetation. An additional feature to note in the Panama data was the contrast in mean chlorophyll concentrations emerging into coastal waters from the estuaries with different forest cover on contributing watersheds (Table 3): larger amounts of chlorophyll were associated with passage through estuaries with more deforested watersheds (Table 3). The concentrations of chlorophyll emerging from the mouth of the estuaries (in water with higher salinity) were modest (Figure 3 bottom row), but similar to the lower range that others found elsewhere in the tropics (Robertson and others 1993; Bouillon and others 2007; Ralison and others 2008). Nevertheless, the exports of chlorophyll constituted a significant addition of cells to the receiving coastal water column, because concentrations of chlorophyll leaving the estuaries were higher than chlorophyll concentrations measured in surface water 1–6 km off estuary mouths (Table 3). Robertson and others (1993) found similar contrasts, with 0.3–5.1 μg chlorophyll l^{-1} measured within estuaries, and only 0.3–0.7 μg chlorophyll l^{-1} outside estuaries. Deforested watersheds therefore made greater contributions of chlorophyll-bearing cells that could then either grow or were consumed in near-shore food webs. Deforestation increased land-to-sea connectivity and subsidies furnished by terrestrial to marine ecosystems.

To approximate the contribution of chlorophyll to total SPM mass, we used a mean ratio of cell weight to chlorophyll of 70 (calculated from data in MacIntyre and others 2002; Li and others 2010; Xiu and Chai 2012; Wang and others 2013; Harrison and others 1997). The calculated mass of phytoplankton ranged 0.07–0.56 mg chlorophyll l^{-1}, expressed as % of SPM mass (which we estimated as 1–30% organic matter, estimated from %C/0.45, Figure 3). The contribution of chlorophyll was therefore quite small compared to the mass of SPM (0.7–40 mg SPM l^{-1}, from Figure 2). Chlorophyll therefore ranges between 0.014 and 0.1% of the SPM. The minor contribution of chlorophyll to tropical estuarine SPM was also found by Robertson and others (1993), Machás and Santos (1999), and Bouillon and others (2007) (Table 4).

Table 4. Chlorophyll Concentrations in Water Samples with Salinity above 27‰, in Sites Within and Outside Estuaries and at 1–3-km Away from Mouth of Estuaries

Samples collected from	% Forest cover on watershed		
	23–29	47–73	91–92
Inside estuaries (stations 1–6)	1.67 ± 0.23	1.46 ± 0.21	0.9 ± 0.13
Outside estuaries (stations 7–8)	1.68 ± 0.17	1.04 ± 0.09	0.7 ± 0.07
Offshore (1–3 km from mouth of estuaries)	0.56 ± 0.04		

Chlorophyll concentrations (μg l^{-1}) in samples of water with salinity >27‰, collected inside (stations 1–6, see methods) and outside estuary mouths (stations 7–9) in estuaries whose watersheds had three different % forest cover, and in samples collected 1–3 km off the estuary mouths (Valiela and others 2012).

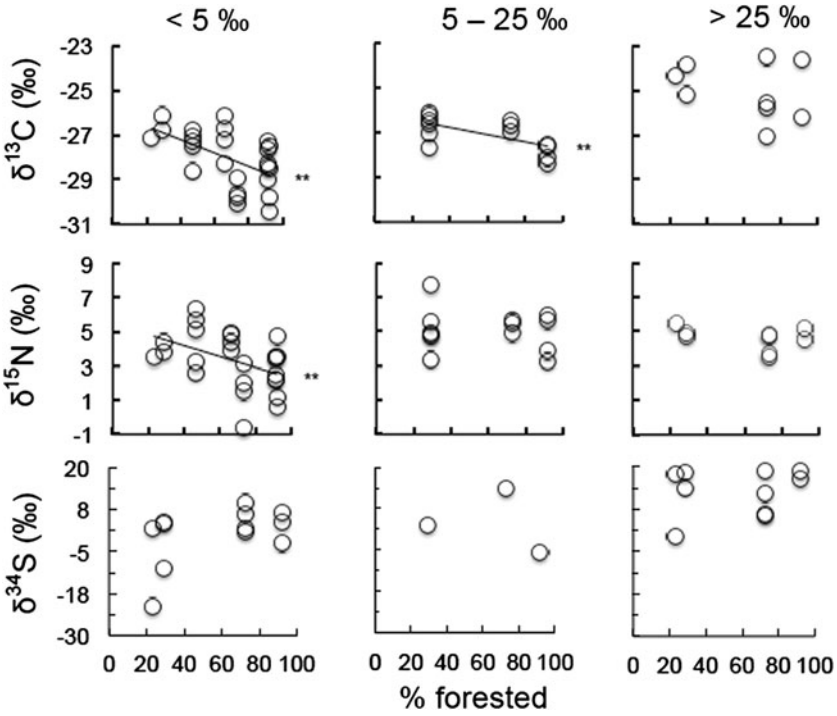


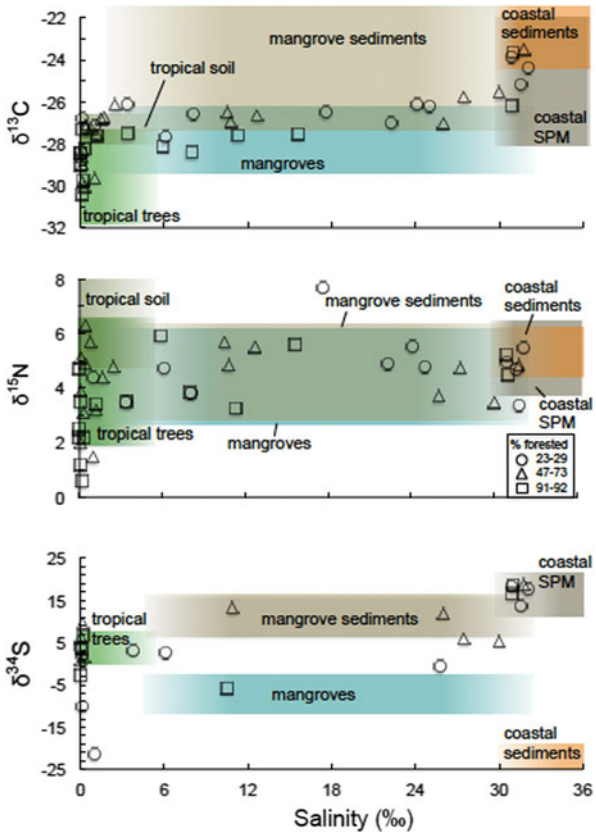
Figure 4. Carbon, nitrogen, and sulfur stable isotope values of suspended particulate matter collected inside estuaries, stratified into three salinity groups (<5, 5–25, and >25‰) to show down-estuary transitions.

Terrestrial and Estuarine Influences on Stable Isotope Values of SPM

Isotopic Comparisons Within Panama Estuaries

To confirm effects of deforestation of land cover, and of down-estuary transformations on SPM, we plotted δ^{13}C, δ^{15}N, and δ^{34}S of SPM versus the % forest cover on the watersheds, for samples collected within salinities below 5, 5–25, and above 25 (Figure 4). δ^{13}C of SPM were significantly enriched in fresher and intermediate reaches of estuaries receiving inputs from more deforested watersheds, compared to SPM sampled from estuaries with more forested watersheds (Figure 4). The terrestrial land cover imprint on δ^{13}C of SPM was erased down-estuary, and in saltier reaches of estuaries, values of δ^{13}C became enriched. δ^{15}N of SPM were also enriched in fresher reaches of estuaries receiving inputs from deforested watersheds (Figure 4). As in the case of δ^{13}C, terrestrial imprint was lost in intermediate and salty reaches. Nitrogen isotopic signatures were variable and remained between 3 and 7 though transit to the sea. δ^{34}S of SPM varied, with no evidence of effect of watershed forest cover, but a suggestion of substantial enrichment down-estuary (Figure 4).

To discern possible sources and processes generating the trends of Figure 4, we tried two approaches. First, we plotted isotopic signatures of SPM versus signatures of likely source materials (mangrove sediment, mangrove leaves, and large particulate matter) (Figure SI 1). Within the Panama estuaries, δ^{13}C of SPM were similar to those of mangrove estuary sediments, were heavier than those of mangrove leaves, and lighter than those of large particulate matter (POM) (Figure SI 1). Iso-



◀**Figure 5.** Carbon, nitrogen, and sulfur stable isotope values of suspended particulate matter (samples from all stations), plotted versus salinity to reveal the down- and outside-estuary spatial gradients. The *shaded bars* show the ranges of values for different potential sources of the SPM; degree of *shading* indicates likely position of source contribution along the gradient from fresh to coastal waters. The ranges of isotopic values for the various sources obtained from our own and published data: *for tropical tree leaves*: Cordell and Sandquist 2008, Courty and others 2011, Domingues and others 2007, Jennerjahn and others 2004, Martinelli and others 1998, Martinelli and others 1999, Muzuka 1999, Nardoto and others 2008, Norstrom and others 2012, Ometto and others 2006, Pessenda and others 2004, Peterson and Howarth 1987, Szpak and others 2013, Tamooh and others 2012; *for tropical soils*: Bouillon and others 2007, Desjardins and others 2006, Gao and others 2012, Nardoto and others 2008, Ometto and others 2006, Alkhatib and others 2007, Alongi and others 1989, Bouillon and others 2002, Bouillon and others 2008, Gonneea and others 2004, Loneragan and others 1997, Okada and Sadaki 1998, Prasad and Ramanathan 2009, Ralison and others 2008, Tue and others 2012, Wooller and others 2004; *for mangrove sediments*: Alkhatib and others 2007, Alongi and others 1989, Alongi and others 2004, Bouillon and others 2002, Bouillon and others 2007, Canfield and others 1998, Gao and others 2012, Jennerjahn and Ittekkot 2002, Jennerjahn and others 2004, Ku and others 1999, Loneragan and others 1997, Norstrom and others 2012, Pereira and others 2010, Pessenda and others 2004, Pessenda and others 2012 (only recent samples), Prasad and Ramanathan 2009, Ralison and others 2008, Ranjan and others 2011, Tamooh and others 2012, Tue and others 2012a; *for coastal SPM*: Alkhatib and others 2007, Bouillon and others 2002, Bouillon and others 2007, Bouillon and others 2008, Bouillon and others 2007a, Cifuentes and others 1996, Dunn and others 2008, Gonneea and others 2004, Jennerjahn and others 2004, Kitheka and others 2005, Loneragan and others 1997, Martinelli and others 1999, Martinelli and others 2012, Maya and others 2011, Miranda and others 2009, Prasad and Ramanathan 2009, Ralison and others 2008, Robertson and others 1993, Tamooh and others 2012, Tue and others 2012a; *for coastal sediments*: Alkhatib and others 2007, Alongi and others 1989, Barros and others 2010, Baumgart and others 2010, Bouillon and others 2002, Boning and others 2004, Bruchert and Pratt 1999, Canfield and others 1998, Dunn and others 2008, Gao and others 2012, Harji and others 2010, Jennerjahn and Ittekkot 2002, Jennerjahn and others 2004, Mazumdar and others 2012, Miranda and others 2009, Muzuka 1999, Norstrom and others 2012, Pereira and others 2010, Peterson and Howarth 1987, Prasad and Ramanathan 2009, Ralison and others 2008, Robinson and others 2012, Sampaio and others 2010, Strauss and others 2012, Tamooh and others 2012, Tue and others 2012a, Wijsman and others 2001, Zhu and others 2013.

topic C signatures of SPM therefore could readily have originated from erosion of sediments [which may make up 70–100% of SPM (Figure 3)], plus a mix of leaf and other plant fragments [leaves tend to have lighter carbon signatures than woody parts (Martinelli and others 1998; Ometto and others 2006; Nardoto and others 2008)]. δ^{15}N of SPM were heavier than those of sediment and mangroves, and generally lighter than those of POM (Figure SI). These results imply that SPM contained nitrogen remaining after some microbial reworking had preferentially removed the lighter isotope of N during transit in the water column.

Second, to make more evident the spatial distribution of the potential sources of SPM, and its fate during transit through and out of estuaries, we plotted the stable isotopic signatures of C, N, and S in SPM versus salinity, and added, for comparison, the ranges in isotopic values, culled from the literature and our own data, for a variety of potential sources (Figure 5). This depiction shows changes during down-estuary trajectories, compares the effects of deforestation, and shows possible links of signatures in SPM to potential sources.

Judging from δ^{13}C values, the SPM that entered the fresh reaches of the streams were a mix of

material derived from terrestrial vegetation and soils. $\delta^{13}C$ values of SPM, regardless of the degree of forest cover on the corresponding watersheds, resembled signatures characteristic of tropical trees and tropical soils. We could have expected some influence of C4 grasses growing on the pastures, but such sources were not in evidence in SPM collected at the fresh reaches of the estuaries (Figure 5). Even in watersheds with only 23% forest cover, the effect of the C4 grasses did not dominate, a result also found by Deegan and others (2011). Whatever trend to heavier carbon isotope signatures may be present, we could not attribute the shift entirely to C4 grasses, as there were algae and C3 aquatic plants present in the fresh reaches that might have contributed carbon.

Figure 5 includes tropical soil data from sites supporting largely C3 vegetation, even though vegetative covers in certain of our watersheds likely held an undetermined portion of C4 plants. Pasture and forest soils are isotopically distinguishable within certain specific inland sites (Bernoux and others 1998; Yonekura and others 2012), but the sorting out of C3 and C4 carbon in watersheds with wet tropical soils is complicated by a number of issues (Powers and Veldcamp (2005). Soils mostly developed under long-term forest cover, carbon added by forest and grassland sources decay and survive at different rates, and tropical pastures often are a combination of C4 and C3 grasses. In addition, in many tropical pastures there are often remnant C3 trees left within or near pastures. Moreover, there is often a riparian edge in many tropical streams, populated with C3 plants, where interception of particulate materials from pastures inland might take place. Because of these complications, it is not surprising to not find a clear-cut C4 imprint in our isotopic data for particulate materials entering fresh reaches of estuaries, and so we did not include data from C4 pasture soils in Figure 5.

The link of stream SPM and tropical trees was rapidly lost as salinity increased (Figure 5 top). The erasure of the terrestrial imprint seemed likely to be a result of the order-of-magnitude increase in total SPM as salinities increased, visible in Figure 2, where the added material, contributed by a mix of mangrove sediment and mangrove biomass, overwhelmed the terrestrial signatures. The dominance of mangrove material extended through the salinity gradient. At higher salinities near the mouth of the estuaries and beyond, $\delta^{13}C$ of SPM became further enriched (and resembled what the literature reports as coastal SPM in many coastal systems). Finally, the $\delta^{13}C$ of some of the SPM in the saltiest part of the gradient matched the $\delta^{13}C$ reported for coastal sediments. The pattern therefore seems to be that terrestrial inputs to upper reaches of streams were distinctive in the relatively clear waters of fresh reaches, but were overwhelmed by larger amounts of particles derived from the mangrove estuary as water became saltier. Once SPM left the estuaries, additional enrichment took place, and carbon signatures of SPM then shifted to levels near those of coastal surface sediments.

The pattern for $\delta^{15}N$ of SPM seemed similar to that of $\delta^{13}C$, but somewhat more variable and less marked (Figure 5 middle panel). There were a number of relatively low values of $\delta^{15}N$ in SPM released into fresh reaches, which suggests the influence of nitrogen fixation (by symbiosis in legumes, orchids, bromeliads, cyanobacteria on tree leaves, and free-living bacteria). There were no other evident effects of degree of deforestation on isotopic signatures of SPM. In studies in much deeper coastal environments, Robinson and others (2012) reviewed the complex possibilities that sharply alter $\delta^{15}N$ of nitrogen within sediments, once SPM was deposited. There may be no such processes operating in the shallow systems we sampled, because the range of $\delta^{15}N$ of SPM we measured overlap comfortably with reported values for coastal surface sediments. This lack of further fractionation merits further study.

The emergent pattern revealed by the carbon and nitrogen isotopic data is that the down-estuary gradients in SPM indeed revealed land-sea linkages in this Panamanian coastal zone. SPM signatures made evident the effects of terrestrial and mid-estuary mangrove sources, of active transformation within the estuaries, and, showed that after transit and export, the isotopic signatures of SPM that managed to be exported from estuaries resembled those characteristic of coastal surface sediments. So far, therefore, the isotopic data demonstrated that SPM transport links land, estuary, and coastal sediments, but do not unambiguously tell us the direction of fluxes: the $\delta^{13}C$ gradient, for example, could have merely resulted from a passive mixing of terrestrial and marine sources.

The down-estuary pattern of the $\delta^{34}S$ signatures (Figure 5 bottom) significantly adds to our interpretation of the fate of land- and mangrove-derived SPM. In fresh reaches, $\delta^{34}S$ of SPM resembled those of terrestrial trees. As water became saltier, the isotopic signatures of SPM spanned a rather variable mix that might have been from mangrove leaves or sediments. The resulting exported SPM, however, converged on higher values (around 15‰), quite similar to values reported for SPM from a variety of coastal environments (Figure 5

bottom). This resemblance points to some common, likely terrestrial-estuarine, sources for SPM found in many coastal sites.

The novel aspect that the sulfur isotope data add is that the exported SPM was, however, notably enriched compared to signatures characteristic of coastal surface sediments (by about 10‰, a significant contrast, Figure 5 bottom). The major point here is that sulfur signatures of SPM measured in our samples, and in those from many other tropical coastal waters, differ from those characteristic of coastal sediments (Figure 5). Coastal sea floor sulfur signatures are usually dominated by reduced sulfide (FeS, FeS_2, or elemental S). This contrast points out that the likely direction of transport, in these Panamanian ecosystems, and probably others elsewhere, is likely to be from land and estuarine toward the coastal seas. If we were, instead, dealing with a passive mixing of estuarine and coastal sediments, we might not find what we found: a large gap in isotopic values between SPM that just emerged from estuaries, and isotopic values on surface sediments under near-shore waters. The estuarine SPM thus seem most likely to flux out of the estuaries, and sink to the coastal sea floor (recall SPM data collected outside estuaries in Figure 2 right). These results suggest that it is the land, and more so, the mangrove estuaries, that export particulate materials to coastal waters. The direction of the ecosystem-level couplings of watershed-mangrove-coastal waters by suspended particulate matter is asymmetrical, with terrestrial and mangrove exports dominating over marine sources.

The results we report on exports confirm the significant exports from estuarine and wetland ecosystems to coastal waters, reported for tropical (Jennerjahn and Ittekkot 2002; Dittmar and others 2006) as well as temperate systems (Valiela and Teal 1979). These papers used a variety of data to make such inferences. In the data of Figure 5 we show a first demonstration of the detailed trajectory of materials that show the mechanisms involved through the couplings of land, estuary and sea, and confirm the suspected exports toward marine ecosystems. Many references conclude that there are significant exports of terrestrial material to coastal waters. Some ambitious efforts are cast at rather large spatial scales, even global estimates (Milliman and others 2008; Mayorga and others 2010). These large-scale efforts focus on mass river transport, and elide over details such as the effects of watershed land covers, or the relative inputs via groundwater versus surface runoff, details that might be important to understand mechanisms that govern land–sea coupling in adjoined watershed–mangrove estuary–coastal water ecosystems. For example, in an earlier paper (Valiela and others 2013) we showed that exports of dissolved inorganic nitrogen from the estuaries studied here differed significantly depending on the land cover on the contributing watersheds. As it turns out, from the results of the present paper, particulate matter exports seem, in contrast, less affected by watershed land covers, at least in the Panama systems. Such contrasts might be important in assessing large-scale budgets.

In more general terms, there is no doubt that mangrove estuaries play a significant function in such land-sea couplings. First, results from this paper and Valiela and others (2013), and those cited elsewhere (Kristensen and others 2008; Breithaupt and others 2012, among others) make the point that there is rather substantial transformations, interception, and sequestering of watershed-derived dissolved and particulate materials within mangrove estuaries. Second, our results, and those of others (Jennerjahn and Ittekkot 2002; Dittmar and others 2006) also suggest that, in spite of the within-mangrove estuary retention and interception, there are exports of particulate matter from the coupled watershed-mangrove ecosystems to adjoined coastal waters, exports that compared to the depauperate condition of the receiving tropical waters are likely to be biologically meaningful. The joint, countering effects of within-estuary interception and the significant export, means that the biogeochemical functioning of these coastal wetland systems is even more quantitatively important than we might have known by just considering exports. Losses of mangrove estuaries, among the largest affecting any environment (Valiela and others 2001) might result in large—and, depending on the trajectories of land cover on the watersheds and rainfall regimes, unpredictable—shifts in sequestration and transfer of land-derived exports to receiving coastal waters throughout the tropics.

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