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Influence of roots and climate on mineral and trace element storage and flux in tropical mangrove soils

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Abstract. The storage and flux of various mineral and trace elements in soils (0–30 cm depth) were examined in relation to monsoonal rains and fine root biomass in four mangrove forests of different age and type in southern Thailand. The onset of the wet SW monsoon resulted in the percolation and dilution of porewater solutes by rainwater and by less saline tidal water, as indicated by shifts in Eh, pH and porewater SO_4/Cl ratios. This is contrary to temperate intertidal environments where seasonal patterns of porewater constituents, and biological and biogeochemical activities, are strongly cued to temperature. Fluxes across the soil–water interface were most often not statistically significant. Concentration of dissolved porewater metals were dominated by Fe, Mn, Al, Mo and Zn. The decreasing order of solid-phase element inventories in these soils, on average, was: Al, S, Fe, Na, Mg, K, Ca, N, P, Mn, V, Zn, Cr, Ni, As, Co, Cu, Pb, Mo, Cd and Hg. There were no gradients in concentrations of dissolved or solid-phase elements with increasing soil depth. This phenomenon was attributed to physical and biological processes, including the presence and activities of roots and tidal recharge of soil water. Fine dead roots were storage sites for most mineral and trace elements, as some elements in roots composed a significant fraction ($\geq$5%) of the total soil pool. Analysis of S and Fe concentration differences between live and dead roots suggested extensive formation of pyrite associated with dead roots; correlation analysis suggested that trace metals coprecipitated with pyrite. An analysis of inventories and release/uptake rates indicate turnover of the N, P, Na and Ca soil pools equivalent to other tropical forests; turnover was slow (decades to centuries) for S, Fe, K and trace elements. Our results indicate that mineral and trace element cycling in these soils are characterized by net storage, with net accumulation of most elements much greater than uptake and release by tree roots.

Introduction

The composition, flux and storage of mineral and trace elements in soils of wetland ecosystems are influenced by rates of sediment accumulation, the origin of inorganic and organic material, primary productivity, bioturbation, and physical disturbance. In intertidal environments where physical processes and atmospheric exposure are dominant, the accumulation and diagenesis of mineral and trace elements is also greatly influenced by the degree of tidal action and microbial activity (Rae 1997).

In wetlands, the presence of extensive below-ground roots and rhizomes are also thought to play an important role in regulating the geochemical composition of soils, mainly by active uptake and release of various solutes, and by oxidation of surrounding microenvironments, including development of metal coatings on root surfaces (St-Cyr and Campbell 1996; Dykyjova and Ulehlova 1998; Sundby et al. 1998). These processes are much better documented for freshwater marshes and swamps and salt marshes than for mangroves. Like other forested ecosystems, mangrove forests have extensive below-ground root systems that often extend to >50 cm beneath the forest floor (Komiyama et al. 1987; Alongi and Dixon 2000). Recent studies have found that most (80–90%) fine roots in mangrove deposits are dead (Robertson and Dixon 1993; Alongi and Dixon 2000; Alongi et al. 2002a). How (and whether or not) dead and live mangrove roots influence the economy of mineral nutrients, trace elements and heavy metals in soils, is not well known. Most studies of metals and trace elements in mangrove soils have focused on their composition and geochemical behavior, rather than on how they effect, or are affected by, below-ground biological processes (Lacerda et al. 1993). Laboratory and field studies have found that some mangroves directly and indirectly trap and retain some heavy metals, functioning as sinks for metals by modifying environmental conditions that promote metal storage (Tam and Wong 1995).

Another factor often overlooked is the role that climate plays on the biogeochemistry of intertidal deposits (Eisma 1998). Ice scouring, storm surges and freezing temperatures are important factors in high latitudes, but in the wet tropics where mangrove forests attain peak abundance, heavy monsoonal rains dominate seasonal climate patterns. The pattern of seasonal monsoons is well understood for southeast Asia, but what impact such periodic heavy floods and precipitation has on element cycling in mangrove sediments is unknown.

As part of a larger study of the role of mangroves in the cycling of carbon and other elements in southeast Asia (Alongi et al. 2001), we examined how biomass of live and dead fine roots (data from Alongi and Dixon 2000) and monsoonal rainfall, influenced dissolved and solid-phase element pools and fluxes in sediments of four different mangrove forests in southern Thailand. We compare these data with coincident measurements of microbial activity and other edaphic characteristics to develop an understanding of factors regulating the cycling, storage and turnover of mineral and trace elements within tropical mangrove ecosystems.

Methods

Site characteristics

Four mangrove habitats were sampled during the dry northeast (April 1999) and the wet southwest (October 1999) monsoons in Sawi Bay, located on the southwestern coast of the Gulf of Thailand. The climate of southern Thailand is dominated by the two monsoon seasons. Water temperatures varied within a narrow range of 27–30°; rainfall was much greater in the wet season (8–34 mm day^{-1}) than in the dry season (0–3 mm day^{-1}) with an annual average of 1800 mm (Wattayakorn et al. 2000). Sawi Bay has mixed semi-diurnal tides with a tidal range of 1.5 m (Wattayakorn et al. 2000). These sites differed in stand age, sediment type and tidal inundation frequency (Table 1).

Table 1. Forest and edaphic characteristics at the four mangrove stands in Sawi Bay, Thailand. Living above- and below-ground biomass and net primary productivity data are from Alongi and Dixon (2000), and sediment granulometry, carbon content and mass sediment accumulation (MAR) rate data are from Alongi et al. (2001). Tidal data was supplied by the Royal Forestry Department. The daily net canopy production rates of Alongi and Dixon (2000) were corrected for night-time canopy respiration (Alongi et al. 2001). Ra = *Rhizophora apiculata*; Cd = *Ceriops decandra*.

Site	Latitude/longitude	Mean tidal inundation frequency (day/month)	Forest type/age	Sediment type	Above-ground biomass (t DW ha^{-1})	Living fine roots (kg DW m^{-2})	Dead fine roots (kg DW m^{-2})	Forest production (tC ha^{-1} year^{-1})	MAR (kg sediment m^{-2} year^{-1})
S1	10°16.8′N, 99°9.8′E	8	Ra, 25year	Coarse silt	344 ± 41	3.6 ± 1.8	4.2 ± 4.4	52.8	7.5 ± 2.0
S2	10°16.7′N, 99°9.8′E	1	Ra, 5 year	Fine sand	42 ± 7	2.3 ± 0.9	11.7 ± 4.0	16.9	7.5 ± 2.0
S3	10°22.4′N, 99°13.2′E	6	Ra, 3 year	Silt/clay	65 ± 15	1.1 ± 0.4	2.6 ± 6.0	37.0	4.4 ± 1.9
S4	10°22.4′N, 99°13.3′E	1	Cd, 3 year	Fine sand	45 ± 6	0.8 ± 0.3	24.9 ± 3.5	22.9	4.4 ± 1.9

Stations S1 and S2 were located on opposite sides of Khlong Sawi, a small tidal river in the southern part of the bay. Station S1 was a mid-intertidal *Rhizophora apiculata* forest partially clear-felled 15 years ago, and allowed to regenerate naturally with *Avicennia alba* as a canopy sub-dominant. Mature trees in this stand were $\approx$25 years old. Above- and below-ground biomass and net canopy production were greatest at this site (Table 1). Station S2 was a high-intertidal *R. apiculata* plantation, manually planted 5 years ago. Above-ground forest biomass and net canopy production were lowest at this site (Table 1).

Stations S3 and S4 adjoined within the same mangrove plantation located in a small tidal estuary, Khlong I Laet, in the northern part of Sawi Bay. This plantation was originally the site of a failed shrimp farm, and was manually replanted 3 years ago. Station S3 was a *R. apiculata* stand within the mid-intertidal zone. Station S4 was located in the high-intertidal zone and was colonized by *Ceriops decandra.*

Soil sampling, redox and pH analyses

Triplicate cores for soil redox potential and pH measurements were taken randomly at each site at low neap tide using a 1.5 m-long (surface area: 28.2 cm^2) stainless steel corer. Cores were taken 1–3 m apart. Each core was extruded into a long plastic bag filled with N_2. Within 1–2 h after collection, measurements were taken using Eh and pH electrodes through puncture holes made at 2-cm intervals. A Model PRFO combination calomel reference-platinum redox electrode and a Model PBFC pH probe were allowed to equilibrate for 10–15 min before readings were taken using a TPS© LC 80 mV-pH–temperature meter. The pH electrode was calibrated using 6.00 and 7.00 standards (NIST scale).

Porewater analyses

Concentrations of porewater solutes were determined from triplicate 40-cm length stainless steel cores (surface area: 35.3 cm^2) taken randomly at each site at low neap tide to a depth of 30 cm. Each corer contained an inner plastic core subdivided into rings that enabled each sample to be cut into 2 cm slices in a N_2-filled glove bag. The slices were placed directly into Teflon porewater extractor cassettes (Robbins and Gustinis 1976) containing a 0.4 μm Nuclepore filter. The slices were squeezed under N_2 to obtain at least 10 ml of porewater per sample. Porewater samples were kept cool and dark in gas-tight plastic tubes until analyzed for elements. Chloride was measured on the same samples using a Radiometer CMT10 Chloride Titrator. Porewater SO_4 from the same slices was collected in tubes containing 1 ml 20% zinc acetate fixative. Sulfate was determined gravimetrically by $BaSO_4$ precipitation and filtration. Average precision was 2% for Cl and 3% SO_4.

Total dissolved Fe, Mn, Al, and Zn were measured on a Varian Liberty 220 ICP atomic emission spectrometer, and total dissolved Pb, Cd, Mo, Cr, Cu, Co, V, and Ni were measured on a Varian Spectra 400 Zeeman atomic absorption spectrometer using the methods detailed in Creed and Martin (1993). Standard reference materials 1643-C and SLRS-2 (National Research Council of Canada) were used to verify the analyses.

Solid-phase analyses

Each soil slice squeezed for porewater was partitioned, with one quarter frozen for later element analysis (lithogenic material + roots) and the remainder used immediately to separate live and dead roots (see procedure in Alongi and Dixon 2000). All root samples were then frozen and returned to the laboratory, where all soil and root samples were dried, ground and analyzed for TOC on a Shimadzu TOC-5000 Analyzer with solid-sampler and for total nitrogen on a Perkin Elmer 2400 CHNS/O Series II Analyzer. The soils and roots were further analysed separately for Fe, Mn, Al, S, Na, Mg, K, Ca, P, V, Zn, Cr, Ni, Cu, Co, Pb, Mo, Cd, Hg and As. Except for Cd measured on the Zieman AAS, the other elements were determined on the Varian Liberty ICP-AES following a modified acidification procedure (Loring and Rantala 1992). Briefly, 0.5 g of each dried (80 °C for 24 h) and ground sample was weighed into a 50-ml digestion tube, digested with HNO_3 and $HClO_4$ at 120° C for 3 h, then refluxed at 180° C for 3 h, and made up to 50 ml in a volumetric tube. The resulting complex was analyzed sequentially. Analytical performance was monitored with standard reference materials NBS 1646 (estuarine sediment) and MESS-2 (marine sediment). Values were always within the certified range. Analytical precision was ± 3%.

Dissolved solute fluxes

Fluxes of dissolved solutes across the soil–water interface were made from three clear and three opaque glass chambers (surface area = 70.9 cm^2) incubated at ambient temperature in a shaded water bath using the river water of each site (Alongi et al. 2001). These small chambers were used to avoid dense roots and crab burrows. Each chamber was inserted into the forest floor at each site to a depth of 5–7 cm and removed with minimal disturbance. Each chamber had a plastic propeller–electric motor unit and a sampling port from which nutrient samples were taken at 30-min intervals for 3 h. Volume of the overlying water varied from 550 to 700 ml. Sample water was replaced by allowing gentle seepage via a semi-closed cap on a smaller sampling port. Samples (10 ml) were filtered (0.45 μm Minisart filters and sterile plastic syringe) and processed as described above for dissolved porewater elements. Due to the small chamber size and analytical error, flux rates were rounded to the nearest hundredth.

Data analysis

Differences in concentrations of dissolved and solid-phase elements were initially tested using three-way (site × depth × season) ANOVA. If differences in one or two

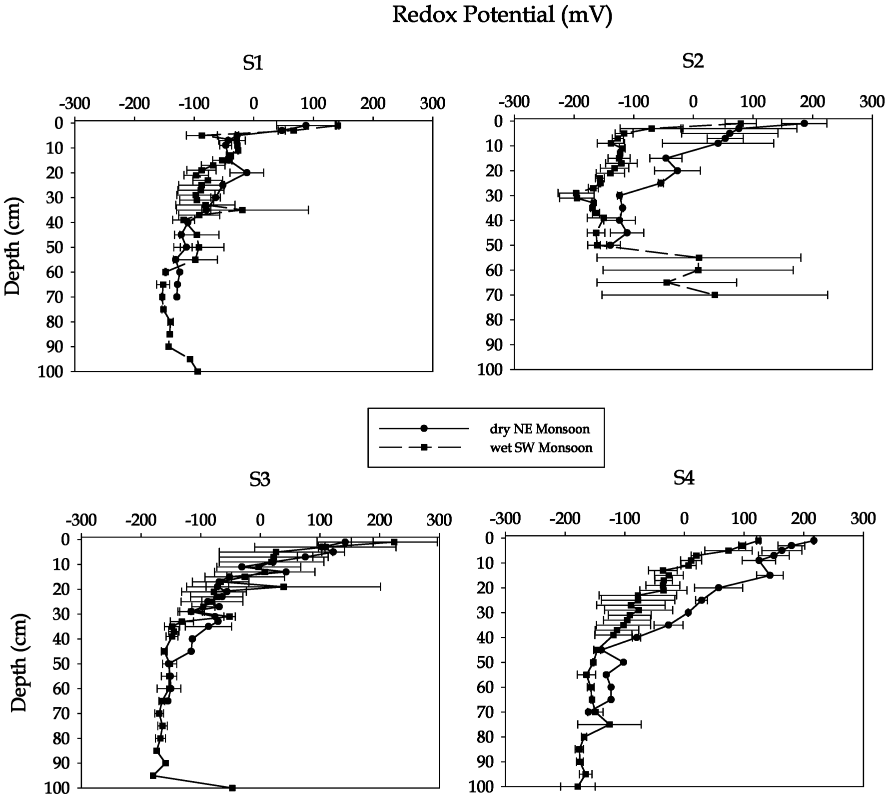

Figure 1. Vertical profiles of sediment redox potential (mV) at Stations S1–S4 during the NE (April 1999) and SW (October 1999) monsoons. Values are mean ± 1 SE.

factors were not significant, the analyses were retested using two-way or one-way ANOVA, followed by Ryan's Q test (Day and Quinn 1989) for multiple comparisons when significant main effects were found. Linear regressions were performed on the flux data to estimate rates of release/uptake. Best-fit regression models were used to examine possible relationships of elements with edaphic characteristics (e.g., pH) and measures of microbial activity. A significance level of $P = 0.05$ was accepted. All tests were performed using methods described in Sokal and Rohlf (1995).

Results

Redox, pH and porewater solutes

Eh profiles at all four sites indicated that soil redox status changed from positive Eh in the upper few centimeters to negative Eh further into the soil (Figure 1). The

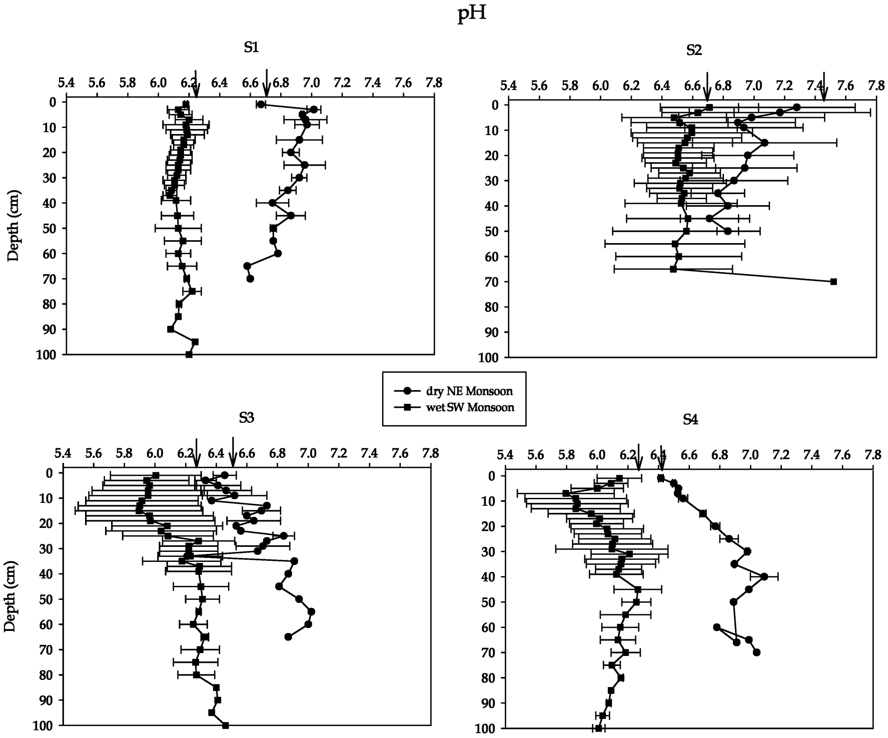

Figure 2. Vertical profiles of sediment pH (NIST scale) at Stations S1–S4 during the NE (April 1999) and SW (October 1999) monsoons. Values are mean ± 1 SE. Arrows depict overlying water-column pH.

ANOVA analyses indicated significant first- and second-order interactions obscuring clear patterns. However, at both high-intertidal forests (Stations S2 and S4), redox levels from the soil surface to a depth of 30 cm were significantly more negative during the wet SW monsoon than the dry NE monsoon (Figure 1).

The temporal patterns of pH were more pronounced (Figure 2) as the ANOVA indicated significant seasonal differences, with soils being more acidic in the wet season; site differences were not significant due to significant interactions with depth. At most depth intervals, soils at the four forests were acidic ($\text{pH} < 7.0$). The pH of overlying water and interstitial water in the 0–2 cm depth horizon were not significantly different at any of the sites during either season.

The molar ratio of porewater SO_4/Cl (Figure 3) was higher at all sites in the wet monsoon season than during the dry NE monsoon. The overlying water-column ratio was not significantly different than the porewater ratio at each site during both seasons.

Concentrations of trace elements in porewater were dominated by Fe, Mn and to a lesser extent, Al, Mo and Zn (Table 2). Concentrations of dissolved V and Pb were always at or below detection limits. There were few consistent differences among

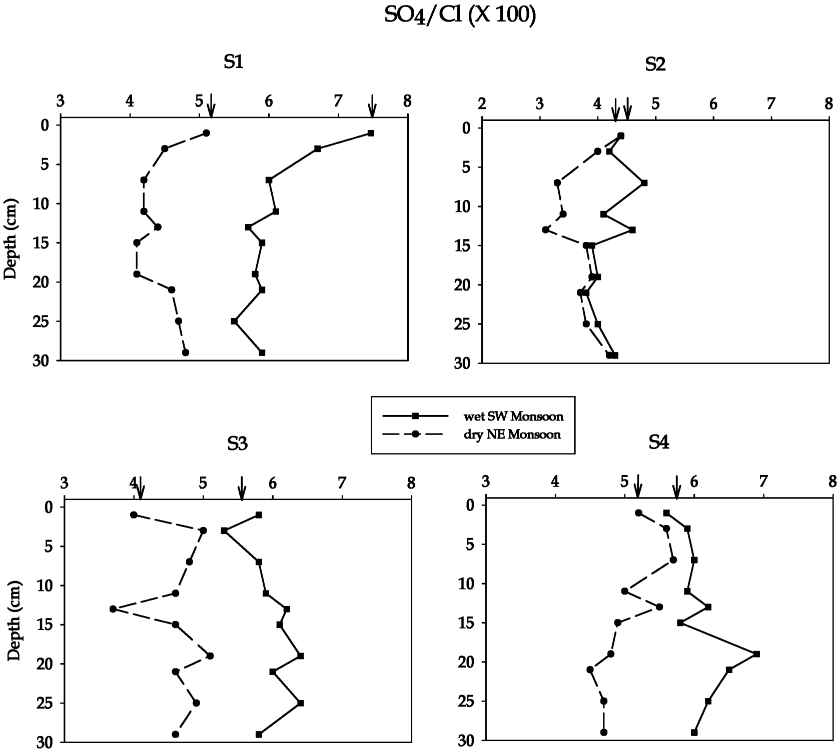

Figure 3. Vertical porewater profiles of molar SO_4/Cl (×100) ratios at Stations S1–S4 during the NE (April 1999) and SW (October 1999) monsoons. Arrows depict overlying water-column ratios. Values are mean ±1 SE.

sites with season and depth (Table 2); nearly all depth profiles were either not significant or irregular. For instance, Al concentrations at Station S2 in April 1999 were significantly greater than concentrations at Station S1, but this difference was not repeated in October 1999. There were some clear patterns among sites: (1) Fe and Mn concentrations at Stations S3 and S4 were greater than at Stations S1 and S2 during both monsoons; (2) Ni and Cr concentrations at Station S1 were significantly less than at the other forests; and (3) Co concentrations were greater at Station S4 than the other sites (Table 2). Seasonal differences, when significant, always indicated greater concentrations of porewater solutes during the dry NE monsoon (Table 2). None of the porewater solutes correlated significantly with pH or Eh.

Soil–water exchange

Fluxes across the soil–water interface were dominated by efflux of Ni and Mo; there were no significant fluxes into the soil (Table 3). Cr flux was measurable at

Table 2. Mean (±1 SE) concentrations of porewater solutes at the four mangrove forests during the dry NE monsoon (April 1999) and wet SW monsoon (October 1999) seasons. Values are means to an average sediment depth of 30 cm in three replicate cores. Concentrations of dissolved V and Pb were nearly always <1 and 9 µM, respectively. Within-sites, NE monsoon values with superscript 'a' are significantly greater those in SW monsoon. Between-site comparisons are discussed in Results text. ∂ = µM; ∞ = nM.

	S1		S2		S3		S4	
	NE	SW	NE	SW	NE	SW	NE	SW
Fe$^{\partial}$	10 ± 3	9 ± 3	53 ± 12^{a}	11 ± 4	39 ± 7	29 ± 32	48 ± 8^{a}	23 ± 10
Mn$^{\partial}$	8 ± 1	6 ± 1	17 ± 16	7 ± 2	51 ± 7^{a}	33 ± 10	69 ± 10	56 ± 11
Al$^{\partial}$	7 ± 3^{a}	1 ± 1	36 ± 6^{a}	3 ± 1	6 ± 3	3 ± 36	13 ± 5^{a}	2 ± 1
Mo$^{\partial}$	14 ± 10^{a}	0.2 ± 0.2	0.6 ± 0.1^{a}	0.3 ± 0.1	2 ± 1^{a}	0.4 ± 0.1	0.9 ± 0.1^{a}	0.1 ± 0.1
Zn$^{\partial}$	0.2 ± 0.2	0.07 ± 0	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.4 ± 0.2	0.2 ± 0.1
Ni$^{\infty}$	86 ± 14	83 ± 29	324 ± 30	297 ± 98	225 ± 58	209 ± 2	360 ± 72	338 ± 77
Cr$^{\infty}$	65 ± 11^{a}	42 ± 10	199 ± 30	539 ± 444	169 ± 87	275 ± 99	258 ± 83	363 ± 99
Cu$^{\infty}$	37 ± 2^{a}	32 ± 1	90 ± 53^{a}	34 ± 1	36 ± 2	35 ± 3	60 ± 9^{a}	35 ± 5
Co$^{\infty}$	28 ± 1	34 ± 9	41 ± 1^{a}	37 ± 2	34 ± 8	70 ± 35	69 ± 82	255 ± 91
Cd$^{\infty}$	8 ± 27	2 ± 0	2 ± 1	2 ± 1	2 ± 1	2 ± 1	5 ± 1	5 ± 1

Detection limits: Fe (54 nmol l^{-1}), Mn (27 nmol l^{-1}), Al (740 nmol l^{-1}), Zn (30 nmol l^{-1}), Pb (10 nmol l^{-1}), Cd (1.8 nmol l^{-1}), Mo (20 nmol l^{-1}), Cr (10 nmol l^{-1}), Cu (31 nmol l^{-1}), Co (17 nmol l^{-1}), V (392 nmol l^{-1}) and Ni (34 nmol l^{-1}).

Table 3. Solute fluxes at each of the four mangrove forests. Only statistically significant fluxes are shown. Detection limits are the same as shown at bottom Table 2. Mn, Zn, Fe, and Al fluxes = μmol $m^{-2} h^{-1}$. Ni, Mo, Cr, Cu, Co and Cd fluxes = nmol $m^{-2} h^{-1}$.

Station	Element	Flux rate
S1	Ni	2500 ± 600 (SW)
	Mo	400 ± 100 (SW)
	Cr	100 ± 100 (SW)
S2	Ni	2200 ± 1400 (NE)
		1400 ± 800 (SW)
	Cu	600 ± 300 (NE)
	Mo	400 ± 200 (NE)
		400 ± 200 (SW)
	Cr	100 ± 100 (NE)
		1200 ± 600 (SW)
S3	Ni	1500 ± 1200 (NE)
	Mo	300 ± 100 (SW)
S4	Al	800 ± 400 (NE)
	Mo	200 ± 100 (NE)
	Ni	6400 ± 2000 (SW)
	Mo	1100 ± 400 (SW)
	Cr	300 ± 200 (SW)
	Co	700 ± 300 (SW)
	Cd	200 ± 100 (SW)

three of the four sites, and flux of dissolved Cu, Al, Co and Cd were measurable only once at different sites (Table 3). In 10 of 16 seasonal comparisons (Table 3), solute fluxes were significantly more rapid during the wet monsoon than in the dry season.

Solid-phase elements in soils and below-ground fine roots

The decreasing order of concentration of elements in these mangrove soils (roots + lithogenic material), on average, was: Al, S, Fe, Na, Mg, K, Ca, N, P, Mn, V, Zn, Cr, Ni, As, Co, Cu, Pb, Mo, Cd and Hg (Table 4). The concentrations of solid-phase Fe, Al, S, P, Zn, Cr, As, Mo and Hg were significantly greater at Station S3 than at the other sites. Stations S3 and S4 had significantly greater concentrations of solid-phase Na, Mg, K, Ca, V, Ni, and Pb than at Stations S1 and S2 (Table 4). None of the elements exhibited clear patterns with increasing soil depth. Most seasonal differences indicated greater element concentrations during the NE monsoon (Table 4); exceptions were Ca at Station S2, Mo at Station S3, and Mn and Mo at Station S4.

The decreasing order of concentration of elements (excluding C and N) in live and dead mangrove roots, on average, was: S, Na, Fe, Mg, Al, Ca, K, P, Mn, V, Zn,

Table 4. Mean (± 1 SE) concentrations of solid-phase elements in soils (lithogenic + root material) at the four mangrove forests during the dry NE monsoon (April 1999) and wet SW monsoon (October 1999) seasons. Values are means (g dry mass) to an average soil depth of 30 cm in three replicate cores. Values with superscript ‘a’ are seasonally higher within-site comparisons; differences between sites are discussed in Results text. $\alpha = \text{mmol g}^{-1}$; $\partial = \mu\text{mol g}^{-1}$; $\infty = \text{nmol g}^{-1}$.

	S1		S2		S3		S4	
	NE	SW	NE	SW	NE	SW	NE	SW
C^{α}	2.5 ± 0.6	2.0 ± 0.4	2.2 ± 0.4	1.9 ± 0.3	6.1 ± 1.4	4.5 ± 0.4	3.6 ± 0.8	3.3 ± 0.8
N^{∂}	85.7 ± 28.5	71.4 ± 21.4	64.3 ± 14.3	57.1 ± 21.4	192.9 ± 21.3	157.2 ± 28.5	114.3 ± 21.4	114.3 ± 21.4
Al^{∂}	651 ± 44^{a}	552 ± 36	601 ± 24^{a}	439 ± 55	1358 ± 18^{a}	1234 ± 17	93 ± 10	124 ± 24
S^{∂}	348 ± 34	336 ± 36	463 ± 54^{a}	356 ± 57	616 ± 83	593 ± 96	171 ± 34	296 ± 135
Fe^{∂}	233 ± 19	227 ± 19	350 ± 27^{a}	203 ± 34	428 ± 40	434 ± 56	210 ± 22	206 ± 24
Na^{∂}	130 ± 12	155 ± 23	164 ± 9	176 ± 20	445 ± 26	466 ± 67	314 ± 25	343 ± 39
Mg^{∂}	129 ± 9^{a}	111 ± 8	123 ± 5	117 ± 15	251 ± 23	253 ± 38	158 ± 5	168 ± 11
K^{∂}	99 ± 5	89 ± 6	90 ± 4^{a}	70 ± 7	169 ± 10	167 ± 23	116 ± 10	125 ± 9
Ca^{∂}	20 ± 3	19 ± 4	19 ± 1	125 ± 5^{a}	51 ± 9	58 ± 5	34 ± 6	45 ± 8
P^{∞}	4059 ± 307^{a}	3289 ± 412	4705 ± 361^{a}	3825 ± 551	6465 ± 529	6190 ± 1025	4407 ± 332	3839 ± 459
Mn^{∞}	2727 ± 374	2812 ± 329	5738 ± 581	4996 ± 1347	3180 ± 422	4949 ± 1081	1673 ± 236	2579 ± 264^{a}
V^{∞}	396 ± 50	355 ± 76	334 ± 39^{a}	211 ± 43	791 ± 55	725 ± 101	552 ± 33	471 ± 66
Zn^{∞}	351 ± 19	305 ± 16	386 ± 18	376 ± 76	625 ± 91	519 ± 61	331 ± 28	350 ± 25
Cr^{∞}	295 ± 22	277 ± 31	300 ± 19^{a}	205 ± 0	458 ± 26	523 ± 66	323 ± 25	386 ± 47
Ni^{∞}	154 ± 11	133 ± 15	155 ± 10	146 ± 51	302 ± 21	283 ± 42	201 ± 19	237 ± 39
As^{∞}	93 ± 7	82 ± 6	138 ± 23	124 ± 35	157 ± 18	157 ± 17	93 ± 15	124 ± 14
Co^{∞}	81 ± 4^{a}	73 ± 1	104 ± 4	108 ± 30	154 ± 109	109 ± 11	90 ± 12	74 ± 9
Cu^{∞}	131 ± 37^{a}	76 ± 8	75 ± 15^{a}	48 ± 8	153 ± 16^{a}	14 ± 13	107 ± 9	99 ± 7
Pb^{∞}	43 ± 7	36 ± 5	38 ± 7	34 ± 6	106 ± 14	105 ± 12	73 ± 8	93 ± 14
Mo^{∞}	34 ± 9	23 ± 2	56 ± 14^{a}	29 ± 14	69 ± 14	94 ± 15^{a}	27 ± 8	47 ± 10^{a}
Cd^{∞}	0.9 ± 0.2	0.7 ± 0.1	0.4 ± 0.1	0.5 ± 0.1	1.0 ± 0.3	0.8 ± 0.1	0.4 ± 0.1	1.0 ± 0.5
Hg^{∞}	0.1 ± 0.01	0.1 ± 0.02	0.08 ± 0.01	0.09 ± 0.02	0.17 ± 0.02	0.16 ± 0.01	0.12 ± 0.01	0.12 ± 0.02

Table 5. Differences in mean (± 1 SE) concentrations of solid-phase elements at the four mangrove forests (combined monsoon data) in live and dead roots (g dry mass) to a soil depth of 30 cm. Values with superscript 'a' are higher concentrations in live versus dead root comparisons for each element. Differences between sites are discussed in Results text. $\alpha = \text{mmol g}^{-1}$; $\partial = \mu\text{mol g}^{-1}$; $\infty = \text{nmol g}^{-1}$.

	S1		S2		S3		S4	
	Live	Dead	Live	Dead	Live	Dead	Live	Dead
C^{α}	28.1 ± 0.9	33.1 ± 0.5^{a}	29.3 ± 1.5	32.4 ± 1.3^{a}	30.9 ± 0.3	34.2 ± 0.6^{a}	29.8 ± 1.1	32.7 ± 1.0^{a}
N^{α}	0.29 ± 0.01	0.56 ± 0.01^{a}	0.37 ± 0.04	0.46 ± 0.01^{a}	0.47 ± 0.02	0.46 ± 0.01	0.47 ± 0.02	0.44 ± 0.04
S^{∂}	811 ± 76	1428 ± 107^{a}	810 ± 83	1927 ± 120^{a}	1127 ± 89	1591 ± 34^{a}	1254 ± 53	2169 ± 114^{a}
Na^{∂}	837 ± 47^{a}	349 ± 21	853 ± 75^{a}	266 ± 12	610 ± 112^{a}	295 ± 42	289 ± 33	313 ± 13
Fe^{∂}	72 ± 11	440 ± 41^{a}	136 ± 15	657 ± 79^{a}	120 ± 10	425 ± 23^{a}	236 ± 25	807 ± 95^{a}
Mg^{∂}	198 ± 12	267 ± 23^{a}	202 ± 19	205 ± 19	171 ± 21	206 ± 10^{a}	139 ± 7	290 ± 2^{a}
Al^{∂}	148 ± 24	182 ± 16	156 ± 42	202 ± 31	220 ± 16	235 ± 20	245 ± 12	241 ± 15
Ca^{∂}	85 ± 1	188 ± 15^{a}	119 ± 23	205 ± 40^{a}	103 ± 6	120 ± 6^{a}	128 ± 8	180 ± 2^{a}
K^{∂}	46 ± 3^{a}	31 ± 3	89 ± 27^{a}	33 ± 4	64 ± 4^{a}	36 ± 2	44 ± 1^{a}	36 ± 2
P^{∂}	11 ± 1	18 ± 2^{a}	14 ± 2	17 ± 6	14 ± 1	14 ± 2	10 ± 1	8 ± 1
Mn^{∞}	1093 ± 28	4212 ± 239^{a}	2137 ± 332	6910 ± 1229^{a}	1167 ± 82	3439 ± 222^{a}	1753 ± 132	10426 ± 1864^{a}
V^{∞}	306 ± 61	701 ± 51^{a}	959 ± 19	1460 ± 167^{a}	701 ± 2	770 ± 21^{a}	1231 ± 82	1574 ± 63^{a}
Zn^{∞}	222 ± 37	492 ± 49^{a}	356 ± 26	724 ± 84^{a}	360 ± 55	473 ± 24^{a}	650 ± 75	895 ± 50^{a}
Cr^{∞}	125 ± 15	200 ± 32^{a}	322 ± 40	658 ± 31^{a}	207 ± 7	207 ± 17	362 ± 17	607 ± 9^{a}
As^{∞}	46 ± 8	270 ± 30^{a}	68 ± 14	322 ± 66^{a}	159 ± 18	397 ± 36^{a}	202 ± 22	766 ± 75^{a}
Mo^{∞}	46 ± 7	193 ± 37^{a}	87 ± 54	153 ± 38^{a}	224 ± 26	417 ± 61^{a}	216 ± 36	468 ± 18^{a}
Ni^{∞}	61 ± 4	132 ± 6^{a}	75 ± 14	145 ± 10^{a}	81 ± 5	153 ± 11^{a}	128 ± 6	334 ± 9^{a}
Cu^{∞}	36 ± 4	83 ± 3^{a}	41 ± 3	87 ± 10^{a}	153 ± 67	102 ± 6	269 ± 72	250 ± 23
Co^{∞}	36 ± 6	127 ± 16^{a}	47 ± 5	177 ± 6^{a}	43 ± 5	136 ± 9^{a}	67 ± 5	283 ± 24^{a}
Pb^{∞}	14 ± 2	34 ± 4^{a}	16 ± 2	45 ± 4^{a}	24 ± 5	62 ± 1^{a}	56 ± 2	191 ± 14^{a}
Cd^{∞}	0.8 ± 0.1	2.5 ± 0.4^{a}	0.5 ± 0.1	1.8 ± 0.3^{a}	1.1 ± 0.2	2.0 ± 0.1^{a}	2.2 ± 0.3	4.0 ± 0^{a}
Hg^{∞}	0.1 ± 0.04	0.22 ± 0.06^{a}	0.10 ± 0.04	0.17 ± 0.02^{a}	0.12 ± 0.03	0.14 ± 0.04	0.17 ± 0.3	1.16 ± 0.05^{a}

Table 6. Mean percentage of the total below-ground pool of each element vested in live and dead root biomass. Seasonal data were combined.

	S1		S2		S3		S4	
	Live	Dead	Live	Dead	Live	Dead	Live	Dead
C	7.4	10.9	2.9	16.1	0.9	23.1	0.7	23.1
N	1.6	14.5	1.4	8.4	0.4	9.4	0.4	9.6
Fe	0.1	1.3	0.1	3.6	0.04	3.5	0.1	9.6
Al	0.1	1.1	0.07	0.5	0.03	0.7	0.02	0.6
S	1.1	9.5	0.5	6.1	0.3	9.7	0.4	1.8
Na	2.4	21.3	1.1	1.7	0.2	2.3	0.08	2.2
Mg	0.8	7.1	0.4	2.0	0.1	2.9	0.07	4.3
K	0.2	2.0	0.3	0.5	0.06	0.8	0.03	0.7
Ca	2.1	18.3	0.04	0.3	0.3	7.4	0.2	9.8
P	1.5	13.0	0.8	5.1	0.4	8.3	0.2	5.7
Mn	1.7	15.3	0.1	1.6	0.04	2.5	0.06	1.0
V	0.4	3.4	1.0	7.8	0.2	3.8	0.2	8.2
Zn	0.3	2.9	0.2	2.1	0.1	3.3	0.2	6.3
Cr	0.2	1.8	0.3	3.6	0.06	1.4	0.08	3.9
Ni	0.2	1.8	0.1	1.1	0.05	1.9	0.05	3.5
As	0.2	2.2	0.1	2.9	0.2	9.1	0.1	15.1
Cu	0.2	1.9	0.2	2.0	0.2	2.6	0.2	6.2
Co	0.2	2.0	0.1	1.8	0.06	4.5	0.08	9.4
Pb	0.2	1.5	0.1	1.5	0.4	2.1	0.05	5.1
Mo	0.9	8.0	0.7	6.0	0.4	16.0	0.4	24.4
Cd	0.5	5.0	1.1	5.0	0.2	9.0	0.2	10.3
Hg	0.4	3.7	0.2	2.9	0.2	9.1	0.1	0.2

Cr, As, Mo, Ni, Cu, Co, Pb, Cd and Hg (Table 5). There were no seasonal differences for any elements at any of the four forests. Site comparisons indicated that greatest concentrations of Fe, Al, S, V, Zn, Ni, As, Cu, Co, Pb, Cd and Hg in live + dead roots were at Station S4 (Table 5). Mo concentrations in live and dead roots were significantly greater at Stations S3 and S4 than at Stations S1 and S2. Concentrations of Na and K were nearly always greater in live roots than in dead roots; there were no differences in concentrations of Al in live versus dead roots (Table 5). In all other comparisons where significant differences were found, element concentrations were greater in dead roots (Table 5).

Some elements in roots comprised a significant fraction of the total below-ground pool (Table 6). Total organic carbon in (mainly dead) roots ranged from 18 to 24% of the total TOC soil pool; for nitrogen the percentages ranged from 10 to 16%. Depending on location, Fe, S, Na, Mg, Ca, P, Mn, V, Zn, As, Cu, Co, Pb, Mo, Cd and Hg comprised at least 5% of the total soil pool (Table 6).

Combining all sites, redox potential correlated significantly with solid-phase Fe ($r = 0.23$), Mn ($r = 0.47$), Zn ($r = 0.46$) and Cu ($r = 0.26$), and live root biomass correlated inversely with solid-phase Hg ($r = -0.38$), Al ($r = -0.61$), Cu ($r = -0.54$), Pb ($r = -0.28$), S ($r = -0.29$), Cr ($r = -0.56$) and Cd ($r = -0.32$). All solid-phase elements correlated positively with TOC (range of $r = 0.47$–0.84) and N (range of $r = 0.23$–0.66).

Root S (live + dead) correlated positively with As ($r = 0.913$), Cd ($r = 0.845$), Co ($r = 0.95$), Cr ($r = 0.753$), Fe ($r = 0.901$), Hg ($r = 0.693$), Mn ($r = 0.911$), Mo ($r = 0.732$), Ni ($r = 0.865$), Pb ($r = 0.783$), Zn ($r = 0.895$) and V ($r = 0.747$). Root Fe (live + dead) correlated positively with As ($r = 0.900$), Cd ($r = 0.836$), Co ($r = 0.979$), Cr ($r = 0.777$), Hg ($r = 0.724$), Mn ($r = 0.964$), Ni ($r = 0.873$), Pb ($r = 0.78$), Zn ($r = 0.883$) and V ($r = 0.75$). Root C (live + dead) correlated only with S ($r = 0.774$), Fe ($r = 0.737$) and Mo ($r = 0.739$).

Discussion

The flux of mineral and trace elements in the mangrove soils of Sawi Bay is dominated by the rapid accumulation of sediments and, to a much lesser extent, by plant uptake. Rates of MAR, estimated from vertical profiles of ^{210}Pb and ^{137}Cs were rapid, ranging from 2.9 to 7.6 kg m^{-2} year^{-1} (Alongi et al. 2001). Assuming a simple mass balance in which total element input to the sediment equals the sum of the total outputs (dissolved release, diagenesis, plant uptake, etc.) and accumulation rate (Berner 1980), we estimated (Table 7) the magnitude of element release and diagenesis relative to the net accumulation rate, and the turnover rate of the soil inventory of the major elements (see legend, Table 7 for details of assumptions and calculations). Our analysis indicates that release/uptake rates were rapid due to high rates of photosynthetic demand, but small relative to net accumulation, as indicated by turnover times often more than a decade, especially for S, Fe, K, Zn, Cu and Mo (Table 7). In contrast, turnover of the N, P, Na, and Ca soil pools were equivalent to those in tropical terrestrial forests, such as in India (Singh 1989), Panama (Golley et al. 1975), Costa Rica (Fassbender 1998) and South America (Vogt et al. 1986) Mangrove forests in other regions (e.g., South America) are similarly net accumulators of solid-phase elements, especially heavy metals, with comparatively little uptake or release from soils (Lacerda et al. 1993).

Soil redox, pH, and organic content are important factors regulating element diagenesis, but the presence and activity of extensive below-ground roots and episodes of heavy monsoonal rain, affected the distribution and concentration of solid-phase and dissolved elements in these mangrove soils. Dilution by monsoonal rain is contrary to the seasonal changes in element chemistry in temperate intertidal sediments where the major regulatory factor is the increase in floral and faunal activities induced by warm summer temperatures (Rae 1997). In these Thai mangrove soils, there was a seasonal shift to more acidic and more reducing conditions, an increase in the porewater SO_4/Cl ratio and a decline in concentration of most other elements in the interstitial water, from the dry to the wet monsoon. This change was most likely due to seepage and dilution of rainwater at low tide and by tidal waters diluted by increased freshwater runoff. Samples were taken at neap low tides when the effects of rainwater were magnified (these sites are more often exposed than inundated, see tidal inundation frequencies, Table 1). Tidal waters were also diluted by the monsoons as surface water salinity in Khlong Sawi ranged from 8 to 10 in April 1999 and from 1 to 2 in October 1999; freshwater discharge

Table 7. Total soil element inventories (mol ha^{-1}), total element release rates (mol ha^{-1} year^{-1}) and estimated turnover times (year) of selected elements at the four mangrove forests. Total soil inventories were estimated to a depth of 30 cm by multiplying the mean concentrations (Table 4) by bulk density and extrapolating from core area to hectare. Release rates were calculated using the mass balance equation, $E_{\text{output}} = E_{\text{input}} - E_{\text{accumulation}}$ (Berner 1980). Accumulation rates were estimated by multiplying the mean concentration of each element (Table 4) by the MAR (Table 1) in Alongi et al. (2001). Inputs were estimated by summing burial rates + solute flux (Table 3) + mineralization rates. Mineralization rates were estimated to equal tree demand, derived by multiplying mean foliage concentrations of each element (Alongi et al. in press and unpublished data for Station S4) by net primary production (Table 1). N demand taken from Table 9 in Alongi et al. (2002b). Turnover was estimated by dividing total soil inventory by total release rate.

	S1			S2			S3			S4		
	Inventory	Release	Turnover	Inventory	Release	Turnover	Inventory	Release	Turnover	Inventory	Release	Turnover
N	450010	129600	3.5	464300	35400	13.1	921440	71900	12.8	657200	40150	16.4
P	21700	3925	5.5	32880	1270	25.9	33560	2500	13.4	22000	1020	21.6
S	2005400	17720	113.2	3143800	4900	641.6	3190500	9900	322.3	1353500	8000	169.2
Fe	1355500	1480	915.8	2127200	100	21272	2283000	125	18264	1154900	50	23098
Na	848300	137100	6.2	1304900	30200	43.2	2422800	67700	35.8	1753000	35100	49.9
Mg	703600	76660	9.2	917500	10800	85.0	1329000	16350	81.3	868100	13400	64.8
K	557600	26400	21.1	767300	6050	126.9	892600	14000	63.8	662400	5800	114.2
Ca	114800	61600	1.9	553900	14000	39.6	291900	37500	7.8	234500	13900	16.8
Zn	1940	12	161.7	2930	4	732.5	3030	6	505	1810	4	452.5
Cu	610	1	610	470	1	470	440	3	146.7	550	2	275
Mn	16300	6077	2.7	41900	350	119.7	21900	1600	13.7	11800	85	138.8
Mo	165	6	27.5	320	1	320	430	1	430	200	1	200

averaged 330,000 and 900,000 $\mathrm{m}^{-3}\,\mathrm{day}^{-1}$ in April and October, respectively (Wattayakorn et al. 2000). In Khlong I Laet, salinity varied from 20–21 during April and from 11 to 12 during October with freshwater discharge averaging 200,000 and 590,000 $\mathrm{m}^{-3}\,\mathrm{day}^{-1}$ in the dry and wet seasons, respectively (Ayukai et al. 2000). Directly or indirectly, rainfall had a pronounced effect on recharge of the soil water deficit. Previous hydrological studies of mangrove soils and tidal creeks in the Indo-Pacific indicate that most rainwater percolates through cracks, burrows and fissures at exposed tide and by diluted tidal waters when the forests are flooded (Wolanski and Gardiner 1981, Ridd 1996). The influence of monsoonal rains on soil biogeochemistry has been observed in other tropical intertidal habitats (Alongi et al. 1999).

The low concentration of dissolved solutes compared with solid-phases and the slow or undetectable rates of flux across the soil–water interface indicate either considerable oxidation and trapping of elements into solid-phases or oscillations in redox conditions that disrupt steady-state diagenesis, or both (Aller 1994). Non-steady state conditions are plausible considering the impact of tides and monsoonal precipitation, and solute uptake and exclusion via roots; interstitial water movements are probably much greater than rates of either molecular or ionic diffusion or biological advection. Some solutes may be lost by lateral tidal drainage, advection or groundwater transport, as burrows, fractures and cracks may serve as conduits for subsurface transport. The forest floor functions like a sponge, being networked with extensive live and dead roots and rhizomes, burrows, fractures, and fissures, and subjected to flooding and drainage by tides and rain. Further, Alongi et al. (2001) noted that these sites drain dry during prolonged periods of tidal exposure, and may undergo oscillations in relation to tidal cycles, with more reducing conditions when submerged.

Evidence exists that mangrove soils frequently experience oscillations in redox induced by biological and physical disturbances (e.g., tidal advection, rainwater seepage) that often preclude buildup or maintenance of free sulfides (Kristensen et al. 1995; Alongi et al. 2001). Mangrove deposits are often characterized by the presence of oxidized surface soils, burrow and tube walls, deep and extensive roots, consistently detectable concentrations of oxidized solutes and the absence or low concentration of CH_4 and H_2S. The lack of complete anoxia or highly sulfidic conditions may be due to the nature of the source material. Trace metals and minerals enter mangrove forests in oxidized forms, especially in association with iron and manganese oxyhydroxides sorbed onto suspended particles that are tidally transported into the forests.

The presence of roots has a considerable impact on soil biogeochemistry, and root activities may account for the lack of vertical solute profiles. An analysis of the mean percentage of the total below-ground pool of each element vested in live and dead roots (Table 6) showed that from 18 to 24% of the total carbon pool is derived from roots. The percentages were smaller for most other elements, but at some forests, percentages exceeded 5% for some elements. Although Na and K concentrations were significantly greater in live fine roots, nearly all other elements were more concentrated in dead roots. This is reminiscent of the role of dead roots in mangroves of arid Western Australia where Alongi et al. (2002a) observed that dead roots in *Rhizophora stylosa* and *Avicennia marina* forests equated to 36–88% by dry weight of total living biomass. The amount of Ca, S, Cl, Na, Si, Fe, Mn, Zn, B, Mo and Cu vested in dead roots of both species was greater than in total living forest biomass. The large reservoir of dead roots was considered a mechanism to conserve various mineral and trace elements, and such may be case in these Thai forests.

A regression analysis of the differences in S and Fe concentrations in live and dead roots indicated that dead roots are loci for pyrite formation and trace metal coprecipitation. A regression line of ΔS (dead minus live root concentrations) versus ΔFe indicated a positive correlation and a slope (2.1) nearly identical to stoichiometric pyrite. Correlation analysis suggested that most trace metals were closely associated with pyritic-dead root complexes. Pyritization of trace metals in sediments is not well understood, but it is known that the transition metals, some class B metals, and As, Hg and Mo can be incorporated into pyrite in anoxic sediments, the rate depending on solute metal availability and organic matter content (Huerta-Diaz and Morse 1992). This is similar to salt marsh plants where iron concretions are the result of precipitation of both insoluble oxides in living rhizospheres and FeS_2 on dead roots (St-Cyr and Campbell 1996; Sundby et al. 1998). The mechanisms fueling pyrite formation and trace metal coprecipitation on dead roots are unknown, but the correlation analyses showed no significant correlation of dead root carbon with any of the trace metals, suggesting that the trace metals were more closely associated with pyrite formation than with immobilization within root tissue. Rates of sulfate reduction correlated significantly with dead root biomass (Alongi et al. 2001) suggesting that carbon in dead roots may be indirectly fostering pyrite formation by providing fuel for the growth of sulfate-reducing bacterial communities which in turn produce free sulfides necessary for the precipitation of FeS_2.

Living fine roots correlated negatively with Hg, Al, Cu, Pb, S, Cr and Cd indicating some impact of metals on the growth of fine roots, or vice versa. Concentrations of Pb, Hg, Cu, Co and Cd were greater in these Thai soils than in other mangrove soils and trees (Lacerda et al. 1993; Tam and Wong 1995; Lacerda 1997). The rapid rates of net primary production in these forests suggest tolerance of heavy metals, perhaps as a result of the formation of root plaques. Lacerda et al. (1993) similarly indicated that mangrove trees seem to be unaffected by the net accumulation of various heavy metals. Our data supports earlier studies suggesting that mangrove ecosystems act as active sinks for mineral and trace elements associated with suspended inorganic and organic matter and soils.

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