BENTHIC FLUXES OF NUTRIENTS AND SOME TRACE METALS IN THE TAMAR ESTUARY, SW ENGLAND

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ABSTRACT

Pore water concentration gradients and fluxes of chemical components have been studied in sediments from six intertidal sites in the Tamar Estuary, SW England over the course of a year. Fluxes of nutrients (ammonia, nitrate, nitrite, phosphate and silicate) and trace metals (iron, manganese, zinc, copper and cadmium) were determined using a laboratory microcosm incorporating *in situ* pore water samplers. Nutrients (except nitrate) were transported out of the sediment throughout the year, but nitrate fluxes were directed into the sediment in the summer (denitrification) and out of the sediment in the winter (nitrification). The activities of benthic macrofauna resulted in enhanced fluxes but these differed between sites depending on population structure and density and whether irrigation or sediment reworking predominated. Fluxes of trace metals were seasonally and spatially variable and specific differences were observed that could be attributed to both chemical and biological activity.

INTRODUCTION

Sediment-water interactions influence estuarine water quality (BAEYENS et al., 1985). They show great spatial and temporal diversity in estuaries (WATSON et al., 1985) because of large variations in the supply and degradation of organic and inorganic components and the influence of physical, chemical and biological processes. Further development and validation of models is dependent on more comprehensive measurements of benthic fluxes and the associated sedimentary system.

In this paper we report measured and calculated benthic fluxes of nutrients and some trace metals in sediments from six sites in the Tamar Estuary, S.W. England determined in a laboratory microcosm over the course of a year. Results are discussed in terms of spatial and seasonal variations and the activities of benthic organisms.

METHODS

The mid and lower Tamar Estuary are characterised by extensive intertidal mud flats (HARTLEY and SPOONER, 1938; BALE et al., 1985) and inputs associated with urban and industrial settlements. Five intertidal sampling sites were chosen along the banks of the lower and mid-estuary and a sixth at the head of a creek in the lower region (Fig. 1) with varying benthic animal activity. Measurements were made on sediments from each of the sites on four occasions: August and December 1990, and March and July 1991.

Sediment characterisation

Cores (6.0 cm dia. x 15 cm long) were collected for measurement of vertical profiles of redox potential (Pt/Ag-AgCl electrode, corrected to Eh), porosity (estimated from water content), total carbon (combustion analysis; Carlo Erba 1106), organic carbon (measured as the difference between
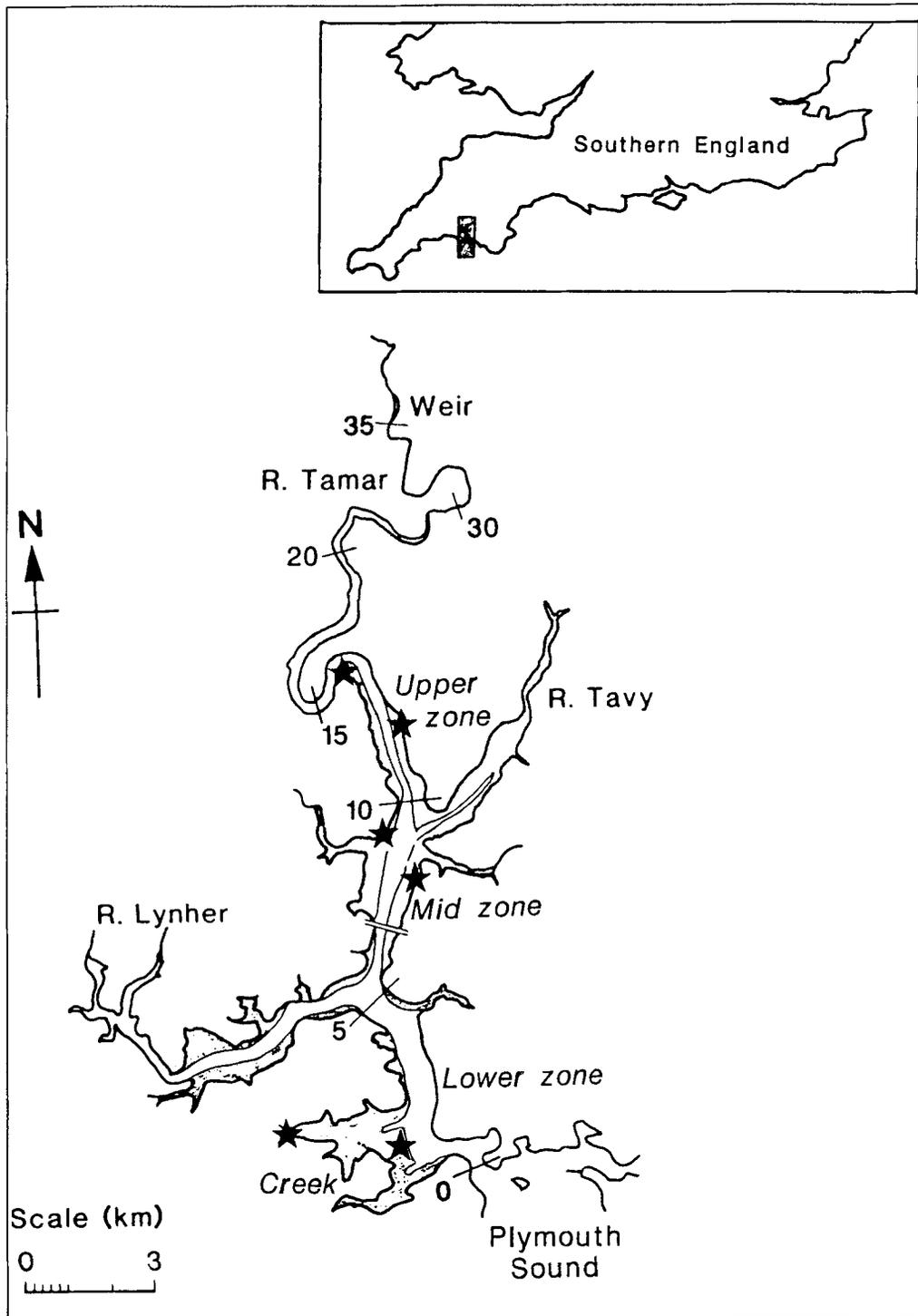
Fig. 1. Location of sediment sampling sites in the Tamar Estuary. Shaded areas represent intertidal mud flats.

total carbon, and total inorganic carbon, after low temperature plasma ashing; Tracerlab LTA- 600) and particle size distribution (percentage > or <63 μm, determined by wet sieving). Macrofauna at each site were sampled using standard coring and sieving procedures (see DAVEY, 1993).

Measured fluxes

Initial field measurements of trace metal fluxes were made at one site using benthic flux chambers consisting of an open, cylindrical, acrylic (perspex) base 60 cm dia., 30 cm long that was pushed into the sediment, and an acrylic, domed lid (fitted with dissolved oxygen, salinity, turbidity and temperature sensors, a variable speed stirrer and sampling ports connected to a vacuum collection system by flexible tubing) together forming a water-tight enclosure with a volume of about 25 l. Bases were installed at low water and as the tidal flow began to cover the sediment the domes were attached and the chambers filled by syphoning in filtered water previously collected from the main channel. This procedure minimised sediment disturbance enabling fluxes to be determined at low turbidities. When the chambers were fully covered samples were collected at hourly intervals for 5-6 h, the overall volume being replenished from a reservoir of the filtered channel water. Stirring was maintained at a rate sufficient to keep the contents mixed without sediment resuspension. The temperature ranged from 15.8-17.1°C during the sampling period. The measured fluxes, calculated from concentration changes in the water within the chamber, were compared with those obtained from sediment cores (20 cm dia. x 20 cm long) collected adjacent to the chambers and incubated in a laboratory microcosm facility. The cores, placed in perspex cylinders in a water tank set to the temperature at the time of sampling (16°C), were supplied with a measured flow of unfiltered, stirred seawater. Sediment-water exchange was determined by

measuring accumulation (or loss) in filtered samples of the overlying water while the input flow was stopped for periods of 5-6h. During this incubation stirring was maintained at a rate sufficient to mix the overlying water column but with no visual sediment disturbance. Agreement between the results was considered satisfactory (see Table 1) and subsequent determinations were made using the microcosm system since this enabled simultaneous flux measurements and coupled pore water sampling, to be carried out on duplicate sediment cores, from each of the six sites, under similar controlled conditions.

Pore water concentration profiles

Pore water samples were collected at 1 cm intervals down to 10 cm; this included both oxic and anoxic horizons and was considered to be a sufficient depth to enable reasonable calculations of diffusive fluxes. Pore waters were collected anaerobically using *in situ* suction samplers (WATSON and FRICKERS, 1990) inserted into each of the microcosm core samples. The samplers were allowed to equilibrate for a minimum of 24 h to minimise the possible effects of atmospheric contamination during implantation. Comparative analyses for dissolved iron, manganese and zinc made on pore waters collected with the *in situ* samplers, in the field, at

Table 1. Comparison of trace metal fluxes (μmol m^{-2} d^{-1}) determined in sediments from the upper zone (14 km from the mouth) (i) in the field (benthic flux chamber) and (ii) in the laboratory (microcosm) in July 1990. Positive fluxes indicate water column gain, negative fluxes water column loss.

| LOCATION | MEAN FLUX [S.D.] n = 3 | | | | | |
	Fe	Mn	Zn	Cu	Ni	Cd
FIELD	37.0	1091	25.7	−8.7	2.9	0.63
	[14.6]	[291]	[9.8]	[0.7]	[1.7]	[−0.33]
LAB	35.0	984	16.8	−7.4	2.3	0.60
	[8.7]	[163]	[7.3]	[0.6]	[1.1]	[0.14]

Table 2. Comparison of mean concentrations of dissolved iron, manganese and zinc (μmol) in pore water samples collected with *in situ* samplers, at two sites in the field (F) and from duplicate cores taken at the same sites and held in a laboratory microcosm (L).

Km FROM MOUTH	Cm DEPTH	Fe(F)	Fe(L)	Mn(F)	Mn(L)	Zn(F)	Zn(L)
9	1	69	96	41	43	0.51	0.49
	2	218	218	44	45	0.50	0.49
	3	269	291	45	45	0.49	0.47
	4	289	328	42	43	0.48	0.50
	5	272	300	41	44	0.41	0.40
	6	187	214	35	38	0.38	0.34
	7	136	123	34	38	0.35	0.32
	8	152	176	33	34	0.40	0.43
	9	123	146	32	33	0.31	0.31
	10	92	90	30	33	0.35	0.32
7.5	1	32	34	21	24	0.40	0.38
	2	33	38	32	26	0.44	0.44
	3	35	36	38	37	0.40	0.44
	4	33	38	28	31	0.36	0.38
	5	24	25	27	27	1.24	1.42
	6	23	23	25	23	0.40	0.37
	7	23	18	28	26	0.77	0.72
	8	18	19	25	26	0.65	0.68
	9	13	12	25	23	0.54	0.51
	10	92	90	27	25	0.32	0.35

two sites at the same time as cores were taken, were in good agreement (see Table 2). However, there was a tendency for the dissolved iron in the field samples to be lower in the 0-3 cm horizon, probably due to slight atmospheric contamination since sampling was carried out within one hour of implantation of the sampler (WATSON and FRICKERS, 1990). Since the microcosm procedure enabled pore water samples to be collected under controlled conditions from the same sediment cores used for the measured flux determinations, it was adopted for all subsequent pore water sampling.

Analytical procedures

Samples for trace metal analysis were acidified to <pH 2 with concentrated nitric acid immediately after collection. Analyses for soluble iron, manganese and zinc were determined by direct flame atomic absorption analysis (Pye Unicam SP9). Analyses for copper, nickel, cadmium and lead were made using ICP-Mass Spectrometry (VG Instruments, Plasmaquad PQ2) following pre-concentration by solvent extraction of APDC/DDDC complexes for flux samples (DANIELSON et al., 1982; STATHAM, 1985) and by coprecipitation of APDC/DDDC complexes using cobalt as a carrier for pore water samples (KLINKHAMMER et al., 1982). Ammonia was determined by semi-automatic flow injection analysis (WILLASON and JOHNSON, 1986) and nitrate, nitrite, silicate and phosphate by standard autoanalyser procedures (Technicon Industrial Systems).

Calculated diffusional fluxes

Concentration gradients derived from pore water profiles were used to calculate theoretical Fickian diffusion fluxes (BERNER, 1980). It was assumed that the gradient between the sediment and the overlying water was linear since it was not possible to obtain samples at greater resolution than 1 cm with the in situ samplers. Sediment diffusion coefficients, adjusted to the sampling temperatures, were derived from seawater values (LI and GREGORY, 1974) and corrected for geometric sedimentary tortuosity using a relationship between porosity and electrical resistivity (ULLMAN and ALLER, 1982).

RESULTS

Sediment characterisation

The sediments at the upper-most and creek sites are poorly sorted medium silts but at the mid and lower sites the sediments are coarser (see Table 3). Sediment organic carbon was higher in the medium silts than in the coarser sediments,

Table 3. Summary of sediment properties. (S) = Summer (August 1990); (W) = Winter (December 1990).

		CREEK	UPPER	MID	LOWER
Wentworth Class		Med. Silt	Med. Silt	Coarse Silt	V. Fine Sand
Mdø		5.76	5.48	4.14	3.71
Porosity	(S)	0.7656	0.8110	0.6550	0.6671
(0-10cm)	(W)	0.8042	0.8099	0.6478	0.6552
% <63 µm		86.6	83.1	52.1	39.9
% Organic	(S)	2.57	2.32	1.47	1.06
Carbon	(W)	1.85	1.78	1.00	1.01
Redox mV	(S)	80	-20	110	90
at 5 cm	(W)	260	225	215	215

and sediment porosity was higher at the upper and creek sites than in the more sandy sediments of the lower regions. The gradient in the organic content was also reflected in the sediment redox potential in the summer, with more reducing conditions at the upper than the lower sites. In the winter there was a marked shift to more oxic conditions, most noticeably at the uppermost and creek sites with further rises in March 1991 up-estuary. In the mid region rises were observed in December 1990 but these had decreased again by March 1991. In July 1991 decreases in redox were observed at all sites, more marked in the upper than in the lower regions.

Macrobenthos

The selected intertidal areas are sites of varying benthic animal activity, mainly deposit feeders (DAVEY, 1993). The uppermost site supports high numbers of the burrowing, irrigating polychaete Nereis diversicolor, varying numbers of the clam Scrobicularia plana and other small surficial dwelling annelids. At the creek site recruitment levels for Nereis are lower. Scrobicularia and the errant polychaete Nephtys hombergi are also present. Moving down the estuary less favourable conditions lead to reduced communities, while nearer to the mouth sediment reworking organisms predominate with populations of Arenicola marina and Nephtys hombergi.

Pore water nutrient concentrations

Despite spatial differences in organic carbon and sediment redox potential, pore water nutrient concentrations over the 0-10 cm profile were not markedly different (Fig. 2 and 3), though nitrite was consistently higher in the upper and creek sites than in the mid and lower regions (not shown). Nitrate was higher at the former sites in winter and at the mid and lower estuary sites in summer.
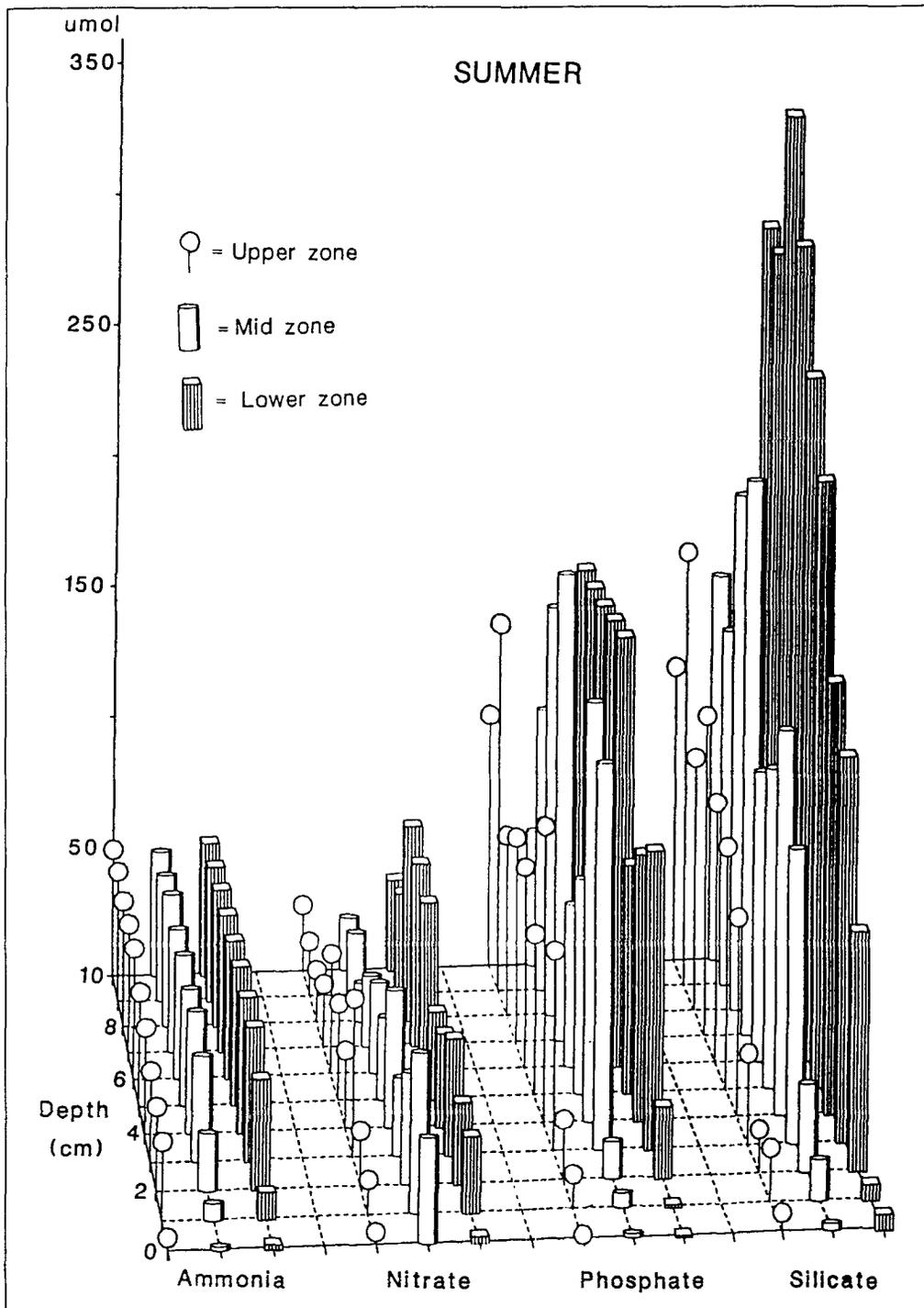
Fig. 2. Depth variation (1-10 cm) in pore water concentrations of nutrients for upper, mid and lower zones in August 1990. Concentration at depth = 0 cm corresponds to that in the overlying water.
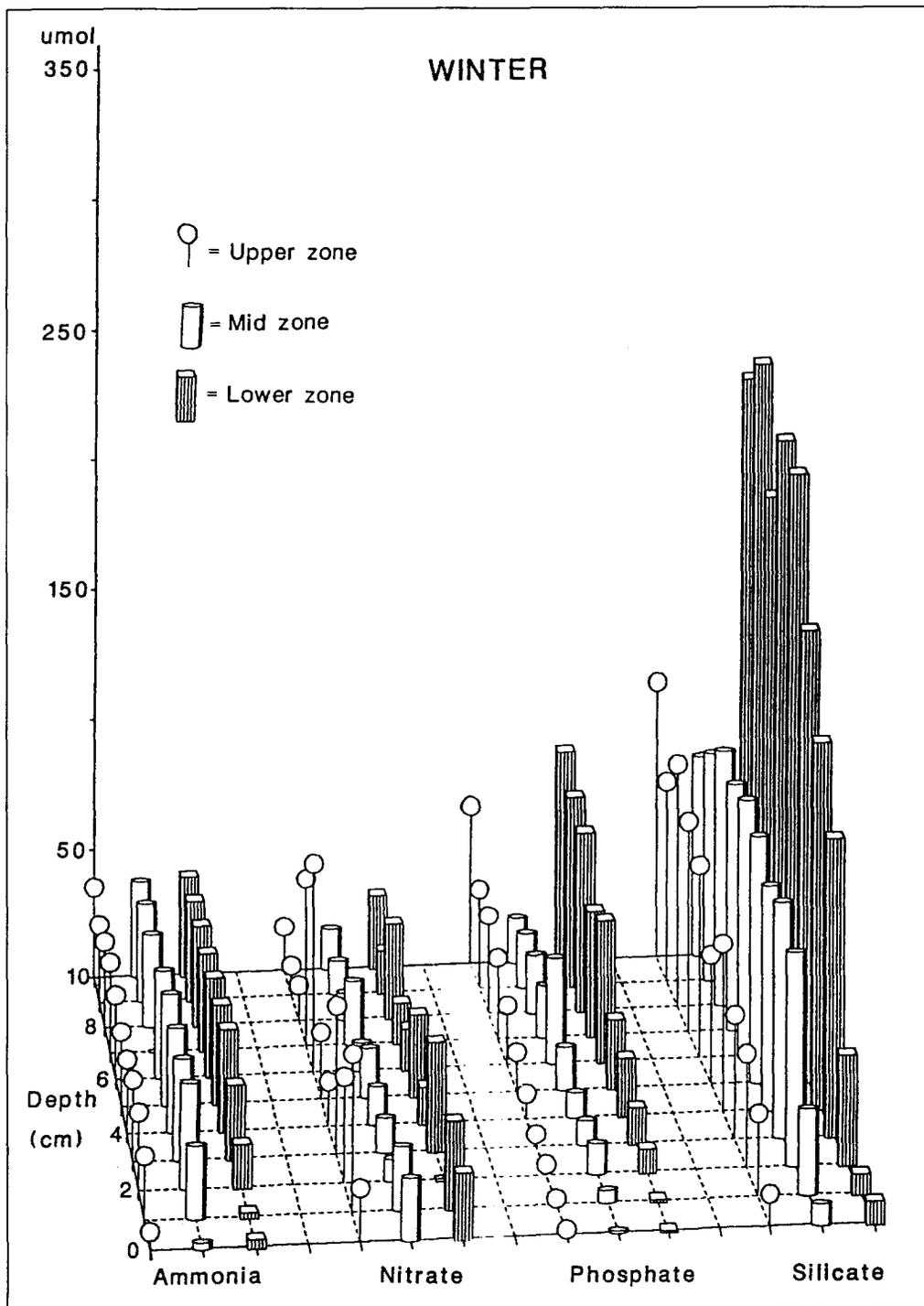
Fig. 3. Depth variation (1-10 cm) in pore water concentrations of nutrients for upper, mid and lower zones in December 1990. Concentration at depth = 0 cm corresponds to that in the overlying water.
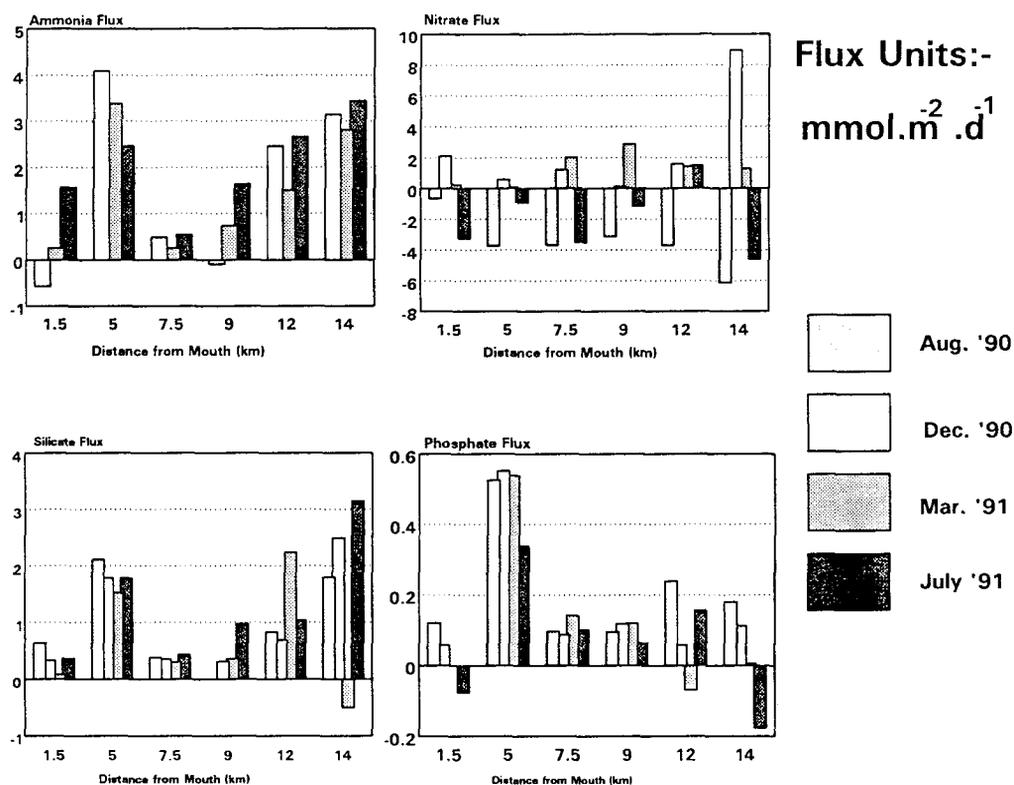
Fig. 4. Seasonal and spatial variation in measured ammonia, nitrate, silicate and phosphate fluxes.

Seasonal variability was also evident for ammonia, nitrite, phosphate and silicate, with pore water concentrations higher in summer than in winter.

Measured fluxes

Spatial differences in measured nutrient fluxes (positive fluxes are defined as sediment loss, negative fluxes as sediment gain) were more marked than seasonal variability (Fig. 4). For all nutrients higher fluxes were determined in the upper and creek sites than at the mid and lower sites. Ammonia, and silicate fluxes were highest in the summer at both regions. Nitrate fluxes showed a striking seasonal reversal (Fig. 4). In the summer when reducing conditions predominated, nitrate was lost from the water column (negative flux). In the winter when the sediments were more oxic, nitrate fluxes were positive. In general the highest positive nitrate fluxes were observed in December 1990, but in the mid-estuary they were higher in March. The largest changes were observed at the site highest up the estuary. Measured fluxes of

nitrite (not shown) were generally elevated in the summer and were markedly high at the creek site.

Phosphate fluxes were high at the creek site (339-552 μmol m^{-2} d^{-1}) compared to a maximum of 239 μmol m^{-2} d^{-1} at the upper and 143 μmol m^{-2} d^{-1} at the mid and lower sites. Silicate fluxes were also higher at the upper and creek sites and were generally lower in March.

Calculated fluxes

Seasonal and spatial variation in measured and calculated fluxes of ammonia, phosphate and silicate are summarised in Table 4. With the exception of nitrite and nitrate, calculated diffusional fluxes of nutrients were always positive since pore water concentrations were greater in the upper 1-2 cm than in the overlying water. Calculated fluxes were seasonally similar. The ratio of measured to calculated nutrient flux was almost exclusively much higher than unity and, with the exception of winter nitrate values, always higher at the upper and creek sites.

Table 4. Comparison of measured (M) and calculated (C) ammonia, phosphate and silicate fluxes (μmol m^{-2} d^{-1}). Positive fluxes represent a net gain, and negative fluxes a net loss, to the water column. ND = Not determined.

Km from mouth	DATE	NH$_4$(M)	NH$_4$(C)	M/C	PO$_4$(M)	PO$_4$(C)	M/C	SiO$_2$(M)	SiO$_2$(C)	M/C
14	AUG 90	ND	164	--	181	33	5	1801	57	31
	DEC 90	3137	82	38	112	3	37	2498	33	75
	MAR 91	2809	82	34	6	2	3	-503	53	--
	JUL 91	3444	62	56	-177	2	--	3150	60	53
12	AUG 90	ND	103	--	239	36	7	833	103	8
	DEC 90	2458	188	13	59	31	2	693	115	6
	MAR 91	1509	116	13	-69	1	--	2245	105	21
	JUL 91	2664	58	46	157	33	5	1038	68	15
9	AUG 90	ND	119	--	96	99	1	0	125	--
	DEC 90	-96	51	--	118	44	3	310	95	3
	MAR 91	739	68	11	119	18	7	366	97	4
	JUL 91	1654	60	28	65	13	5	984	65	15
7.5	AUG 90	ND	61	--	97	9	11	385	97	4
	DEC 90	485	100	5	87	10	9	359	81	4
	MAR 91	245	68	4	143	5	29	305	57	5
	JUL 91	550	65	8	102	18	6	438	78	6
5 (Creek)	AUG 90	ND	34	--	526	65	8	2116	43	50
	DEC 90	4087	81	51	552	84	7	1790	139	13
	MAR 91	3377	54	63	539	33	16	1523	60	25
	JUL 91	2462	51	49	339	23	15	1790	51	35
1.5	AUG 90	ND	111	--	121	31	4	643	122	5
	DEC 90	-574	42	--	59	8	7	336	82	4
	MAR 91	251	75	3	0	10	--	82	57	1
	JUL 91	1567	83	19	-76	18	--	370	150	3

Table 5. Comparison of measured (M) and calculated (C) iron and manganese fluxes (μmol m^{-2} d^{-1}). Positive fluxes represent a net gain, and negative fluxes a net loss, to the water column.

| Km from mouth	DATE	Fe(M)	Fe(C)	M/C	Mn(M)	Mn(C)	M/C
14	AUG 90	26	106	0.3	230	19	12
	DEC 90	84	28	3	491	15	32
	MAR 91	273	43	6	773	57	14
12	AUG 90	173	194	0.9	353	37	10
	DEC 90	153	112	1.4	35	117	0.3
	MAR 91	27	182	0.2	9	63	0.1
9	AUG 90	-31	90	--	10	22	0.5
	DEC 90	27	87	0.3	8	19	0.4
	MAR 91	116	28	4	10	25	0.4
7.5	AUG 90	36	38	1	6	8	0.7
	DEC 90	50	26	2	24	25	1
	MAR 91	32	40	0.8	-23	25	--
5 (Creek)	AUG 90	42	51	0.8	65	2	33
	DEC 90	37	126	0.3	59	7	8
	MAR 91	97	142	0.7	-240	5	--
1.5	AUG 90	149	244	0.6	2	17	0.1
	DEC 90	42	90	0.5	5	8	0.7
	MAR 91	7	74	0.1	3	25	0.1
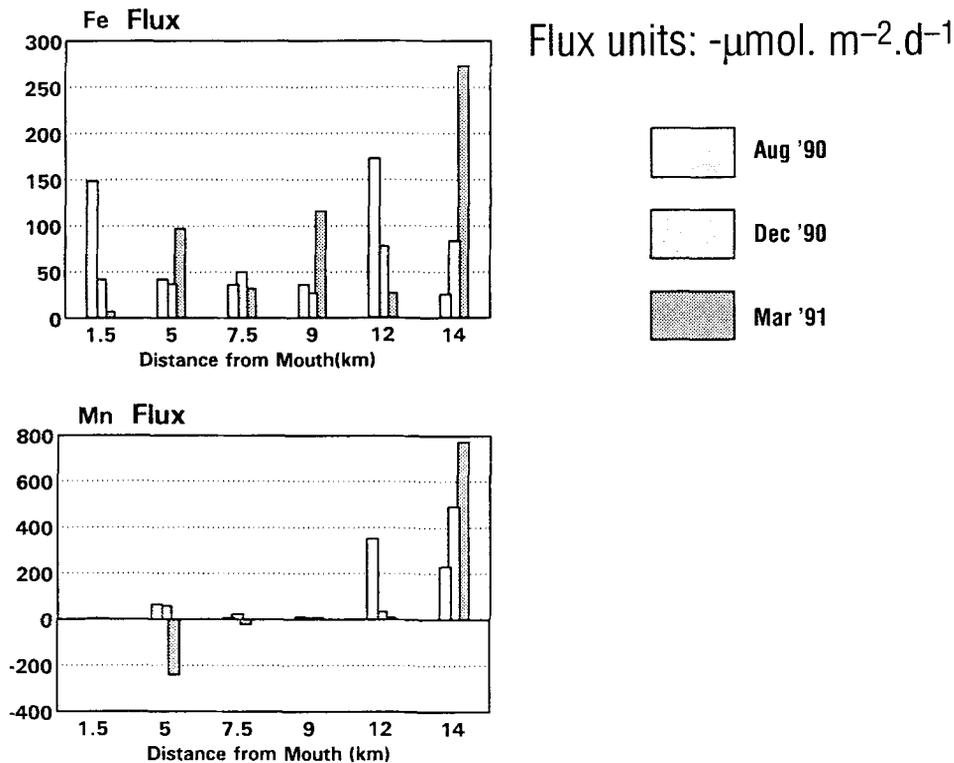
Fig. 5. Seasonal and spatial variation in measured iron and manganese fluxes.

Measured metal fluxes

High positive fluxes of iron and manganese (Fig. 5) were determined in the sediments from the upper sites and, for iron in the summer, in the sediment from the estuary mouth. Summer fluxes of zinc were generally high especially in the sediments from the mid regions (Fig. 6). In contrast copper fluxes were generally low or negative in the summer, and in the winter at the upper and creek sites, but at the mid and lower sites positive fluxes of copper were observed in the winter. Measured fluxes of cadmium were always positive and generally higher in the summer.

Calculated metal fluxes

The calculated diffusive flux of iron was higher for the upper site sediments and, in the summer, for those at the mouth, than for those in the mid region (Table 5). However, the ratio of measured to calculated flux was not markedly different between the two regions and in many cases was less than unity. Calculated fluxes of manganese were also generally higher up-estuary (though not at the creek site) but the measured to calculated ratios were notably greater for both the upper and creek site sediments than for the lower (Table 5). Calculated fluxes of zinc (not shown) were highest in winter in the upper regions and in summer at the mid and lower sites. Calculated fluxes of copper and cadmium showed no marked spatial or seasonal trend.

DISCUSSION

Temporal variations in estuarine sediment-water exchange are due to a range of rates and processes many of which are not well defined. In summer organic matter inputs and sediment diffusion coefficients are higher so that diffusive fluxes of pore water solutes are potentially higher. But increased microbial activity and oxygen consumption result in lowered redox potentials favouring loss of nitrate by denitrification, and the formation of insoluble metal sulphides closer to the
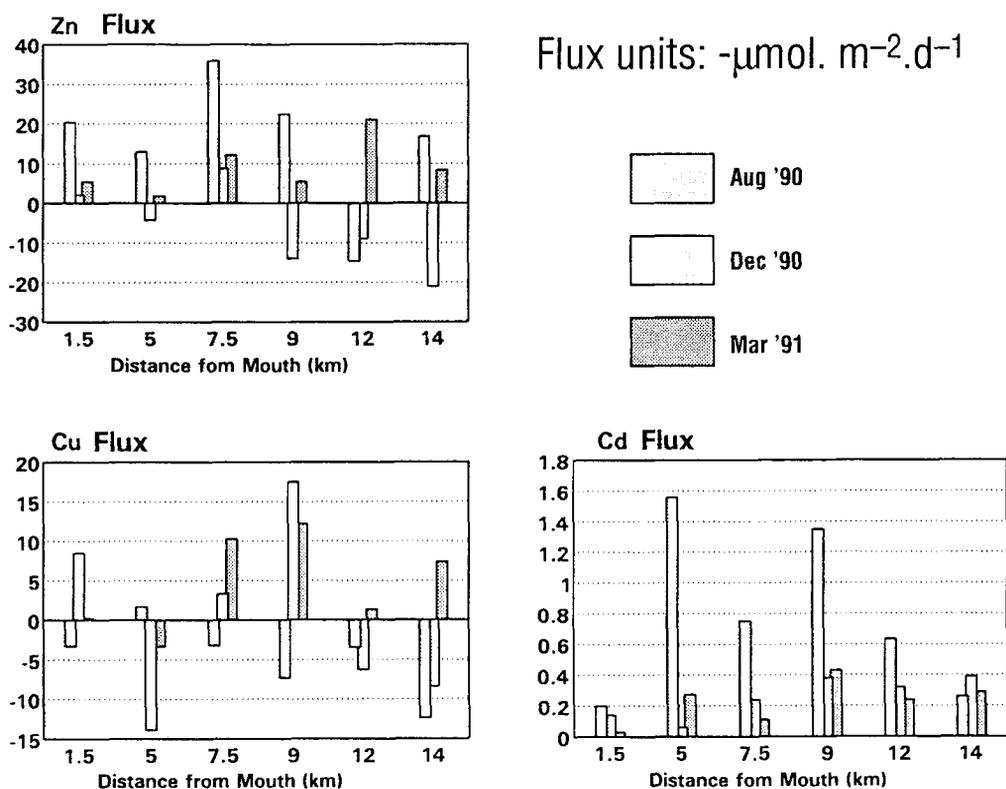
Fig. 6. Seasonal and spatial variation in measured zinc, copper and cadmium fluxes.

sediment surface. In addition to these factors, sediment-water exchanges are affected by seasonally variable physical disturbance and by the burrowing and irrigation of benthic organisms (ALLER, 1982; ALLER et al., 1983).

In this study observed fluxes of ammonia and silicate (Fig. 4) were higher in summer when organic carbon levels were higher and redox potentials lower, but phosphate fluxes were more variable. Extensive nitrate reduction was observed in summer accompanied by high ammonia and nitrite fluxes, providing evidence of both ammonification and denitrification processes (KRISTENSEN, 1988). In the winter measured fluxes were generally lower but the shift to more oxic redox potentials, particularly in the surficial sediment zone, was accompanied by positive nitrate fluxes resulting from nitrification. The trend for nutrient fluxes to increase higher up the estuary and at the creek site where more silty sediments with a higher organic content were present, was not reflected in higher pore water concentration gradients and calculated

diffusive fluxes. It is clear that the observed seasonal changes in sediment organic carbon levels and limited variability in pore water concentration gradients are insufficient to explain the spatial variability in measured nutrient fluxes. Transport of ammonia, nitrite and silicate out of the sediment was considerably higher at the upper and creek sites than in the mid and lower regions. While sediment uptake of nitrate (Fig. 4) was generally similar in the summer (though highest at the most up-stream site), positive nitrate fluxes in the winter resulting from nitrification processes, were more variable. The nitrate flux at the uppermost site was very high in December, in the mid region fluxes were higher in March while at the creek site nitrate fluxes were low at both these times though nitrite fluxes were high. Measured fluxes of ammonia and silicate were far higher than calculated fluxes for sediments from the upstream and creek, than at the mid and lower sites (see Table 4). Fluxes calculated from pore water profiles may differ from measured fluxes due to lack of precision in determining

concentration gradients, in particular close to the sediment surface. However pore water profiles were determined at similar resolution (1 cm intervals) in the sediments from all the sites and it is unlikely that concentration gradients were sufficiently different to explain the spatial variation observed in calculated fluxes. Another potential source of error lies in estimating sediment diffusion coefficients, especially if these are modified by sediment mobilisation or the activities of benthic organisms. All measured flux determinations were made in the absence of physical sediment disturbance but the upper and creek sediments are the habitat of large populations of burrowing and irrigating macrofauna and the high measured to calculated flux ratios at these sites demonstrate that spatial trends in nutrient fluxes are strongly influenced by bioturbational activity. These enhanced fluxes also provide an explanation for the apparent absence of higher pore water nutrient concentrations in the more organic-rich sediments in the upper and creek sites, since increased production is masked by the higher transport out of the sediment. At the most upstream site there was an extensive winter increase in the population density of *Nereis diversicolor* and cores taken at this time contained high levels of juveniles. The irrigational activity of these, particularly in the more surficial oxic sediment, may account for the particularly high nitrate fluxes observed at this time.

Lower down the estuary benthic populations are smaller and sediment reworking rather than irrigation predominates. In this region the winter shift to more oxic redox potentials was less marked and positive nitrate fluxes were higher in March. The *Nereis* community at the creek is not as large as that at the upper site. Recruitment levels are lower, and the population is dominated by large, deep burrowing adults. The shift to more oxic conditions in the winter was more marked in the surface layers, and did not persist to the March sampling. It is possible that surface water is carried by irrigation to deeper, less oxic layers in these sediments, than by the juvenile dominated population at the upper site. If this is so, complete oxidation of ammonia to nitrate (nitrification) could be inhibited at the nitrite intermediate stage (HENRIKSEN and KEMP, 1988), leading to accumulation and the high nitrite fluxes (300-500 μmol m^{-2} d^{-1}) observed at this site, compared to the upper (50-100 μmol m^{-2} d^{-1}) and mid (20-50 μmol m^{-2} d^{-1}) sites.

Phosphate fluxes were generally higher upestuary (60-239 μmol m^{-2} d^{-1}) and particularly in the creek sediments (340-550 μmol m^{-2} d^{-1}). The overall range of measured fluxes was comparable to that reported by CLAVERO *et al.*, 1991, for the Palmones Estuary in Spain (200-500 μmol m^{-2} d^{-1}), despite higher concentrations of phosphate in the Tamar pore waters at depth (up to 150 μmol l^{-1} below 5 cm compared to a maximum of only 30-40 μmol l^{-1} in the Spanish sediment). *Nereis* populations at the creek site were lower (200-500 m^2), but those at the upper site were much greater (2500-4000 m^2) than in the Spanish estuary (300-900 m^2). The reason why much higher phosphate fluxes were not observed at the more bioturbated upper site may also be due to the high proportion of juveniles in the *Nereis* population of these sediments. The surficial burrowing of these juveniles results in oxidation of the surface sediments in the vicinity of the burrow openings with the result that phosphate, transported from the deeper burrows by the adults, is trapped by adsorption onto iron oxides.

The measured fluxes of iron and manganese were also higher in the sediments from the more bioturbated sites although pore water concentration ranges were not spatially very variable. Measured to calculated flux ratios were generally less than unity for iron because of oxidation losses close to the sediment surface, or in the water column during incubations. For manganese, for which oxidation kinetics are slower, measured to calculated ratios were high at the upper and creek sites. Zinc fluxes to the water column were also generally high in the summer, though sediment uptake was observed, particularly at the more bioturbated sites, in the winter. Zinc is strongly associated with iron and manganese oxides (KERSTEN, 1988) and may be released along with these elements in the summer when reducing conditions dominated. However, in the winter when the sediment was more oxic, negative fluxes at the bioirrigated sites may be due to adsorption onto iron and manganese oxide layers at the extended surfaces formed by burrow walls. Copper fluxes were generally low in the summer. Copper is associated with sulphide/organic phases (KERSTEN, 1988) and these may have provided adsorption sites close to the sediment surface in the more anoxic summer conditions. Measured cadmium fluxes were particularly elevated in the mid-estuary and creek site sediments under summer conditions, probably associated with the high iron and zinc transport observed at this time.

CONCLUSION

Laboratory microcosm studies have shown that nutrients (except nitrate) and trace metals are transported out of estuarine sediments under sum-

mer and winter conditions. While temporal differences in nutrient fluxes accord with seasonal factors marked spatial variations were also observed.

Bioturbation resulted in enhanced fluxes, both positive (out of the sediment) and negative (into the sediment), but there were differences between sites where the distribution of adult and juveniles in the *Nereis* population differed and where irrigation or sediment reworking was the predominant activity. Fluxes of trace metals were also seasonally and spatially variable, and specific differences were observed that could be attributed to both chemical and biological activity.

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