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Notes and Discussions

Variations in the Natural Abundance of ^{15}N in Estuarine Suspended Particulate Matter: A Specific Indicator of Biological Processing

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In this study, the $^{14}N : ^{15}N$ ratio of suspended particulate material collected from the Tamar river estuary, south-west England, is described. Three populations of particles, distinguishable by their ^{15}N content, were observed. This investigation has shown that populations of estuarine particles are generated by biological transformations *in situ* and that the ^{15}N content of estuarine particles does not merely reflect hydrodynamic mixing of the freshwater and seawater source particulate material.

Introduction

The composition of particle populations suspended in estuaries is controlled not only by the intermixing of source materials of marine and riverine origins but also by significant *in situ* hydrodynamic selectivity (Schubel, 1969; Officer, 1980), and chemical (Sholkovitz & Price, 1980; Loring *et al.*, 1983) and biological (Morris *et al.*, 1982*c*) modification. The interactions of these mechanisms are complex and there is an urgent need for the identification of particulate constituents which serve as specific indicators of the sources and/or *in situ* processing of estuarine particles. The measurement of the stable isotope ratios of nitrogen ($^{14}N : ^{15}N$) has made a significant contribution to knowledge of the sources and sinks of particulate material in a variety of environments (for example, see Rau, 1981; Saino & Hattori, 1980; Sweeney & Kaplan, 1980; Wada *et al.*, 1981); there is, however, no information on the variations in the natural abundance of ^{15}N in estuaries.

Materials and methods

Descriptions of the Tamar river estuary can be found elsewhere (Morris *et al.*, 1981; 1982*a*, *b*, *c*). In this study, suspended particulate material was collected at intervals along

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an axial section of the estuary from a research vessel fitted with a sub-surface pump which provided water to the shipboard laboratory. Continuous measurements of salinity, dissolved oxygen and turbidity were made using the methods described in Morris *et al.* (1981; 1982*a, b, c*). All other measurements were made on discrete samples collected from a manifold in the pump system. The total nitrogen and ^{15}N content of particulate material were determined simultaneously on GF/C glass fibre filters (previously combusted at 450 °C for 24 h) using the automatic nitrogen-analyser mass-spectrometer apparatus described by Preston & Owens (1983). The ^{15}N content of samples was compared with the isotope composition of local atmospheric nitrogen (LAN) and $\delta^{15}N‰$ calculated as shown in the legend to Figure 1. Phytoplankton biomass was determined by direct microscopic count and measurement to give a volume which was converted to biomass by assuming a density of 1 g cm^{-3}. NH_4 was determined in duplicate on GF/C filtered samples by a modification of the indophenol blue technique (Mantoura & Woodward, 1983).

Results and discussion

The $\delta^{15}N$ values of particulate material collected from the marine (salinity 33·8‰) and freshwater ends of the estuary were respectively, $+4{\cdot}96 \pm 1{\cdot}03‰$ and $+2{\cdot}29 \pm 2{\cdot}23‰$ (values are means of duplicate analyses of triplicate samples and 95% confidence intervals of the mean, see Figure 1). Similar values have been obtained for other surveys in this estuary. At sites intermediate between the freshwater and seawater ends of the estuary, $\delta^{15}N$ values ranged from $+1{\cdot}79 \pm 1{\cdot}63‰$ to $+14{\cdot}73 \pm 0{\cdot}7‰$. The marked difference in ^{15}N content between the estuarine and end-member source particulate material is a clear indication, for the nitrogen fraction at least, that the composition of the estuarine particulate material cannot be accounted for by hydrodynamic mixing of the end-member source particles alone.

A marked turbidity maximum, similar to the one shown in Figure 1, is a consistent feature of this estuary although its location within the estuary and the absolute turbidity vary over both tidal and seasonal scales (Morris *et al.*, 1982*a, b, c*). It can be seen that the highest $\delta^{15}N$ values coincided with the turbidity maximum. The hydrodynamic mechanisms which lead to the formation of estuarine turbidity maxima entrain particulate material thereby effectively increasing the residence time of particles in the estuary. Morris *et al.* (1982*c*) have suggested, based on the measurement of the carbon content of particles, that the material entrained in the turbidity maximum undergoes at least partial microbial degradation. The $\delta^{15}N$ data presented here confirm these observations since isotope fractionation theory predicts, and a study by Wada (1980) has shown, that the microbial mineralization of organic nitrogen leads to a relative enrichment (increase in $\delta^{15}N$) of the refractory nitrogen. In the Tamar estuary this refractory material becomes concentrated in the turbidity maximum (see Morris *et al.*, 1982*c*) and gives rise to the high $\delta^{15}N$ values observed there. A number of other observations presented in Figure 1 provide evidence that the turbidity maximum is a zone of net degradation of organic nitrogen. First, there was a minimum in the percentage nitrogen content (w/w) of particulate material in the turbidity maximum. Second, the distribution of ammonium, a by-product of microbial organic nitrogen mineralization, exhibited a maximum at and seawards of the turbidity maximum (see also Morris *et al.*, 1982*c*). Third, the marked sag in oxygen concentration downstream of the turbidity maximum is indicative of net

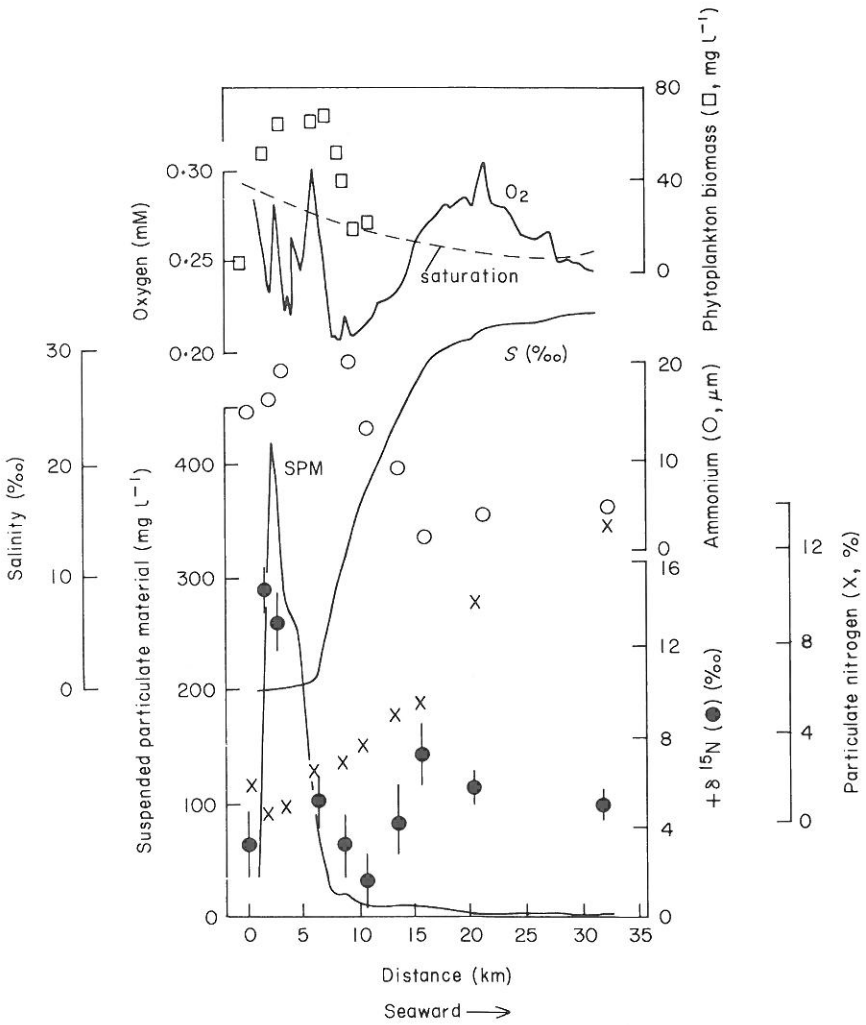

Figure 1. The axial distribution of $\delta^{15}N$ of suspended particulate matter and selected chemical variables in the Tamar river estuary, south-west England, 27 July 1982. The abcissa indicates the distance, seawards, from the upper limit of tidal influence. Suspended particulate material (mg l^{-1}). O_2 (mM) and salinity (‰) were measured continuously during an up-estuary transect on a research vessel fitted with a subsurface pump. The remaining measurements were made on discrete water samples collected on the same transect: $\delta^{15}N$ (mean of six determinations $\pm$ 95% confidence intervals); particulate nitrogen (% by weight); phytoplankton biomass (mg l^{-1}); NH_4 (μM). $\delta^{15}N$(‰) is given by:

$$\delta^{15}N = \left[\frac{^{15}N/^{14}N_{sample} - ^{15}N/^{14}N\ LAN}{^{15}N/^{14}N\ LAN} \right] \times 1000,$$

where LAN is local atmospheric nitrogen.

respiration. It is to be expected that the dissolved tracers of catabolism, for example ammonium and dissolved oxygen, would have a different distribution in the estuary from particulate matter since dissolved species are advected downstream from the turbidity maximum whilst particulate matter is largely constrained within the turbidity maximum zone.

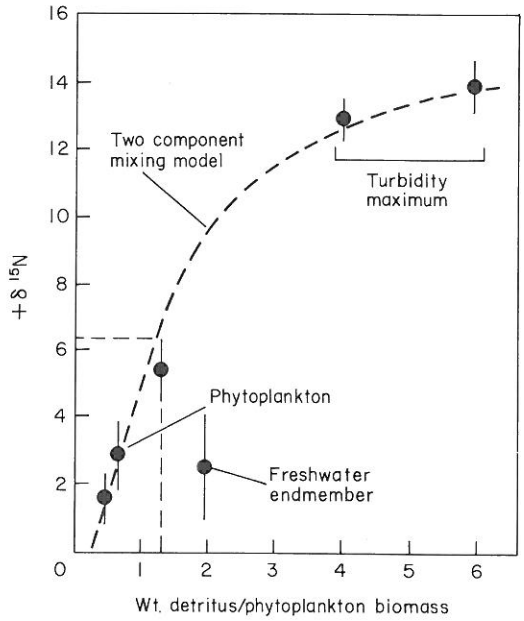

Figure 2. The relationship between the $\delta^{15}N$ (‰) of suspended particulate matter and the ratio of the detrital component of the suspended particulate load (total suspended load − phytoplankton biomass; mg l^{-1}) to the phytoplankton biomass (mg l^{-1}) observed in the Tamar estuary, 27 July 1982. The dotted curve represents the distribution of $\delta^{15}N$ assuming mixing of two components—see text and equation 1. The freshwater endmember material was taken to be the material collected at 0·3 km—see Figure 1.

Particulate material depleted in ^{15}N was found both immediately up and down the estuary from the turbidity maximum. The low $\delta^{15}N$ values (+1·8‰ to +5·4‰) are similar to those of typical terrigenous material, reflecting the dominance of atmospheric nitrogen ($\delta^{15}N \simeq 0$‰) as the ultimate source of nitrogen for terrestrial ecosystems. It can be seen, however, that the low $\delta^{15}N$ values are apparent only where the phytoplankton biomass represents a significant proportion of the total suspended load, suggesting that the low $\delta^{15}N$ material may be phytoplanktonic rather than an accumulation of terrestrial material. In order to distinguish the relative contribution of the various possible sources of particulate material, the ^{15}N data have been compared with a simple two component mixing model (see Figure 2) where:

$$\delta^{15}N = \delta^{15}N_{det} + \left[\frac{1}{1-R}\right]\left[\delta^{15}N_{phyto} - \delta^{15}N_{det}\right], \quad (1)$$

in which the two components are assumed to be phytoplankton ($\delta^{15}N_{phyto}$) and the detrital component of the total suspended particulate load ($\delta^{15}N_{det}$); R is the ratio of the biomass of the two components. In the absence of measured data on the values of $\delta^{15}N_{phyto}$ and $\delta^{15}N_{det}$, a linear least squares regression was performed of R on the $\delta^{15}N$ values observed in the 0–10 km section of the estuary. The regression explained 93·7% of the variance and generated realistic values for the $\delta^{15}N_{phyto}$ and $\delta^{15}N_{det}$ of −5·38‰ and +17·04‰, respectively. These values were used in equation (1) to generate Figure 2. The closeness of fit between the model and the observed $\delta^{15}N$ values indicates, first, that

during this survey the turbidity maximum was composed of only two distinct populations of particles and, second, that the material of low ^{15}N content was phytoplanktonic and distinct from the freshwater end-member material which, clearly, did not conform to the model. The low $\delta^{15}N$ values are in accord with studies of phytoplankton in culture which have demonstrated isotope fractionation effects which give rise to phytoplankton depleted in ^{15}N (Wada & Hattori, 1978); ^{15}N depleted particulate material observed in the surface waters of the Indian Ocean has also been attributed to phytoplankton growth (Saino & Hattori, 1980). Little is known about phytoplankton in the low salinity regions of estuaries; however the $\delta^{15}N$ values presented here are strong evidence for the autochthonous development of phytoplankton in the freshwater–brackishwater interphase of this estuary.

The data for the lower estuary, seawards of the 12 km point, are less clear. The $\delta^{15}N$ values observed of $+4{\cdot}5$‰ to $+7{\cdot}5$‰ were similar to the seawater end-member material ($+4{\cdot}9 \pm 1{\cdot}0$)‰) suggesting that mid-estuarine particles may have been of marine origin. However, the mid-estuarine material was characterized by a high percentage nitrogen composition and coincided with oxygen concentrations above saturation which together indicated that the mid-estuary was a zone of net biogenic production and not merely a sink for marine particles. However, in the absence of data on the ^{15}N content of dissolved inorganic nitrogen in order to establish a mass-balance for ^{15}N these data are equivocal.

The combined evidence, therefore, points to the existence of distinct regions in the Tamar estuary where biologically mediated catabolism and anabolism of organic nitrogen give rise to distinct populations of particles. A compartmentalization of organic carbon in the St Lawrence estuary, Canada, has been shown recently by Tan & Strain (1983) using variations in the natural abundance of ^{13}C. The observations presented here clearly have implications concerning the biogeochemical processes which occur in an estuary. For example, the variability observed in the rate of removal of manganese from solution in an estuary has been attributed to the natural variability in the surface chemistry of particles (Morris & Bale, 1979). The distribution of high molecular weight polyaromatic hydroarbons (PAH) is also linked closely with the distribution of the suspended particulate load (Readman *et al.*, 1982) which has been demonstrated to have potentially significant effects on the bioavailability and toxicity of PAH to invertebrates (Harris *et al.*, 1984).

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