# Particle dynamics, particulate carbon and the oxygen minimum in an estuary

Estuaries Turbidity Particle dynamics Particulate carbon Oxygen depletion

Estuaires Turbidité Dynamique des particules Carbone particulaire Épuisement d'oxygène

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# ABSTRACT

Profiles of suspended particulate load and its organic and inorganic carbon contents as well as salinity, dissolved oxygen, ammonia and divalent manganese have been recorded throughout the mixing region of the Tamar Estuary, Southwest England, in late summer when there was pronounced net oxygen consumption. The results indicate that trapping of particulate organic detritus (of both riverine and marine origins) within the high turbidity zone contributes to the localisation and buffering of the seasonal oxygen demand exerted within the low salinity region of the estuary.

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# RÉSUMÉ

Dynamique des particules, carbone particulaire et minimum d'oxygène dans un estuaire.

Des profils de la charge particulaire en suspension et de sa teneur en carbone organique et minéral aussi bien que des profils de salinité, oxygène dissous, ammoniac et manganèse divalent, ont été enregistrés vers la fin de l'été, lorsqu'il y avait une importante consommation nette d'oxygène, dans la région de mélange de l'estuaire du Tamar, au sud-ouest de l'Angleterre. Les résultats indiquent que le piégeage de détritus organiques particulaires (de provenance fluviale aussi bien que marine) dans la zone de turbidité élevée, contribue à la localisation et au tamponnement de la demande saisonnière en oxygène exercée dans la zone de faible salinité de l'estuaire.

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### INTRODUCTION

Partially stratified to well mixed estuaries usually exhibit a zone of high turbidity within the upper estuary where concentrations of suspended solids can reach several orders of magnitude greater than those carried by the contributory freshwater and marine sources. Postma (1967) and Schubel (1969) have described these features and discussed the combination of hydrodynamic factors which leads to their formation and maintenance; partial analytic treatments have been developed by Festa and Hansen (1978) and by Officer (1980). Significantly, it appears that the maximum turbidity zone acts as a particle trap which retains selected fractions of influxing materials either in suspension or cycling between suspended and deposited states. The Tamar Estuary, Southwest England, generally has a pronounced turbidity maximum in the low salinity region (Morris *et al.*, 1982*a*) which accords closely with the descriptions given by Postma (1967) and by Schubel (1969).

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Geochemical studies of the estuary (Loring *et al.*, 1981) have shown distinctive spatial differences in suspended particle composition indicating particle selectivity within the high turbidity zone.

Progressively from spring to late summer, the Tamar Estuary is subject to oxygen depletion of steadily increasing intensity which maximises in late August to early September. The shapes of the oxygen profiles indicate that the oxygen demand is exerted mainly in the low salinity region (Morris et al., 1982a). This seasonality, together with the closer geographical coupling of the oxygen sag to salinity than to turbidity and the absence of significant local sewage inputs, led to the conclusion that the oxygen distributions could have arisen from immediate net respiration of halophobic freshwater phytoplankton following their advection into the estuary (Morris et al., 1978). However, it is also possible that particulate organic detritus becomes trapped within the high turbidity zone, thereby increasing both the concentration and local residence time of degradable organic material within the low salinity region of the estuary. Evidence that this process contributes significantly to oxygen consumption within the estuary is examined in this work.

## **METHODS**

Sampling was carried out underway during axial traverses of the estuary along the cruise track indicated on the sketch map shown in Figure 1. Water, pumped from a depth of 0.5 m using a submersible centrifugal pump, was passed through a rapidly flushing, constant level reservoir which contained sensors for dissolved oxygen (Yellow Springs Instrument Co. Inc., Model 57 Oxygen Meter), chloride (Philips IS 550-C1 specific ion electrode) and suspended solids concentration (Partech Electronics Ltd., Suspended Solids Monitor, Model



Figure 1

Sketch map of the Tamar Estuary. Bars drawn at 5 km intervals along the axis of the estuary define the distance scale used for the surveys. LP-740-3R). A second reservoir contained the sensing head of an Electronic Instruments Ltd, Salinity Temperature Bridge, Type MC5.

The chloride electrode was used to indicate salinities at low levels ( $<10^{\circ}/_{\infty}$ ). Salinities greater than  $1^{\circ}/_{\infty}$  were recorded using the MC5 Bridge which was calibrated by measuring the salinities of discrete samples, collected at regular intervals throughout each traverse, using an Autolab Inductively Coupled Salinometer. The chloride electrode response was calibrated by direct comparison with the output of the MC5 Bridge. The output of the Partech instrument was calibrated by gravimetric analysis of the discrete samples. Full details of the sampling strategy and analytical methodologies have been reported elsewhere (Morris, 1978; Morris *et al.*, 1978; Morris *et al.*, 1982 *a*).

A subsidiary stream, tapped from the pumped flow, supplied water to an autoanalytical system for the continuous recording of ammonia concentration using a modification of the indophenol blue procedure. Calibration was achieved using the method of standard additions applied to the discrete samples. Samples for manganese analysis were abstracted from the subsidiary flow, filtered through a 0.45  $\mu$ m pore sized membrane filter, acidified to pH <2 with analytical grade hydrochloric acid and stored in polyethylene vials for subsequent analysis by flameless atomic absorption using the method described by McArthur (1977).

Samples for the determination of particulate carbon were collected by filtering measured volumes of estuarine water through combusted (24 hours at 450°C) and weighed Whatman GF/C glass fibre filters which were sealed in aluminium foil during storage and transport. After washing with deionized water, freeze-drying and weighing, each filter was halved and one portion was ashed in an oxygen plasma (IPC 1101 Low Temperature Asher). The samples were then individually ground and homogenised in an agate ball-mill prior to analysing for carbon using the Carlo-Erba 1106 Elemental Analyser. The unashed portion provided an analysis of total carbon. Organic carbon was obtained as the difference between the two assays. Appropriate blank corrections were used.

Surveys of the estuary were carried out during spring tide on the 27 and 28 August, 1980. On the first day, a single axial traverse of the estuary from the mouth to within 3 km of Weir Head (31.3 km above the mouth) was performed. On the second day, repetitive traverses were made through an approximately 10 km stretch of the estuary covering the high turbidity zone. A more extensive penetration into the fresh water than was practicable on the previous day was also achieved. Ammonia determinations and dissolved manganese sampling were confined to the first day; other properties (salinity, dissolved oxygen, suspended load and particulate carbon content) were measured on both days.

# RESULTS

Figure 2 shows the distributions of salinity, suspended solids concentration, oxygen, ammonia, manganese and particulate organic carbon per unit weight of suspended



#### Figure 2

Distributions of salinity  $(^{\circ}|_{\infty})$ , suspended load (mg|l), oxygen  $(^{\circ})$  saturation), ammonia (µg at N|l), dissolved manganese (µg/l) and the organic carbon content (mg/g) of suspended particulates in the Tamar Estuary on 27 August, 1980. Freshwater extensions to the profiles were obtained on the following day at an equivalent time with respect to tidal state.

solids in estuarine profiles measured on 27 August, 1980. The freshwater extensions to these profiles were recorded on the subsequent day, at the equivalent time with respect to tidal state. Both the fresh-water and marine (>  $30^{\circ}/_{\infty}$  salinity) sections of the system had low suspended particulate loads (<2.5 mg/1) comprising highly variable proportions of inorganic and organic carbon. The fractional contributions made by organic carbon to the particulate compositions were generally high in the marine and freshwater sources. Over the two days of this investigation, overall ranges of 75-170 mgC/g in the marine water and 45-107 mgC/g in the freshwater were encountered. Within the estuary, the suspended load increased to ca. 10 mg/1 as the salinity decreased from 30 to  $5^{\circ}/_{\infty}$  and the fractional contribution of organic carbon decreased in approximately linear correlation with decreasing salinity. Below  $5^{\circ}/_{\infty}$  salinity, suspended solids increased sharply with decreasing salinity to a maximum of 271 mg/l at  $0.12^{\circ}/_{\infty}$ salinity and thereafter decreased sharply towards the low value characteristic of the freshwater. Although the concentration of organic carbon increased considerably within the core of this high turbidity zone, concomitantly with the increase in suspended solids concentration, the proportion of organic carbon per unit weight of suspended solids minimised (<40 mgC/g). The upestuarine limit of enhanced turbidity coincided with the limit of marine salt penetration.

Dissolved manganese and ammonia were present in low concentrations in the freshwater and marine contributions to the estuary relative to the high values attained in the low salinity region. Maxima in these constituents coincided some 5 km down-estuary of the turbidity maximum. These distributions could not be attributed to the effects of subsidiary estuarine inputs. Oxygen concentrations exceeded 100% saturation in the freshwater and marine sources. The oxygen concentration carried by the river water decreased sharply in the seaward direction from a point coincident with the limit of salt intrusion. Minimum oxygen (63% saturation) was encountered in the low salinity region, somewhat down-estuary of the turbidity maximum and in approximate coincidence with the ammonia and manganese peaks. Thereafter, oxygen saturation levels increased fairly regularly with respect to increasing salinity towards the supersaturated levels prevalent at the marine boundary.

Repetitive profiling on the second day of the investigation showed that the highest particulate loads occurred consistently within the salinity range 0.1 to  $0.3^{\circ}/_{\infty}$  throughout the tidal cycle but varied markedly in intensity. The most elevated loads (>600 mg/l) coincided with strongest tidal currents whereas the least elevated loads (100-300 mg/l) occurred some 1 to 2 hours after slack water. Clearly, the turbidity maximum was being periodically reinforced at times of high current velocity by scouring of sediment, with net sedimentation at other times.

Variations in the inorganic, organic and total carbon contents of the suspended solids with changes in suspended solid loading, for samples containing greater than 10 mg/l of suspended solids during both days of sampling, are combined in Figure 3. The fractional contributions made by inorganic and organic carbon to the suspended load were highly variable but overall trends were clear. The inorganic carbon content of the particles decreased with increasing suspended load for concentrations less than ca. 100 mg/l, minimised in the range 100-300 mg/l and increased slightly with increasing particulate concentrations above this level. The organic carbon content decreased sharply as particulate concentrations increased up to ca. 200 mg/l and thereafter continued to decrease, but at a much reduced rate with respect to increasing particulate concentration. Total particulate carbon content correspondingly exhibited a slight minimum at around 200 mg/l suspended load.



Figure 3

Organic, inorganic and total carbon contents of the particulate load in the Tamar Estuary on the 27 and 28 August, 1980 as a function of total suspended load for all samples of greater than 10 mg/l total suspended load.

#### DISCUSSION

High fractional contributions of organic (and inorganic) carbon to the total suspended material and oxygen supersaturation in both the riverine and marine inputs to the estuary indicated that living and/or relatively under graded primary production products comprised a high proportion of the particulate inputs to the estuary during this summer investigation. In contrast, resuspended material within the zone of maximum turbidity, predominant at very high suspended loads, was characterised by much lower fractional proportions of organic and inorganic carbon. However, the temporal and spatial variabilities in the suspended load and its inorganic and organic carbon contents within the estuary were not compatible with admixtures of two contributory components only. Under relatively quiescent tidal conditions, when the resuspended contribution to the particulate load within the turbidity maximum was minimal, estuarine turbidities remained high relative to those of the marine and riverine sources indicating the presence of a sub-population of particles persisting more or less permanently in suspension within the turbidity maximum zone. This sub-population had an organic carbon content which was intermediate between the high values characteristic of the inputs and the low values shown by the material undergoing continuous cycling between sedimented and suspended states: its inorganic carbon content was lower than both. These results indicate that the turbidity maximum was acting as a selective particle trap within which degrading organic material of marine and riverine origins tended to remain, initially in suspension, and inorganic carbon was preferentially lost from suspension, presumably by relatively rapid settlement. Duinker et al. (1980) have recently described a similar subpopulation of suspended particles of relatively high organic content in the high turbidity region of the Varde Å Estuary.

The extent to which flocculation of river-borne organic colloids (Sholkovitz, 1976) contributes to the organic carbon content of suspended material trapped within the turbidity maximum zone cannot be ascertained from the present data. Granulometric studies have proved inconclusive on this point although they provide further evidence of particle selectivity. Particle sizing by laser Fraunhofer diffraction (Bale et al., 1982) has shown that particles within the turbidity maximum zone show distinctive size distributions. These are essentially unimodal with a modal size, on a weight-percentage basis, which increases from around 20 µm diameter for the least elevated loads to around 50 µm for loads in excess of 200 mg/l. Elsewhere in the estuary, there is a tendency towards multimodal size distributions in which predominant modes occur at sizes greater than 50 µm diameter.

Investigations of temporal and spatial variabilities in the distributions of dissolved manganese in the Tamar Estuary have shown that pronounced maxima of this constituent in the water column, similar to that reported here, are generated by infusion of sediment pore water during active resuspension of sediment (Morris *et al.*, 1982 b). This process has been identified as an important contributor to manganese cycling in estuaries (Sanders, 1978; Duinker *et al.*, 1979; Sundby *et al.*, 1981).

Moreover, correlations between the distributions and concentrations of ammonia and dissolved manganese in this estuary, as shown by the present data, have served to demonstrate that mid-estuarine inputs of ammonia have the same source (Knox et al., 1981). High concentrations of dissolved manganese in the pore waters are generated by reductive solubilization of particulate manganese. Ammonia is probably produced by bacterial decomposition of organic detritus: inputs of marine and riverine organic detritus must provide the continuous supply of nitrogen required to maintain this process. The geographical displacements of the extreme concentrations of these dissolved constituents from the peak turbidity levels can be attributed to their continuous net seaward transport following generation in comparison with the persistent hydrodynamic confinement of particle resuspension and trapping to the vicinity of the freshwater-brackish water interphase. The distribution of dissolved oxygen observed in this work suggests that oxygen depletion processes evident in the low salinity region of the estuary were related to the ammonia and dissolved manganese generative processes. Oxygen demand can be exerted either by chemical and bacterial oxidative regeneration of the permanently suspended and cyclically resuspended particulate organic detritus which is trapped within the turbidity maximum region or by chemical and bacterial oxidation of reduced chemical species (ferrous iron, ammonia and divalent manganese, for example) which are generated within the anoxic sediment and released by sediment resuspension. Since oxygen concentrations in the low salinity region appear to be well buffered [that is, short-term concentration changes correlatable with semi-diurnal and spring-neap tidal periods are not pronounced (Morris et al., 1982 a)], the more or less permanently suspended trapped particles appear to be the predominant oxygen consumers.

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Oxygen demand exerted within the zone of maximum turbidity can generate a sharp drop in estuarine oxygen concentration, relative to increasing salinity, seaward of the limit of salt intrusion. Thus, although an instantaneous oxygen demand created by influxing riverborne organic particles may, at times, appear quantitatively sufficient to account for the sharp drop in oxygen concentration in the immediate vicinity of the freshwater-brackish water interphase (Morris *et al.*, 1978), this process appears to be less important than the persistent slower degradation or organic detritus which has become trapped within the turbidity maximum zone.

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