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**The Chemistry of the Severn Estuary and the Bristol Channel**

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In an appraisal of water quality in the Severn Estuary, this issue of *Marine Pollution Bulletin*, Owens provides information about the concentrations of nutrients, metals and other determinands. My intention here is to make some brief comments on a few aspects of chemical processes and to suggest a few of the topics which require further research.

**Oxygen**

Owens draws attention to the oxygen sag which is found in the upper reaches of the estuary, especially under summer conditions of low flow and high temperature. The sources and mechanisms controlling the extent and location of the oxygen demand in this part of the estuary have not been fully characterized. Oxidizable inorganic species (nitrite, ammonia, divalent manganese) which are carried into the estuary by the Severn River are mostly lost within the low salinity zone, but their potential oxygen demand accounts for only a very small proportion of the observed oxygen utilization. Furthermore, the riverine flux of dissolved organic carbon is distributed conservatively within the estuary (Mantoura & Woodward, 1983). It is
probable that the oxygen demand is exerted predominantly by particulate organic materials, of natural and anthropogenic origins, which are hydrodynamically localized within the low salinity region, either in suspension or oscillating tidally between suspended and deposited states.

### Dissolved Nutrients and Metals

The waters of the Severn Estuary and Bristol Channel do not constitute a simple two-component mixing gradient between the primary river input and offshore waters. The Severn River supplies only about a quarter of the total freshwater input to the system. The remainder enters through a multiplicity of additional natural and man-made discharges located throughout the system but concentrated around the Outer Severn Estuary (Joint, in this issue of the Bulletin, provides a chart showing the regional subdivisions of the estuary, in his Fig. 1).

Figures 1 and 2 show concentrations of some nutrients and metals within the Inner and Outer Severn Estuary plotted against salinity. Despite the complexity of inputs to the system, it is apparent that some dissolved constituents do show synoptic linear relationships with salinity within this part of the estuary, either consistently (nitrate, dissolved organic carbon) or at certain times (silicate in winter). The primary requirements for this type of distribution are (1) a large proportion of the total input of the dissolved constituent is contributed by rivers and streams, (2) temporal variability in the freshwater concentrations of the constituent is not pronounced and (3) the constituent behaves conservatively or near-conservatively within the estuary. Additionally, any industrial and domestic inputs of such constituents are not highly localized. Under these circumstances, linear correlation with salinity throughout the Severn Estuary can arise because the flow-dominant rivers (Severn, Wye, Avon) are not widely disparate in composition, and differences that occur are largely ameliorated during mixing within the individual sub-estuaries. Estuarine components of predominantly riverine origin which do not show linear correlations with salinity are subject either to pronounced estuarine reactivity (Mn,
Fig. 2) or to appreciable variability, especially seasonally, in their riverine source concentration (phosphate and silicate in summer).

Rivers and streams are the predominant sources of silicate and oxidized inorganic nitrogen (SETWP, 1980). The concentrations of both these nutrients in the influent Severn are higher in winter than in summer. Oxidized nitrogen shows a linear correlation with salinity as does silicate in the winter (Fig. 1), indicating conservative mixing. Utilization of nutrients for diatom growth is severely restricted by the high turbidity of the water in the Inner and Outer Estuary but further seaward there is depletion by primary production in summer, especially within the more productive bays (Abdullah et al., 1973; Morris & Mantoura, 1980; Joint & Pomroy, 1981). The contribution of nitrate to the total oxidized nitrogen is minor everywhere except the highly productive areas of the Bristol Channel in summer (Morris & Mantoura, 1980). The concentrations of dissolved organic carbon consistently show a strongly linear inverse correlation with salinity, indicating conservative behaviour, but with noticeably elevated concentrations in areas of enhanced primary production (Mantoura & Mann, 1978; Mantoura & Woodward, 1983).

The retention time for freshwater within the combined Inner and Outer Severn Estuary ranges from about 45 days under high run-off conditions to about 120 days in summer. The characteristic shapes and temporal variations of the silicate-salinity relationships (Fig. 1) arise from changes in the freshwater loading of silicate over comparable or shorter time scales. The variable curvature in the phosphate-salinity relationships for the upper Severn Estuary is similarly induced by seasonal changes in freshwater phosphate loading, but is also influenced by the appreciable industrial and domestic phosphate inputs to the Outer Estuary; these give rise to a consistent inflexion in the phosphate-salinity relationship, within the range 18 to 25%o, which is often more pronounced than in the examples of Fig. 1.

The distributions of dissolved metals in the Inner and Outer Severn Estuary are largely determined by the magnitude of their riverine flux relative to that delivered through outfalls and by atmospheric deposition, mainly to the Outer Estuary. Metals predominantly of riverine origin (Ni) decrease in concentration regularly with increasing salinity (Fig. 2). The concentrations of metals with sources dominated by anthropogenic outfalls and atmospheric deposition to the Outer Severn Estuary (Zn, Cd) increase with increasing salinity (Fig. 2) through the Inner and Outer Estuary and then decrease, in approximately linear fashion relative to increasing salinity, through the Bristol Channel. Other metals with a more balanced distribution of sources (Pb, Cu) are poorly correlated with salinity within the Inner and Outer Estuary but decrease with increasing salinity further seaward. Apart from cadmium, these trends are much more clearly demonstrated (Fig. 2) by time-averaged data than by the results of individual synoptic surveys, indicating considerable temporal variability in inputs.

Inputs of dissolved Ni via industrial and domestic outfalls are relatively minor, although some of the rivers and streams, especially in the Swansea Bay area, are polluted with Ni from metal processing (SETWP, 1980; Chubb et al., 1980; Vivian, 1980; Abdullah & Royle, 1974). In the case of Cd, and especially Zn, atmospheric inputs account for a large proportion of the total. The predominance of inputs of Cd to the Outer Estuary gives rise to a characteristic distribution with a pronounced peak in water of salinity 18 to 25%o but this fell from 3 µg l⁻¹ in 1975 to less than 1 µg l⁻¹ in 1978 (Fig. 2), indicating a lessening of industrial discharges in the Outer Estuary.

Of the two metals in Fig. 2 which show poor relationships with salinity, a large proportion (58%) of the Pb in solution comes from the atmosphere, two-thirds of the total falling on the Outer Severn Estuary; however, this does not produce a distinctive pattern of distribution although there are locally elevated levels in the vicinity of coastal effluents. Copper, on the other hand, is mainly carried into the region by rivers and streams but, imposed on this, are significant local perturbations by subsidiary inputs and atmospheric fluxes.

Rivers and streams bring 73% of the Mn to the system, roughly equally divided between particulate and dissolved forms (SETWP, 1980). Dissolved Mn from the influent River Severn (average about 40 µg l⁻¹) is mainly lost from solution during transport through the Inner Estuary (Fig. 2); seaward of this zone the concentrations are consistently less than 2 µg l⁻¹, except near coastlines where local effects can be pronounced (Abdullah & Royle, 1974). Two outfalls provide about half of the total supply of Hg (SETWP, 1980; Chubb et al., 1980), one to Swansea Bay and the other to the Outer Estuary where the highest dissolved concentrations (> 50 ng l⁻¹) have been recorded, but this reduced to < 10 ng l⁻¹ in the Central Bristol Channel, increasing to 30–50 ng l⁻¹ in the Outer Channel (Gardner & Riley, 1973). Particulate Hg exceeded 200 ng l⁻¹ in the Outer Severn Estuary, decreasing to 20 ng l⁻¹ in the Outer Bristol Channel. These distributions were attributed to locally pronounced adsorption of Hg by the high particulate loadings of the Outer Estuary.

Seaward of the Inner Bristol Channel, inputs are much less significant in controlling the concentrations of solutes which, in many cases, are distributed in a manner which indicates conservative or near-conservative behaviour during mixing between Celtic Sea water and water characteristic of the Outer Severn Estuary, although localized coastal perturbations of this general pattern are common, especially in the vicinity of larger rivers and their bays. However, biogeochemical processing of elements, which is insignificant within the Severn Estuary, becomes increasingly significant seawards, and is evidenced by seasonal changes in nutrient concentrations and in suspended particulate composition (Abdullah et al., 1973; Abdullah and Royle, 1974). These chemical variations are primarily attributable to primary production within the Bristol Channel which thrives on the rich nutrient supply emanating from the highly turbid, and correspondingly unproductive, Severn Estuary.

The combination of widely distributed sources, temporal variability in anthropogenic inputs and, especially for the nutrients, seasonal variability in riverine concentrations, coupled with the long estuarine flushing time, severely restricts the use of synoptic distributions of dissolved constituents for qualitative and quantitative deductions.
concerning chemical behaviour within the waters of the Inner and Outer Severn Estuary. Under these circumstances, a time-variant modelling approach, such as that used for Cd by Radford et al. (1981), is essential for characterizing and quantifying internal chemical reactions. Cadmium provides a relatively simple example because its dominant inputs are very localized and are not highly variable over short to seasonal time-scales. To treat similarly constituents, like Zn, which have a wide dispersion of significant inputs showing appreciable temporal variability in fluxes, would require a greater discrimination, in both time and space, of inputs and of distributions than is presently available.

**Sediments and Suspended Particulate Materials**

In the course of a multi-element analysis of sediments and suspended material in the Bristol Channel, Hamilton et al. (1979) found that the particulates were mainly rounded quartz grains, limestone, shell fragments and aluminosilicates. Illite dominated the clay fraction, there was abundant iron floc and coal particles were ubiquitous. Appreciable quantities of plastic spherules have also been found in the suspended load and sediments (Kartar et al., 1973; Morris & Hamilton, 1974).

The average bulk chemical composition of silty and sandy sediments is closely similar to world-averaged data and the spreads about the means are small, presumably reflecting a thorough mixing of particles from diverse sources by the great tidal energy of the system. Enrichment of some elements (Li, B, C, N, F, Zn, Br, I, Pb) in suspended materials was attributed to adsorption by iron flocs or to the inclusion of industrial mineral debris and other waste products. However, Hamilton et al. (1979) concluded that the sediments and suspended materials in the Bristol Channel and Severn Estuary were not greatly contaminated in any element. A similar conclusion was reached by Chester & Stoner (1975) who examined the <61 μm diameter fraction of the sediments from the lower Severn Estuary and Bristol Channel; a wide range of elements (Mn, Fe, Cu, Ni, Ga, V, Cr, Ba, Sr) had average concentrations similar to, or lower than, those typically found in unpolluted near-shore regions. However, Sn, Zn and Pb were considerably in excess. The highest concentrations of Zn and Pb (with excesses residing in the non-detrital fraction) were found in the lower Severn Estuary, with intermediate levels in Swansea Bay, suggesting industrial sources. The distribution of Sn was more complex, with relatively high concentrations in the Outer Bristol Channel, away from sources of pollution.

Clifton & Hamilton (1979) measured metal concentrations in dated sediment cores from Newport Deep, Bridgwater Bay and Swansea Bay. The cores from the first two locations had a relatively constant 210Pb activity, indicating unstable deposits (>100 cm deep). The core from Swansea Bay revealed steady accumulation, averaging 0.17 g cm⁻² yr⁻¹; Fe, Zn and Cu in the accreting sediment increased sharply early in the second half of the nineteenth century, coinciding with the industrialization of the region. Since then, there has been a slightly declining trend in Fe and Cu but Zn has continued to increase and there was a sharp increase in deposition of Pb around 1900 followed by a continuing increase to the present time. Isotopic analysis of the Pb burden indicate that 70–75% is carried by coal debris of local origin, the remainder coming from industrial use of imported ores (Hamilton & Clifton, 1979).

Clearly, the estuary has a very large capacity for assimilating particulate contaminants and this generally obviates the use of particulate compositions, and their spatial characteristics, for elucidating aspects of chemical reactivity within the Severn Estuary. The non-detrital character of the excess Pb and Zn suggests hydrogenous activity and the historical evidence provided by sediment cores indicates local industrial and domestic origins. Nevertheless, even for these constituents, elucidation of retention mechanisms and transport routes, enabling precise mass budgets to be formulated, is not at present feasible.

**Organic Compounds**

There have been a few studies of molecular organic constituents, dealing with pollutants rather than natural organic compounds. Analyses for common industrial organochlorine compounds were included in the survey of inputs (SETWP, 1980) but only γ-hexachlorocyclohexane and dieldrin were detected frequently at >2 ng l⁻¹ John et al. (1979), who examined sediments of the drainage system of the estuary, found that nine of the common polycyclic aromatic hydrocarbons were ubiquitous but most abundant in areas of recent coal mining. Cooke et al. (1979) detected several alkanes and polynuclear aromatic hydrocarbons in intertidal sediments but significant levels of polychlorinated naphthalenes, DDT and related species, were not found. Thompson & Eglington (1976, 1978, 1979) concluded that the hydrocarbon content of the sediments is mainly of pollutant origin; the aliphatic hydrocarbon fraction resembled that of biodegraded crude oil, whereas the polycyclic aromatic hydrocarbon fraction was similar to the products of combustion of fossil fuels, especially petroleum.

**Trace Metals in Organisms**

There have been many reports of trace metals in marine organisms from the Bristol Channel and Severn Estuary; see, for example, Fuge & James (1974) and Morris & Bale (1975) dealing with *Fucus vesiculosus*; Butterworth et al. (1972), Nickless et al. (1972), Peden et al. (1973) and Bryan et al. (1980) dealing with invertebrates; Hardisty et al. (1974a,b) and Badsha & Sainsbury (1977, 1978) dealing with fish. Regional variations in metal content of organisms tend to be related to ambient concentrations of the metals in dissolved form but there are exceptions. More studies are needed of the biochemistry of metabolism, accumulation and detoxication; see, for example, Noël-Lambot et al. (1980), dealing with the part played by metallothioneins in the accumulation of cadmium in the tissues of limpets from the Bristol Channel. The levels and forms of metals in organisms must be investigated also in terms of their physiological and ecological implications, through fundamental studies of the performance of organisms in relation to environmental variability.


