

# Processes controlling chemical distributions in the Firth of Clyde (Scotland)

Biogeochemical cycles  
Trace metals  
Coastal waters  
Firth of Clyde  
Principal component analysis

Cycles biogéochimiques  
Métaux traces  
Eaux côtières  
Firth of Clyde  
Analyse en composantes principales

François L.L. MULLER<sup>a</sup>, Philip W. BALLS<sup>b</sup> and Martyn TRANTER<sup>c</sup>

<sup>a</sup> Department of Oceanography, The University, Southampton Oceanography Centre, Southampton SO14 3ZH, United Kingdom.

<sup>b</sup> SOAFD Marine Laboratory, P.O. Box 101, Victoria Road, Aberdeen AB9 8DB, United Kingdom.

<sup>c</sup> Department of Geography, University of Bristol, Bristol BS8 1SS, United Kingdom.

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## ABSTRACT

A total of 28 chemical variables were measured on water samples taken on an approximately longitudinal section of the Firth of Clyde in August 1989, November 1989, March 1990, July 1990 and March 1991. The data were integrated in a study of the overall processes acting on these variables.

The sampling section crossed two mixing zones, *i.e.* the Clyde Estuary Plume ( $30 < S < 32$ ) and the Clyde Sea ( $32 < S < 34$ ), with mixing times of 4-25 days and 60-150 days respectively. The interpretation of the distributional data was complicated in July 1990 by the penetration of an "older" water mass originating from one of the five sealochs bordering the Firth of Clyde. Heterogeneous reactions within the Clyde Estuary Plume generally modified the export fluxes of dissolved trace metals to the Clyde Sea in the order: Fe, Pb > Mn, Co > Zn, Cd, Cu, Ni. In the deep layers of the sealochs, dissolved Pb was scavenged by newly formed hydrous Mn oxides following Mn(II) diffusion from the underlying sediments. Resuspension of bottom sediments was a permanent feature of the inner Firth, although it did not significantly affect the solid-solution partitioning of trace metals. Organic matter decomposition promoted a tight inverse relationship between O<sub>2</sub>-% and pCO<sub>2</sub> in the deep layers (especially in November 1989 and July 1990), as did photosynthetic activity in the surface layers in July 1990. The latter process also manifested itself in the surface depletion of dissolved PO<sub>4</sub>, NO<sub>3</sub>, Si, ΣCO<sub>2</sub>, Fe, Zn and Cd. A ratio P:N:Si:C of 1:9:6:68 was obtained in relation to the uptake of these elements by phytoplankton. Gas exchange at the air-sea interface – coupled with turbulent vertical mixing – was the main process controlling O<sub>2</sub> and CO<sub>2</sub> concentrations in the surface layers in March 1990 and 1991. At wind speeds below 8 m s<sup>-1</sup>, *i.e.* in the absence of bubble-induced gas exchange, O<sub>2</sub> reached saturation in the outer Firth but pCO<sub>2</sub> remained above its atmospheric equilibrium value of 350 ppm. At wind speeds above 12 m s<sup>-1</sup> (March 1990) pCO<sub>2</sub> was close to 350 ppm while O<sub>2</sub> became supersaturated.

Water composition should be examined not only in relation to that anticipated from instantaneous mixing between end members but also in relation to the transit times of water masses. An application of this approach suggests that the inner Firth, situated at the triple junction Clyde Estuary-Sealoch System-outer Firth, is the area where the rates of heterogeneous reactions are fastest.

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## RÉSUMÉ

## Phénomènes contrôlant les répartitions d'éléments chimiques dans le Firth of Clyde (Écosse).

L'alcalinité, l'oxygène dissous, le carbone minéral et organique, les éléments nutritifs ( $\text{PO}_4$ ,  $\text{NO}_3$ ,  $\text{NO}_2$ ,  $\text{NH}_4$ , Si) et les métaux traces dissous et particuliers (Fe, Mn, Zn, Pb, Cd, Co, Cu, Ni) ont été mesurés à cinq reprises entre août 1989 et mars 1991 dans la voie navigable principale du Firth of Clyde. L'ensemble des résultats obtenus peut s'expliquer en fonction d'un nombre restreint de processus physiques, chimiques ou biologiques qui, dans l'ensemble, tendent à produire des gradients de concentration, soit horizontaux, soit verticaux.

Les variations dans l'espace les plus importantes résultent de l'apport des eaux de l'estuaire de la Clyde ( $30 < S < 32$ ) qui se répandent vers le sud et perdent leur identité en débouchant après 4-25 jours sur le Firth extérieur. Au nord et à l'ouest, une troisième masse d'eau – peu souvent renouvelée – occupe les couches profondes des lochs. Dans cette dernière, on observe un excès de Alk,  $\Sigma\text{CO}_2$ ,  $\text{PO}_4$ ,  $\text{NO}_3$  et Mn (dissous et particulaire) et un déficit de  $\text{O}_2$ , Fe, Pb et Cd (dissous) qui sont dus aux actions conjuguées de trois processus: oxydation de la matière organique, diffusion de Mn (II) à partir des sédiments, et réactions d'échange à l'interface solide-liquide de la matière particulaire en suspension. Les échanges solide-liquide à l'intérieur du panache estuarien modifient les apports à la Mer de Clyde de façon plus ou moins importante selon l'élément considéré: Fe, Pb > Mn, Co > Zn, Cd, Cu, Ni. L'oxydation de la matière organique se traduit par une relation inverse entre  $\text{O}_2$ -% et  $\text{pCO}_2$  qui se prolonge vers des valeurs ( $\text{O}_2$ -% > 100 %,  $\text{pCO}_2 < 350 \mu\text{atm}$ ) lors de blooms phytoplanctoniques. Les rapports d'assimilation de juillet (P:N:Si:C = 1:9:6:68) indiquent que les diatomées ne sont pas l'espèce dominante à cette époque de l'année.

La variabilité du régime hydrographique complique l'interprétation des résultats d'autant plus que le transport des masses d'eaux s'effectue à des échelles de temps très différentes. Lorsque ce facteur est pris en compte, il apparaît que le Firth intérieur (qui communique avec l'estuaire, le Loch Long et le Firth extérieur) représente la région la plus active du système en ce qui concerne les réactions d'échange solide-liquide.

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## INTRODUCTION

The Firth of Clyde is a partially enclosed coastal basin on the south-west coast of Scotland (Fig. 1). It is bordered in the north by five sealochs and the Clyde estuary. The basin receives two thirds of its total freshwater input, together with a wide range of potential pollutants, from the Clyde Estuary (Mackay and Leatherland, 1976; Muller *et al.*, 1994). In the southwestern part of the basin a sill at a depth of 50 m restricts the exchange of water and sediments with the adjacent continental shelf seas. For most of the year a hydrographic front persists on the sill (Dooley, 1979; Edwards *et al.*, 1986), separating the normally stratified waters of the Firth of Clyde from the tidally well mixed waters of the adjoining North Channel. This stable front is produced by comparable contributions of buoyancy supplied by seasonal heating and by freshwater (Simpson and Rippeth, 1993). These geographical and hydrological constraints produce a typical fjordic regime whereby the discharge of freshwater in the northern part of the system creates a low-salinity plume flowing seaward and a compensating inflow of seawater over the sill. In addition, large volumes of high-salinity water may be cut off from

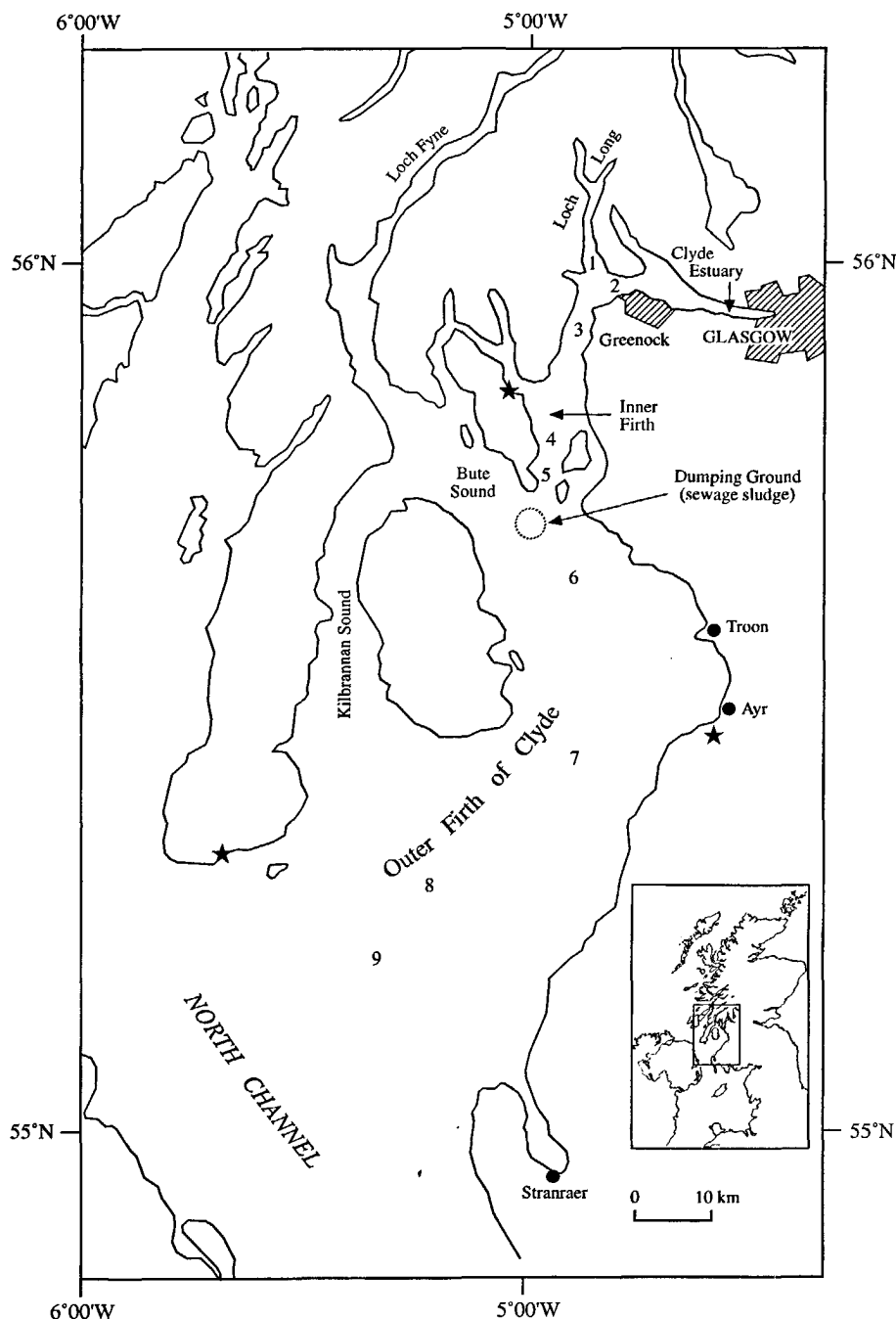
this circulation as they lie stagnant in the deep layer of the sealochs. Therefore the interpretation of element-salinity relationships is likely to require not only a basic understanding of the water masses present at the time of sampling but also of their mixing history. While these characteristics may restrict the unambiguous use of salinity as a mixing indicator, the weakness in the barotropic tidal stirring acting near the bottom (Simpson and Rippeth, 1993) and the presence of the frontal zone at the marine boundary help preserve the integrity of distinct water masses. Their spatial and temporal separation provides an ideal opportunity for examining the processes controlling the behaviour of minor and trace elements in a coastal environment, provided the rates of these processes are not much slower than mixing rates.

There are very few studies of the oceanographic processes controlling the chemical distributions (inorganic and organic carbon, nutrients, trace metals) observed at different times of the year in an estuary or a shelf sea. In part, this is because of a failure (*e.g.* this study) to identify or measure the key physico-chemical variables controlling specific microscopic processes. Certainly, measurements of the changes in overall variables cannot provide the key to specific mechanisms. Another difficulty is that large data sets

Figure 1

Map of the Firth of Clyde with sampling stations 1-9.

Localisation des stations de prélèvement occupées dans le Firth of Clyde en 1989-1991.



are often broken up in order to produce several papers, thus placing on the reader the burden of reconstructing the important oceanographic processes which act across the whole range of variables. This study is an attempt to rationalize our extensive chemical observations of the Firth of Clyde, between August 1989 and March 1991, in terms of the main physical and biogeochemical processes producing those observations. As a means of presenting and interpreting a large data set, this approach has obvious advantages over that which consists of cataloging the distributional data for the individual variables. In addition, we hope that it will assist the reader in conceptualizing the "behaviour" of the Firth of Clyde as a chemical system.

In the pictorial representation of the data by the above approach, no more than three variables at a time could be examined. Although a preliminary data analysis based on scatter diagrams did show several bivariate relationships,

we also examined relationships among the original set of variables by principal component analysis. We carried out this analysis with the aim of providing a two-dimensional representation of the entire data set which still retained most of the original information. The significance of this procedure is that it revealed the grouping of variables according to characteristics of the system which were not explicitly measured (Meglen, 1992). We show that these characteristics are consistent with the oceanographic processes studied independently.

## MATERIALS AND METHODS

Vertical sampling of the water column took place in Loch Long (station 1), the inner Firth (stations 2-5) and the main waterway of the outer Firth of Clyde (stations 6-9) on the fol-

lowing dates: 20-21 August 1989 (outer Firth excluded), 20-22 November 1989, 20-25 March 1990, 2-4 July 1990 and 1-5 March 1991. At each station five samples were taken to provide a resolution commensurate with the expected characteristics of the water column. We used Teflon-lined 2.5 litre Go-Flo sampling bottles, modified and rigorously cleaned to reduce the contamination potential for trace metals, deployed on a Kevlar line for use with custom-made PTFE messengers (August 1989) or on a stainless steel hydrowire (all other times). Samples for pH, salinity, alkalinity, nutrients and dissolved trace metals were pressure-filtered directly from the Go-Flo bottles through in-line 0.4  $\mu\text{m}$  Nuclepore filters, while keeping the receiving bottles and custom-made PTFE filter blocks enclosed in clean plastic bags. A complete description of initial sample processing and handling, as well as subsequent analyses in the land-based laboratory, is given by Muller *et al.* (1994). In all, 28 variables were measured: salinity, dissolved oxygen, pH, alkalinity (Alk), dissolved and particulate organic carbon (DOC, POC), nutrients ( $\text{PO}_4$ ,  $\text{NH}_4$ ,  $\text{NO}_3$ ,  $\text{NO}_2$ , Si), total dissolved and total particulate trace metals (Fe, Mn, Zn, Pb, Cd, Co, Cu, Ni) and suspended particulate matter (SPM). Detection limits and precisions are given in Table 1. Accuracy was tested with each extraction batch by measurement of CASS-2 reference seawater. Quality control for all chemical data is crucial to the accurate measurement of input and output fluxes, the construction of annual mass balances for the system of interest (Muller *et al.*, 1995), and to the evaluation of its sensitivity to any scenario of modification to these inputs. The Firth of Clyde is a case in point, as the dumping of industrial wastes is being phased out while the dumping of sewage sludge off Garroch Head (Fig. 1) is to continue until the end of 1998 when all licences for disposal of sewage sludge at sea will be terminated (MAFF, 1992; MAFF, 1994).

## RESULTS AND DISCUSSION

Only the most representative data is presented below as an illustration of specific processes. Copies of the complete

data set, *i.e.* 181 samples  $\times$  28 variables, are available on request from the first author.

### Mixing of waters of different origins

The seasonal cycle of stratification and mixing in the Firth of Clyde has recently been studied by Simpson and Rippeth (1993). They point out that the entire system may be regarded as a ROFI (Region Of Freshwater Influence) in which seawater from the adjoining North Channel ( $S = 34.0$  psu) is measurably diluted by rain and runoff to salinities between 30 and 34 psu. The zone of direct influence of the Clyde Estuary, thereafter referred to as the Clyde Plume, is characterized by the lowest salinities within this range on account of the fact that two thirds of all freshwater inputs to the system pass through the Clyde Estuary. Alkalinity-salinity relationships provided the only reliable method of determining the exact boundaries of the Clyde Plume. At salinities lower than 32 psu, a linear relationship showing significant seasonal variations was observed (Fig. 2). These variations were caused by the dilution of freshwater alkalinity exported from the estuary at times of high precipitation and river discharge. Above 32 psu a permanent relationship was observed, which implied that variations in freshwater alkalinity supplied to that part of the system referred to as the Clyde Sea were averaged out over the residence time of freshwater in the Clyde Sea. The breakpoint occurred at  $S = 31.9$  psu – except in July 1990 when it occurred at 32.8 psu – and marked the boundary of the Clyde Plume, *i.e.* the region directly influenced by inputs of dissolved constituents from the Clyde Estuary. At any period of observation other than March 1991 the relationship within the plume was highly linear, which in turn implied that the mixing time in the plume was shorter than the time scale of variations in the EZS (effective zero-salinity) alkalinity. Although the frequency of our measurements did not allow us to resolve this time scale, we note that it must relate to some characteristic frequency in rainfall or freshwater runoff and that both records show a peak at approximately 1 cycle per 45 days (Muller *et al.*, 1995), *i.e.* in addition to the anticipated annual frequency. A cha-

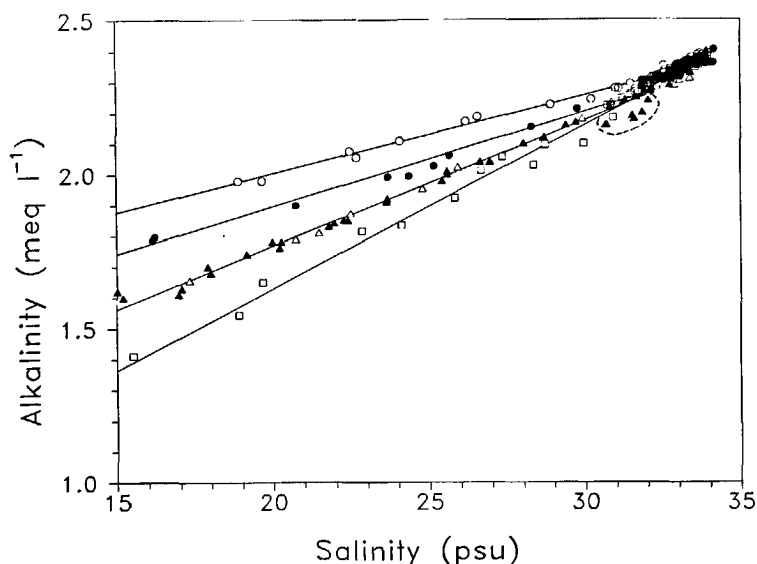


Figure 2

Alkalinity relationships in the Firth of Clyde ( $30 < S < 34$ ) and the lower Clyde Estuary ( $15 < S < 30$ ) over the following sampling periods: ( $\Delta$ ) 20-21 August 1989, ( $\bullet$ ) 20-22 November 1989, ( $\square$ ) 20-25 March 1990, ( $\circ$ ) 2-4 July 1990, ( $\blacktriangle$ ) 1-5 March 1991. Note that the August 1989 ( $\Delta$ ) and March 1991 ( $\blacktriangle$ ) relationships are undistinguishable.

Relations alcalinité-salinité pour les échantillons du Firth of Clyde ( $30 < S < 34$ ) et de l'estuaire de la Clyde ( $15 < S < 30$ ) collectés au cours des périodes suivantes : ( $\Delta$ ) 20-21 août 1989, ( $\bullet$ ) 20-22 novembre 1989, ( $\square$ ) 20-25 mars 1990, ( $\circ$ ) 2-4 juillet 1990, ( $\blacktriangle$ ) 1-5 mars 1991. Les tracés pour août 1989 ( $\Delta$ ) et mars 1991 ( $\blacktriangle$ ) se superposent.

racteristic time scale of 45 days would indeed exceed the flushing time of the estuary + plume (8-30 days, as shown in Fig. 3), as estimated by the method of Kaul and Froelich (1984) from daily river discharge data and salinity measurements at stations 2-5 (Muller *et al.*, 1995). This is not to argue that variability in EZS values do not also occur on time scales shorter than mixing time. Rather, it would seem that such time scales are probably too short (minutes-hours) to have a major influence in perturbing the relationship of alkalinity – or any other conservative property – with salinity. The arguments presented above help explain why a steady-state balance between input and mixing terms is approached most of the time. Nevertheless, especially during the very short transition periods from persistent high flow to very low flow conditions, deviations from steady-state may occasionally be observed. As an example, heavy rainfall over a short period at the end of February 1991 contributed to a 10-fold increase in freshwater discharge immediately prior to our survey. The cluster of points circled in Figure. 2 originated from a buoyant lens of fresher water left over from the short-lived high flow

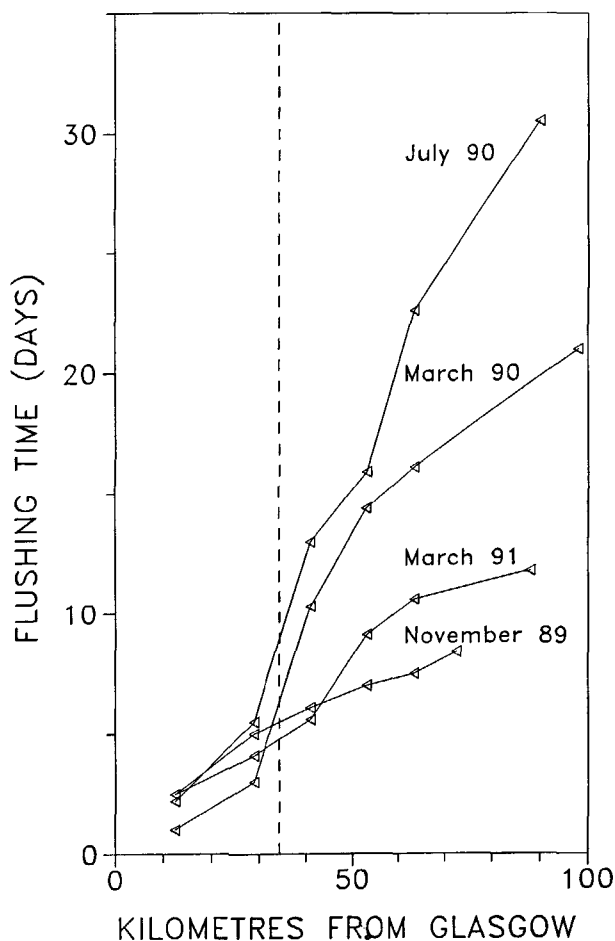


Figure 3

Cumulated flushing time diagram for the fresh water flowing from the mouth of the Clyde Estuary (dashed line) to a distance measured from the head of the estuary, i. e. in central Glasgow.

Temps de résidence moyen dans le système (estuaire + zone côtière) d'un volume élémentaire d'eau douce, en fonction du point kilométrique compté à partir du centre de Glasgow. La ligne brisée verticale indique la limite de l'estuaire.

regime. They are not related to any *in situ* process removing alkalinity and, as a result, do not form a distinct grouping when alkalinity is plotted versus a constituent whose EZS variations with freshwater discharge parallel those of alkalinity (Fig. 4a). An indication that mixing time in the plume was short is given by the fact that, only nine days after the peak discharge, the new Alk-S relationship was again represented by a straight line (Fig. 2).

As noted earlier, large volumes of high-salinity water may be trapped for the greatest part of the year or longer in the deep troughs running through the sealoch system as well as the Bute and Kilbrannan Sound (Dooley, 1979). A combination of surface cooling and wind stirring, usually in late autumn, is known to weaken the density stratification and favour the exchange between these protected deeper waters and the waters of the outer Firth of Clyde (Simpson and Rippeth, 1993). Least expected, however, was the presence

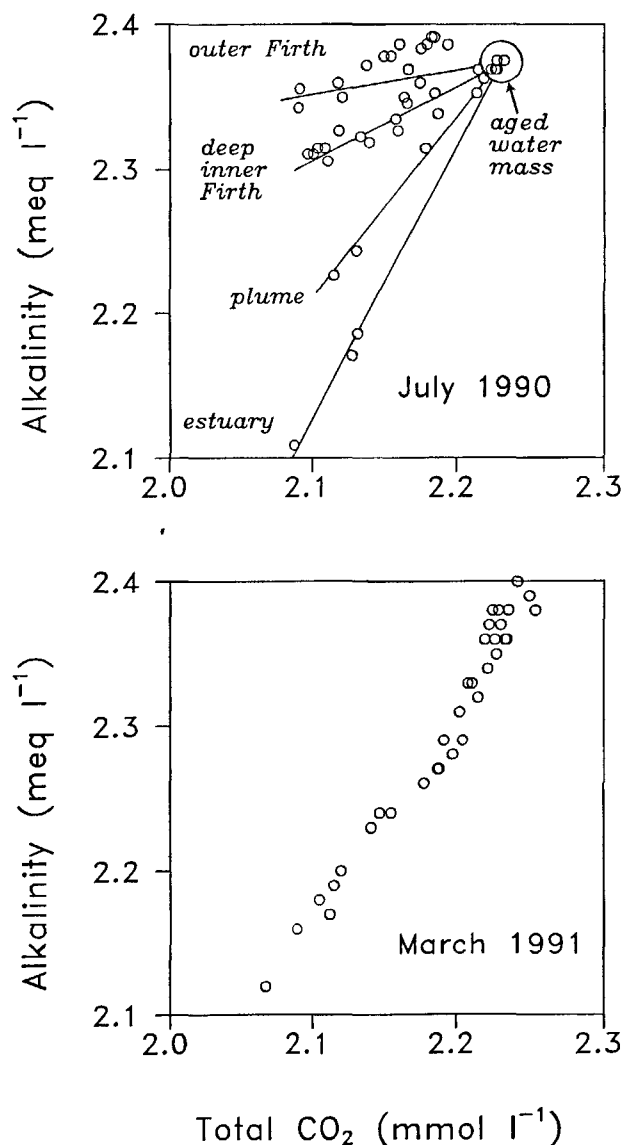


Figure 4

Alkalinity- $\Sigma\text{CO}_2$  mixing relationships in the Firth of Clyde in July 1990 and March 1991.

Relations alcalinité-salinité pour l'ensemble des échantillons prélevés en juillet 1990 et en mars 1991.

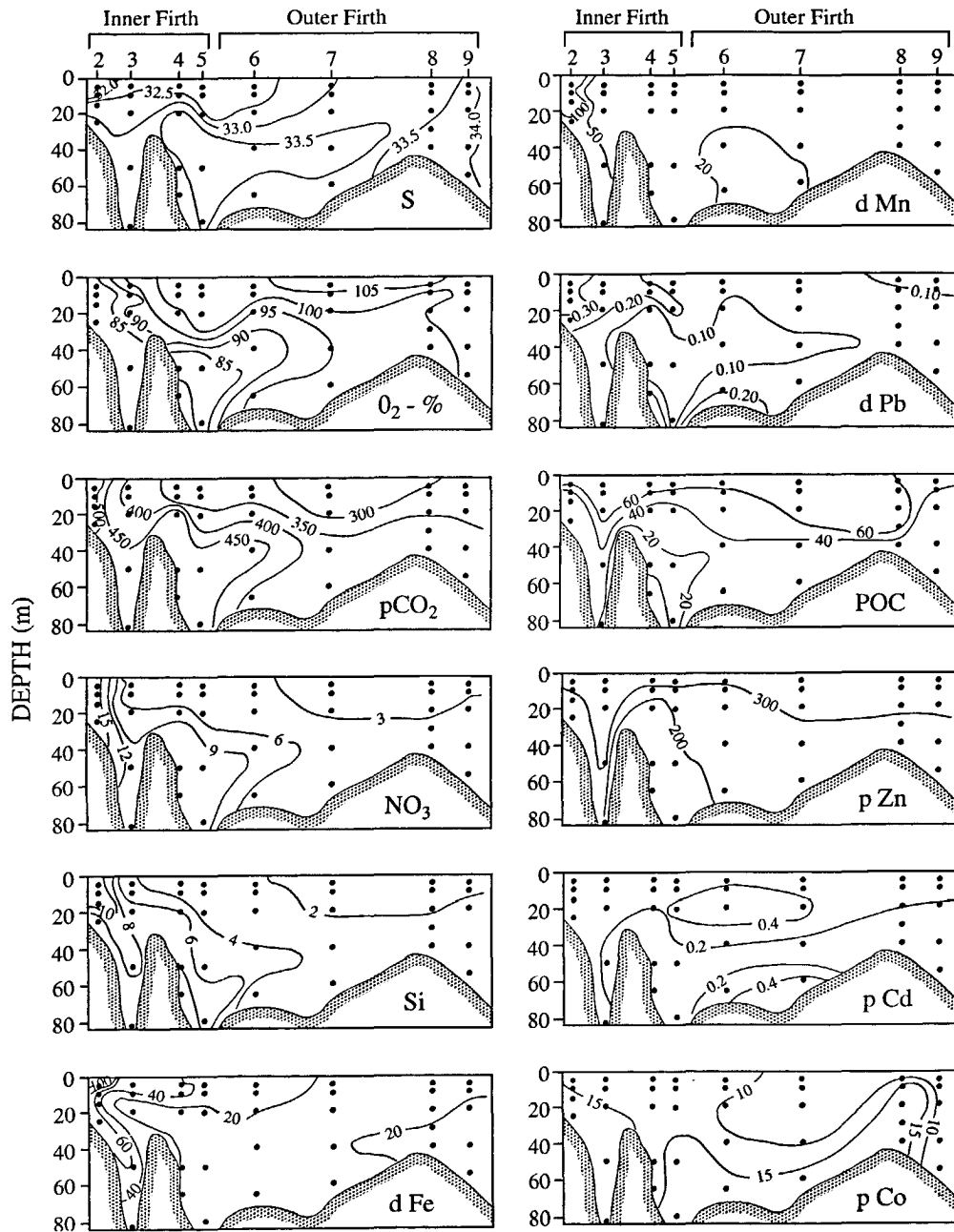


Figure 5

Hydrographic section of the main basin of the Firth of Clyde (July 1990) showing,  $S$  psu,  $O_2$ -% (of the value at saturation),  $pCO_2$   $\mu$ atm,  $NO_3$   $\mu$ mol  $l^{-1}$ ,  $Si$   $\mu$ mol  $l^{-1}$ , dissolved  $Fe$  nmol  $l^{-1}$ , dissolved  $Mn$  nmol  $l^{-1}$ , dissolved  $Pb$  nmol  $l^{-1}$ ,  $POC$  %, particulate  $Zn$  mg  $kg^{-1}$ , particulate  $Cd$  mg  $kg^{-1}$ , particulate  $Co$  mg  $kg^{-1}$ . Station numbers correspond to those given in Figure 1.

Coupe verticale du Firth of Clyde (juillet 1990) montrant :  $S$  (psu),  $O_2$ -% (% de la valeur à saturation),  $pCO_2$  ( $\mu$ atm),  $NO_3$ , ( $\mu$ mol  $l^{-1}$ ),  $Si$  ( $\mu$ mol  $l^{-1}$ ),  $Fe$  dissous (nmol  $l^{-1}$ ),  $Mn$  dissous (nmol  $l^{-1}$ ),  $Pb$  dissous (nmol  $l^{-1}$ ),  $C$  organique particulaire (en % de la matière particulaire en suspension),  $Zn$  particulaire (mg  $kg^{-1}$ ),  $Cd$  particulaire (mg  $kg^{-1}$ ),  $Co$  particulaire (mg  $kg^{-1}$ ).

of a density inversion (higher salinity and lower temperature) in mid-water observed at stations 4, 5 and 6 during the July 1990 survey, especially since it was not picked up by Simpson and Rippeth (1993) in their higher-resolution survey conducted two weeks earlier throughout the entire Firth of Clyde. We believe that some unspecified hydrological and meteorological conditions resulted in high-salinity water from the Bute Sound to spill into the main stem of the Firth of Clyde (perpendicularly to, and into, the Figure 5 section) and progress as an intrusion along the

main axis of the inner and outer Firth of Clyde, at about 50 m depth. This intrusion event had a profound influence on the chemical distributions in the main basin (Fig. 5). Compared with isohaline waters of the "normal" circulation cell, from which it is decoupled, this water mass was enriched in  $\Sigma CO_2$  and nutrients but depleted in dissolved oxygen and most dissolved trace metals. The juxtaposition of this older water with (a) estuarine water, (b) Clyde Plume water modified by photosynthetic activity, and (c) outer Firth surface waters, likewise modified, resulted in a com-

plex mixing pattern as illustrated by the Alk- $\Sigma\text{CO}_2$  diagram (Fig. 4b). The core of the older water had temperature and salinity characteristics ( $S = 33.65$  psu;  $T = 10.0^\circ\text{C}$ ) very close to those measured by Simpson and Rippeth (1993) in the Bute Sound deep water ( $S = 33.73$  psu;  $T = 9.5^\circ\text{C}$ ), and indeed to the ones we had measured on the Great Plateau (station 9) 14 weeks earlier ( $S = 33.65$  psu;  $T = 9.6^\circ\text{C}$ ). In Table 2 the chemical composition of the older water (July 1990) is presented, together with that of water flowing from the North Channel and that we assume to have propagated up the length of the outer Firth of Clyde in March 1990. From the apparent utilisation of  $\text{O}_2$  and production of  $\text{PO}_4$ ,  $\text{NO}_3$  and  $\Sigma\text{CO}_2$ , an overall stoichiometry of the elemental composition of the material undergoing oxidation in the deep layers is obtained, namely

$$\text{P:N:C:-O}_2 = 1:12:270:570$$

By comparison, the Redfield ratio revised by Takahashi *et al.* (1985) is 1:16:122:172, while the average composition of soil-derived organic matter is in the range 1:12-23:130-510: - (Buffle, 1988; Hecky *et al.*, 1993). The latter ratios are closer to the present observations. This indicates the importance of (a) oxidation of organic matter derived from the surrounding land masses, or (b) respiration by benthos, fish, bacteria etc., by comparison with (c) oxidation of material of marine origin.

### Particle-solution interactions involving trace elements

Although the gradients in physico-chemical parameters such as salinity and pH are less pronounced in the Firth of Clyde than in the Clyde Estuary, the residence time of water increases in the order Clyde Estuary (3-7 days) < Clyde Plume (4-25 days) < outer Firth of Clyde (60-150 days), which potentially allows heterogeneous reactions to become significant in the Firth of Clyde. Consequently, we examined the potential of heterogeneous reactions to influence the distribution of trace elements and their particle-solution partitioning in the two water masses discussed above, namely the Clyde Plume (all seasons) and the older water intrusion of July 1990. It is important to mention at the outset that SPM concentrations in the plume were confined, in time and space, to a relatively narrow range ( $0.4\text{-}1.0 \text{ mg l}^{-1}$ ). Under these conditions, it seemed legitimate to try and relate the extent to which dissolved trace metal fluxes were modified by addition or removal in the plume to the hydraulic residence time of the latter.

Figure 6 gives an indication of the extent to which dissolved metal fluxes are modified through particle-solution interactions during transit in the Clyde plume. For example, a  $F_P/F_E$  ratio of 1 indicates that the net export flux  $F_P$  is essentially equal to the primary estuarine flux  $F_E$ . For the purpose of calculating its flushing time, the plume was divided into a series of four boxes straddling sample positions 2-5 and the lower and upper estuary were repre-

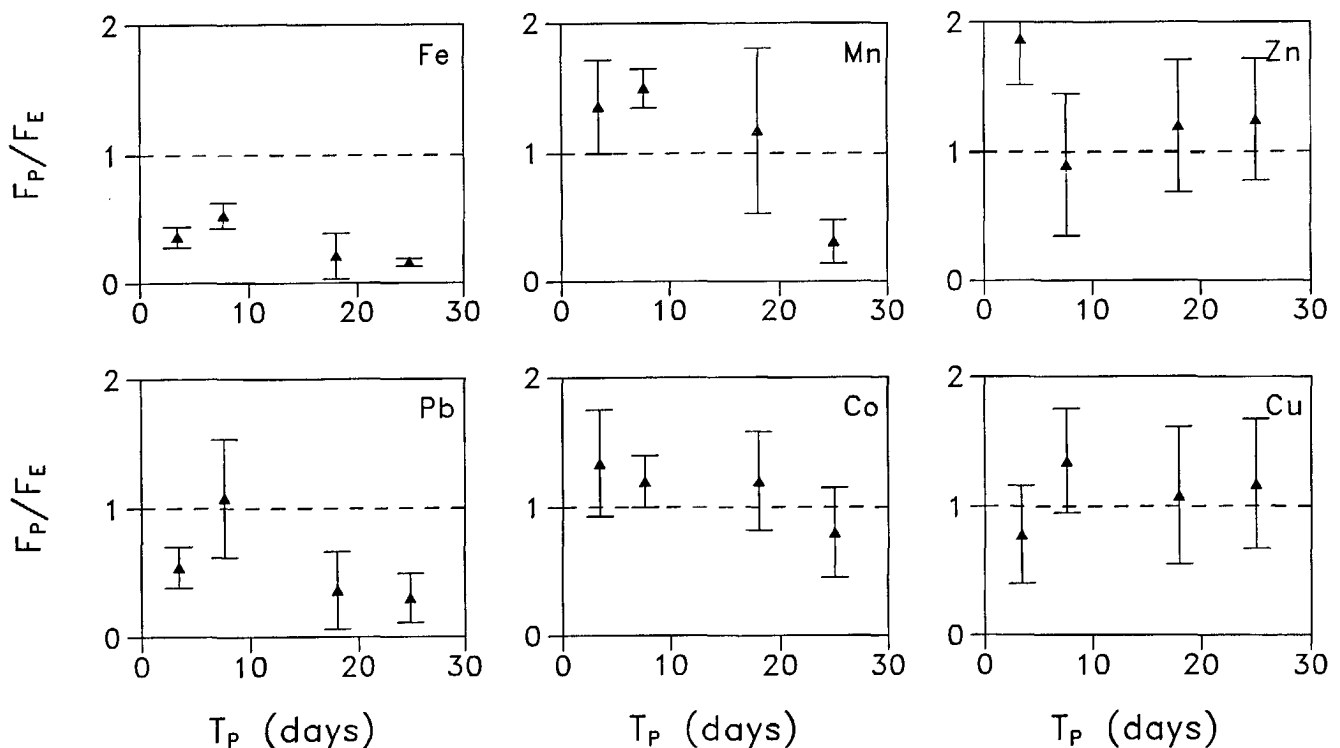


Figure 6

The ratio of the metal flux across the plume boundary to that across the mouth of the estuary is shown as a function of the residence time of water in the system (estuary + plume).

Le rapport entre le flux d'un métal à l'interface (panache estuarien → Mer de Clyde) et son flux à l'interface (estuaire → panache) est indiqué en fonction du temps de résidence dans le système (estuaire + panache).

sented by another two boxes. Each box was considered sequentially from the upper estuary to the leading edge of the plume. The volume of freshwater locked up in each box and the time required to provide this volume were estimated from salinity and river discharge data according to the method proposed by Kaul and Froelich (1984). It follows that the flushing times of Figure 6 are the cumulative transit times of Figure 3. Export fluxes from the plume,  $F_p$ , were estimated as the product of the "effective zero-salinity" (EZS) end-member concentration by the mean freshwater discharge creating the plume. The EZS concentrations were obtained by extrapolation to zero salinity of the metal concentration vs salinity relationships established over a 2 psu salinity range around the discontinuity value of 31.9 (or 32.8) psu. A combination of limited salinity range used in this calculation together with non-conservative behaviour of the elements investigated produces the large relative errors seen in Figure 6. Nevertheless, it can be concluded from Figure 6 that a large fraction of the Fe and Pb estuarine exports are scavenged from solution during their residence time in the plume. The behaviour of Mn, Zn and Co is less predictable, as processes operating in the plume can modify the estuarine fluxes either way. It is perhaps reassuring to find that Cu fluxes were not significantly modified in any of the five surveys, given that Cu tends to be strongly bound to natural organic ligands and, as such, is least likely to be affected by sorption (Van den Berg *et al.*, 1987). For the particle-reactive elements (Fe, Mn, Pb, Co) a longer residence time would be expected to lead to a greater removal and hence a lower  $F_p/F_E$  ratio. Although Figure 6 is not inconsistent with this prediction, it is also clear that the ratio  $F_p/F_E$  shows little sensitivity to  $T_p$  and, above all, no indication of yielding the expected value of 1 when extrapolated to zero  $T_p$ . This implies either that  $T_p$  plays no important role in producing the  $F_p/F_E$  observations or that an initial rapid (less than four days) uptake (Fe, Pb) or release (Mn, Co) reaction is followed by a longer-term slower uptake, in accordance with the kinetic model proposed by Nyffeler *et al.* (1984). The latter explanation, although more likely, appears inconsistent with the observation that the same metals behave conservatively in the lower Clyde Estuary (Muller *et al.*, 1994), *i.e.* an environment characterized by  $T_E \sim 4$  days and SPM  $\sim$  five times that in the plume. It must be concluded that some important factor other than  $T_p$  or SPM controls the dissolved metal concentrations in the plume. It seems reasonable to expect that this factor may be related to the surface characteristics of the particles, as well as to the metal-binding properties of the unidentified dissolved or colloidal components that are invariably present in marine and estuarine waters.

The role played by hydraulic residence time remains ambiguous even when the longer residence time ( $T > 14$  weeks) of the "aged" intrusion water of July 1990 is considered. Evidence for scavenging of dissolved Fe, Pb and Cd and their concurrent depletion in the SPM was found from a comparison of the "initial" solid/solution composition as measured at the marine boundary (station 9) in March 1990 and the composition measured in the core of the departing old water (station 4, 50 m; station 5, 80 m) 14 weeks later. This scavenging may have been assisted by the enrichment

Table 1

Mean values of the detection limits and precision estimates for the analytical methods. The detection limit was calculated as three times the standard deviation of the blank. The precision was calculated from the standard error on the slope of a calibration line generated by spiking a seawater sample at analyte concentrations spanning those found throughout the Firth of Clyde.

Limites de détection et précisions moyennes relatives aux modes opératoires et techniques analytiques. La limite de détection est définie comme trois fois l'écart-type des blancs. La précision des résultats est reliée à celle de la pente de la droite d'étalonnage, laquelle est définie par quatre ajouts standards.

| Analyte          | Dissolved               |               | particulate             |                            |
|------------------|-------------------------|---------------|-------------------------|----------------------------|
|                  | Detection limit         | Precision (%) | Detection limit         | Precision <sup>a</sup> (%) |
| Fe               | 2.1 nM                  | 14            | 11 nM                   | 16                         |
| Mn               | 0.8 nM                  | 11            | 2.6 nM                  | 15                         |
| Zn               | 0.4 nM                  | 13            | 2.0 nM                  | 24                         |
| Pb               | 0.009 nM                | 8             | 0.05 nM                 | 15                         |
| Cd               | 0.02 nM                 | 8             | 0.07 nM                 | 22                         |
| Co               | 0.03 nM                 | 12            | 0.05 nM                 | 16                         |
| Cu               | 0.2 nM                  | 8             | 0.25 nM                 | 20                         |
| Ni               | 0.2 nM                  | 6             | 0.08 nM                 | 15                         |
| OC               | 0.1 mg l <sup>-1</sup>  | 10            | 0.02 mg l <sup>-1</sup> | 7                          |
| Alk              | 0.1 meq l <sup>-1</sup> | 0.06          |                         |                            |
| pCO <sub>2</sub> | 10 µatm                 | 2             |                         |                            |
| PO <sub>4</sub>  | 0.02 µM                 | 5             |                         |                            |
| NH <sub>4</sub>  | 0.1 µM                  | 5             |                         |                            |
| NO <sub>3</sub>  | 0.1 µM                  | 15            |                         |                            |
| NO <sub>2</sub>  | 0.05 µM                 | 20            |                         |                            |
| Si               | 0.2 µM                  | 10            |                         |                            |
| SPM              |                         |               | 0.07 mg l <sup>-1</sup> | 9                          |

<sup>(a)</sup> based on SPM = 0.5 mg l<sup>-1</sup>.

in particulate Mn (Tab. 2) resulting from the long contact time of that water mass with Mn-diffusing sediments. Different though the modes of formation, physico-chemical conditions and time scales may have been between the two water masses, the changes in dissolved Fe, Mn, Zn, Pb, Co and Cu concentrations during aging of the isolated water mass in Bute Sound are strikingly similar to the corresponding changes in fluxes which occurred during the transit of freshwater within the Clyde Plume (compare Fig. 6 and Tab. 2). This suggests that the same dominant process(es) may have been at play in both cases.

### Remobilization of redox-sensitive elements in sediments

The behaviour of Mn in estuarine and shelf environments is dominated by the effects of transformations between the (+II) oxidation state, in which the element is mobile in solution, and higher oxidation states (+III, +IV) in which it is strongly particle-reactive. In turn, these transformations may influence trace metal concentrations in this (above section) and other coastal environments (Eaton, 1979; Morris *et al.*, 1982). Significant correlations between reactive particulate Mn and other reactive particulate metals is usually taken as an indication that the Mn hydrous oxide phase actively scavenges trace metals from solution, parti-



Table 2

The chemical composition of the marine intrusion of March 1990 (measured at station 9) is compared with that of the water mass propagating from the Bute Sound along the 50 m horizon of the main basin in July 1990. Both had the same (T, S) signature and are assumed to represent the same water body (see text). The last column then gives the apparent utilization (-) or production (+) of the quantities used to calculate the stoichiometry of organic matter decomposition.

Comparaison entre les caractéristiques chimiques des eaux collectées à la station 9 en mars 1990 et celles de la masse d'eau en provenance du Bute Sound qui, en juillet 1990, s'étendit sous forme de panache à une immersion de l'ordre de 50 m. Leurs caractéristiques (T, S) étant identiques, il s'agit vraisemblablement de la même masse d'eau dont on peut suivre l'évolution temporelle.

|       | Quantity                                 | 25 March 1990 | 3 July 1990 |       |
|-------|--|---------------|-------------|-------|
|       | O <sub>2</sub> (μmol l <sup>-1</sup> )   | 275 ± 3       | 218 ± 3     | -57   |
|       | pH (SWS, 25°C)                           | 7.92 ± 0.02   | 7.86 ± 0.02 |       |
|       | Alk (meq l <sup>-1</sup> )               | 2364 ± 6      | 2375 ± 6    | +11   |
|       | PO <sub>4</sub> (μmol l <sup>-1</sup> )  | 0.88 ± 0.02   | 0.98 ± 0.02 | +0.10 |
|       | NO <sub>3</sub> (μmol l <sup>-1</sup> )  | 11.0 ± 0.2    | 12.2 ± 0.2  | +1.2  |
|       | ΣCO <sub>2</sub> (μmol l <sup>-1</sup> ) | 2196 ± 8      | 2230 ± 8    | +27*  |
|       | DOC (mg l <sup>-1</sup> )                | 0.8 ± 0.05    | 0.9 ± 0.05  |       |
|       | POC (%)                                  | 26 ± 8        | 14 ± 2      |       |
| diss  | Fe (nmol l <sup>-1</sup> )               | 27 ± 23       | 17 ± 7      |       |
|       | Mn (nmol l <sup>-1</sup> )               | 7 ± 2         | 32 ± 5      |       |
|       | Zn (nmol l <sup>-1</sup> )               | 12 ± 1        | 15 ± 2      |       |
|       | Pb (nmol l <sup>-1</sup> )               | 0.14 ± 0.03   | 0.04 ± 0.02 |       |
|       | Cd (nmol l <sup>-1</sup> )               | 0.25 ± 0.02   | 0.15 ± 0.04 |       |
|       | Co (nmol l <sup>-1</sup> )               | 0.10 ± 0.01   | 0.08 ± 0.04 |       |
|       | Cu (nmol l <sup>-1</sup> )               | 6.6 ± 1.3     | 6.6 ± 0.9   |       |
|       | Ni (nmol l <sup>-1</sup> )               | 4.7 ± 0.3     | 6.3 ± 1.5   |       |
| part. | Fe (%)                                   | 4.1 ± 1.4     | 0.9 ± 0.3   |       |
|       | Mn (mg kg <sup>-1</sup> )                | 2190 ± 330    | 3990 ± 540  |       |
|       | Zn (mg kg <sup>-1</sup> )                | 150 ± 40      | 167 ± 23    |       |
|       | Pb (mg kg <sup>-1</sup> )                | 150 ± 15      | 86 ± 36     |       |
|       | Cd (mg kg <sup>-1</sup> )                | 0.4 ± 0.2     | 0.1 ± 0.1   |       |
|       | Co (mg kg <sup>-1</sup> )                | 15 ± 5        | 17 ± 4      |       |
|       | Cu (mg kg <sup>-1</sup> )                | 72 ± 16       | 67 ± 4      |       |
|       | Ni (mg kg <sup>-1</sup> )                | 90 ± 12       | 84 ± 6      |       |

\* The apparent ΣCO<sub>2</sub> production is calculated as (2230 - 2196) - (11 + 1.2)/2, where the corrective term removes the effect of CaCO<sub>3</sub> dissolution (Takahashi *et al.*, 1985).

cularly when calculations of diffusive (release from sediments) and deposition fluxes already point to a rapid recycling of Mn between the sediments and the water column (Paulson *et al.*, 1988). Within the Firth of Clyde, the release of Mn(+II) from underlying anoxic sediments was most likely to be detected in the sealoch system because of the longer contact time of bottom waters with Mn-diffusing sediments. Indeed, we found elevated bottom concentrations of Mn – measured ~ 5 m above the seabed – only at station 1 (Fig. 7). The benthic signal was present in both dissolved (~ 40% of total Mn) and particulate (~ 60% of total Mn) Mn vs depth profiles. It was much more pronounced in August and November 1989, probably as a result of the reductive dissolution of Mn oxides brought about by the accumulation of biogenic organic matter in the summer months. Dissolved and particulate Fe concentrations at station 1 are also shown in Figure 7. Because Fe (+II) is relatively rapidly oxidized, its behaviour is more highly dominated by the chemistry of Fe (+III) and particularly its occurrence in microcolloids (< 0.4 μm) which undergo aggregation into 0.4 μm-filterable particles

(Honeyman and Santschi, 1991; Benoit *et al.*, 1994). The Fe concentration profiles of Figure 7 indicate that 80-95% of Fe was particulate and that, in general, the partitioning was more heavily weighted towards the particulate phase in the bottom samples. However, the interpretation of the benthic signal is not as straightforward for Fe as for Mn. For example, it is hard to reconcile the fact that bottom particulate Fe peaked in July 1990 when Mn concentrations were low.

Away from the sealochs, at stations 2-9, dissolved Mn or Fe were rarely found to increase towards the sediments. On the other hand, a marked summer maximum in the dissolved Mn inventory of the outer Firth of Clyde was observed (Tab. 3; Fig. 5), in line with that found in other UK shelf seas at that time of year (Dehairs *et al.*, 1989; Tappin *et al.*, 1993; Tappin *et al.*, 1995). Remobilization of Mn from the underlying sediments may, at first sight, seem like a plausible explanation for the elevated Mn concentrations in the water column. In reality, the average Mn concentration for stations 6-9 systematically falls short of the value predicted by assuming simple mixing between an effective freshwater concentration of 1250 ± 720 nmol l<sup>-1</sup> (Muller *et al.*, 1994) and a variable marine concentration as measured at station 9. Furthermore, the average Mn concentration of the outer Firth (stations 6-9) appears to be positively, although nonlinearly, related to that of its marine end-member (station 9). It seems reasonable to conclude that (a) the remobilization of Mn from outer Firth sediments is outweighed by its removal from solution by oxidative processes, and (b) the excess Mn observed in the summer is not generated *in situ* but rather carried in from the North Channel. On the basis of <sup>137</sup>Cs measurements, Baxter *et al.* (1979) estimated that about 40% of low-activity nuclear releases into the Irish Sea actually pass through the Firth of Clyde. They further calculated that about 90% of Clyde seawater originates from the Irish Sea, as opposed to the North Atlantic. Therefore it would seem that the Irish Sea is the likely source of the excess Mn observed in the water column of the outer Firth of Clyde during the summer.

### Resuspension of sediments

The distributions of SPM loadings suggested to us that some resuspension of bottom sediments, inferred from elevated SPM values, occurred most of the time at the inner Firth stations 2-5. It would be difficult to generalize about the elemental composition of the SPM, but there was a trend for higher Fe and Co and lower OC (organic carbon) Zn and Cd contents in the SPM sampled near the bottom (*see*, for example, Fig. 5, Fig. 8). This would be anticipated, given that crustal material is enriched in Fe and depleted in OC and Cd relative to other sources of SPM (Taylor, 1964; Martin and Whitfield, 1983), and it is consistent with the better-defined patterns already observed in the inner Firth and sealoch system (Balls, 1990). Note that in Figure 8 (March 1990) characteristic differences in the composition of SPM are observed not only on vertical but also on horizontal scales as particles collected near the open waters of the North Channel are enriched in organic carbon and depleted in most trace metals.

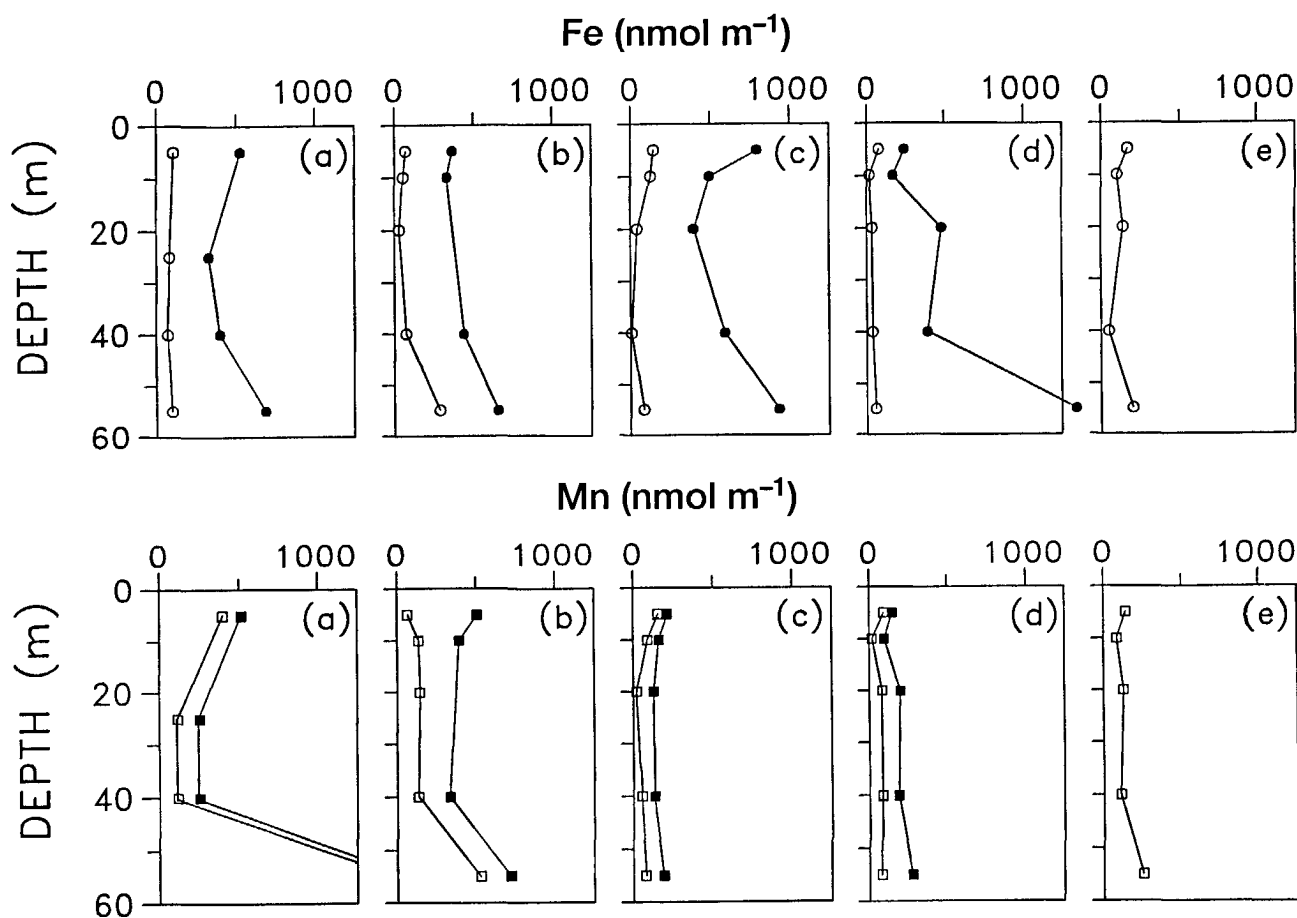


Figure 7

Vertical profiles of (○) dissolved Fe, (●) particulate Fe, (□) dissolved Mn, (■) particulate Mn, at station 1; (a) 21 August 1989; (b) 23 November 1989; (c) 21 March 1990; (d) 4 July 1990; (e) 2 March 1991.

Profils des concentrations de Fe dissous (○), Fe particulaire (●), Mn dissous (□), Mn particulaire (■) à la station 1; (a) 21 août 1989; (b) 23 novembre 1989; (c) 21 mars 1990; (d) 4 juillet 1990; (e) 2 mars 1991.

Although tidal stirring was weak in all parts of the system (Dooley, 1979; Simpson and Rippeth, 1993) it was probably responsible for the permanent resuspension signal in the inner Firth. By contrast, resuspension in the outer Firth was an episodic phenomenon associated with the intrusion of North Channel water which was triggered, in March 1990, by a combination of very strong south-westerly winds and high freshwater input (compare particulate constituents in Fig. 5 and Fig. 8). The nature of the event implies that this "resuspension" signal was probably a composite of SPM either locally resuspended or carried in by the intrusion water. Interestingly, since the loading and composition of SPM at the time were similar in the outer Firth and in the adjacent North Channel, the deep water renewal event of March 1990 did not result in the net import or export of a significant quantity of particulate material (Muller *et al.*, 1995).

#### Remineralization of organic matter

We showed earlier ("Mixing of water masses...") that dissolved  $O_2$ ,  $CO_2$  and nutrients were useful chemical variables not only for tracking the penetration of an older

water mass into the main basin, but also for estimating the global stoichiometry of oxidative processes (Tab. 2). These estimates were based on the differences between the pre-

Table 3

The average dissolved Mn concentration in the Clyde Sea is compared with the concentration estimated as a weighted average between a constant "effective zero salinity" value of  $1250 \pm 720 \text{ nmol l}^{-1}$  (freshwater end-member) and a variable "salinity = 34" value (marine end-member).

Tableau comparatif montrant que les concentrations moyennes du Mn dissous dans la Mer de Clyde ([Mn] obs) sont systématiquement inférieures aux valeurs qu'on attendrait ([Mn] est) d'un simple mélange entre les eaux dessalées de l'estuaire et celles du North Channel ( $S = 34$  psu). Elles se rapprochent davantage – et sont corrélées positivement – avec les concentrations moyennes observées à  $S = 34$  psu.

| Cruise        | S (psu) | [Mn] observed (nmol l <sup>-1</sup> ) | [Mn] estimated (nmol l <sup>-1</sup> ) | [Mn] at S = 34 (nmol l <sup>-1</sup> ) |
|---------------|---------|---------------------------------------|--|--|
| November 1989 | 33.24   | 15 ± 1                                | 32 ± 16                                | 4.6 ± 0.5                              |
| March 1990    | 32.74   | 14 ± 1                                | 50 ± 26                                | 3.6 ± 0.7                              |
| July 1990     | 33.45   | 27 ± 3                                | 45 ± 11                                | 25.5 ± 4.3                             |
| March 1991    | 33.11   | 18 ± 2                                | 41 ± 18                                | 8.7 ± 1.7                              |

formed concentrations (in the sea water entering the system at depth) and the observed concentrations (in the same water re-emerging after decomposition of organic matter has taken place). However, the same procedure cannot be applied to gain insight into the oxidative processes occurring in the Clyde Plume or in the bottom layers of the Clyde Sea. Indeed, this type of analysis will, in general, be thwarted by lack of knowledge on source concentrations (varying rapidly through time in the case of the freshwater end member) and mixing proportions among waters of different origin.

Alternatively, it may be useful to relate percent saturation of dissolved  $O_2$  to partial pressure of dissolved  $CO_2$  (Simpson, 1985). In the absence of complicating processes, the

data should cluster near the coordinate (100 %, 350  $\mu\text{atm}$ ) representing equilibration with the atmosphere. The data in Figure 9 show that  $O_2$ -% and  $pCO_2$  generally departed from their equilibrium values. The combination of mixing, organic matter decomposition, air-sea gas exchange and photosynthetic activity produced the negative relationships seen in Figure 9. Although the contributions of the different processes could not be separated on the strength of our data set, we found it instructive to subdivide the data into Clyde Plume and Clyde Sea regions. A rather scattered diagram emerged from the Clyde Plume data, reflecting the fact that all four processes were at play and that the  $O_2$  and  $\Sigma CO_2$  contents of the freshwater end-member varied with time. By contrast, a tight interdependency between  $O_2$ -%

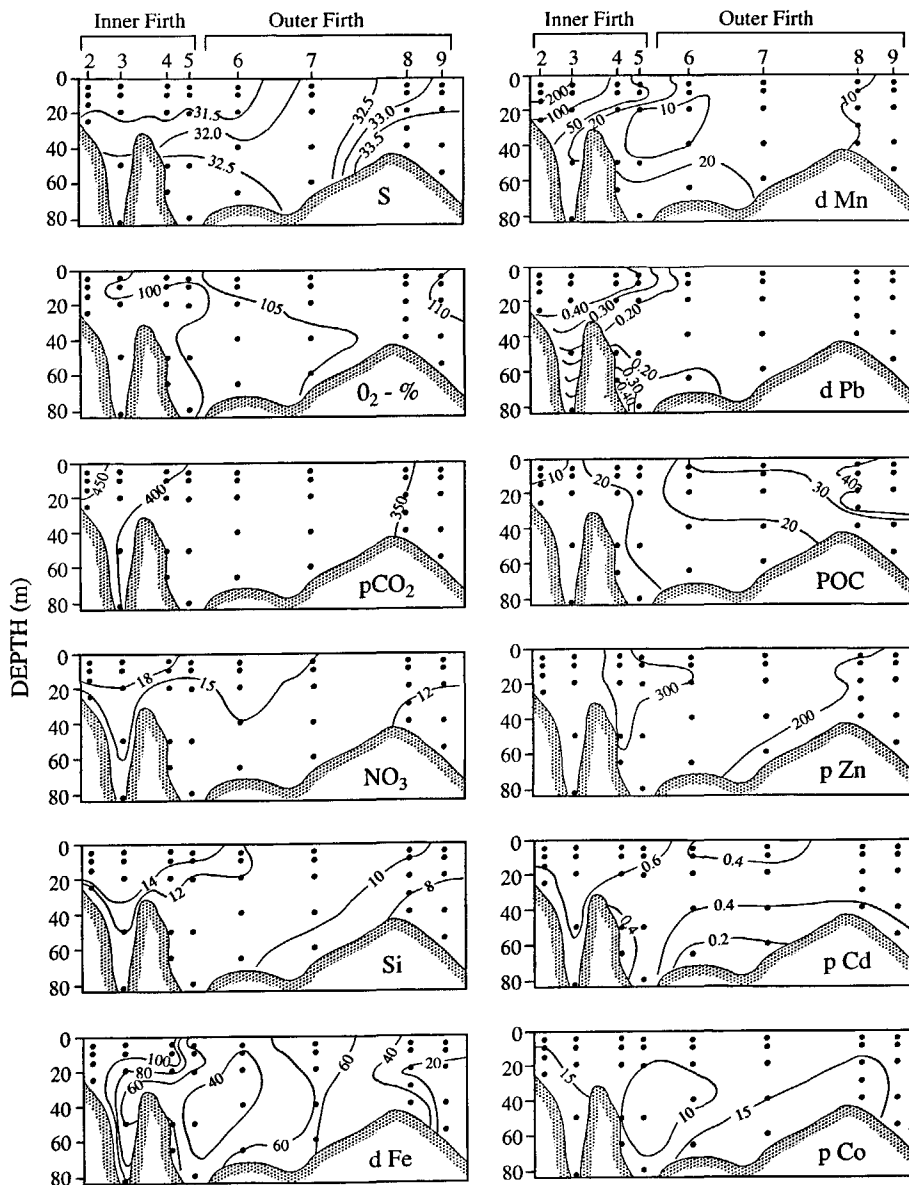


Figure 8

Hydrographic section of the main basin of the Firth of Clyde (March 1990) showing, S psu,  $O_2$ -% (of the value at saturation),  $pCO_2$   $\mu\text{atm}$ ,  $NO_3$   $\mu\text{mol l}^{-1}$ , Si  $\mu\text{mol l}^{-1}$ , dissolved Fe  $\text{nmol l}^{-1}$ , dissolved Mn  $\text{nmol l}^{-1}$ , dissolved Pb  $\text{nmol l}^{-1}$ , POC %, particulate Zn  $\text{mg kg}^{-1}$ , particulate Cd  $\text{mg kg}^{-1}$ , particulate Co  $\text{mg kg}^{-1}$ . Station numbers correspond to those given in Figure 1.

Coupe vertical du Firth of Clyde (mars 1990) montrant : S (psu),  $O_2$ -% (% de la valeur à saturation),  $pCO_2$  ( $\mu\text{atm}$ ),  $NO_3$  ( $\mu\text{mol l}^{-1}$ ), Si ( $\mu\text{mol l}^{-1}$ ), Fe dissous ( $\text{nmol l}^{-1}$ ), Mn dissous ( $\text{nmol l}^{-1}$ ), Pb dissous ( $\text{nmol l}^{-1}$ ), C organique particulaire (en % de la matière particulaire en suspension), Zn particulaire ( $\text{mg kg}^{-1}$ ), Cd particulaire ( $\text{mg kg}^{-1}$ ), Co particulaire ( $\text{mg kg}^{-1}$ ).

and  $p\text{CO}_2$  emerged from the Clyde Sea data. Two factors help explain this: (a) the deeper waters were much less vigorously mixed and ventilated and the interdependency was promoted by the dominating influence of remineralization which set in as soon as the water entered the system, and (b) the outer Firth surface waters were generally influenced by only one major process such as photosynthesis (July 1990) or air-sea exchange (November 1989, March 1990, March 1991).

#### Air-sea gas exchange

This process is best illustrated by the March 1990 and 1991 situations (Fig. 9b and 9d) since remineralization was a significant process in November 1989 and July 1990 while photosynthesis also played an important part in the latter case. In March 1991 the mean wind speed over, and shortly before, the study period was  $4\text{--}8\text{ m s}^{-1}$ . In March 1990 it was  $13\text{--}17\text{ m s}^{-1}$ . Fig. 9b may therefore be viewed as a continuation of Fig. 9d, *i.e.* into the gas transfer velocity regime where bubbles produced by breaking waves contribute significantly to the exchange (Liss, 1983; Merlivat and Memery, 1983). Proceeding seaward from the inner to the outer Firth, it is seen from Fig. 9d that  $\text{O}_2$  saturation was reached at a point where the waters still contained some excess  $\text{CO}_2$ . This implies faster kinetics of gas exchange for  $\text{O}_2$  than for  $\text{CO}_2$ , as some previous investigations (Hoppema, 1991; Thomas *et al.*, 1993) have suggested. Further equilibration with the atmosphere did bring  $p\text{CO}_2$  down to near its equilibrium value while  $\text{O}_2$  remained at 100 % saturation: hence the cluster of points observed on the X axis in both diagrams. This cluster in fact represents the intersection between the two scatter diagrams. In the absence of air-sea gas fluxes due to bubbles (March 1991) it corresponds to the waters of the outer Firth of Clyde. As windspeeds exceeded  $10\text{ m s}^{-1}$  (Liss, 1983; Keeling, 1993) more  $\text{O}_2$  was transferred into these waters through the additional mechanism of bubble dissolution, leading to  $\text{O}_2$  supersaturation (Fig. 9b). At the same time,  $\text{O}_2$  saturation took place over the inner Firth of Clyde where whitecap coverage remained negligible. Another notable feature of the March 1990 survey, in addition to the strong winds, was the consistently high rainfall values during the preceding two months. In many estuaries this sort of event has a profound and beneficial effect on dissolved oxygen concentrations. In the lower Clyde Estuary, however, the elevated oxygen concentrations of March 1990 have been unambiguously related to equilibration with the atmosphere (Muller *et al.*, 1994) so that we do not need to seek any alternative explanation for the higher  $\text{O}_2$ -% values in the plume in March 1990 compared with March 1991. In summary, it appears that the data points in Figs. 9b and 9d are distributed along a single path representing: (a) a rapid reoxygenation of the estuarine waters by  $\text{O}_2$  input from the atmosphere as they mix with Clyde Sea water; note that while  $\text{O}_2$  replenishment is achieved within the mixing time of the Clyde Plume,  $\text{CO}_2$  excess is not fully eliminated (Fig. 9d); (b) a gradual elimination of the  $\text{CO}_2$  excess in the outer Firth; and (c) the development of  $\text{O}_2$  supersaturation in the surface waters of the outer Firth under conditions of intense wind mixing. We note

that the high wind regime modifies  $\text{O}_2$ -% but not  $p\text{CO}_2$ . This is because bubble induced dissolution tends to favour gases with lower solubilities (Liss, 1983; Keeling, 1993).

#### Phytoplankton photosynthesis

The July 1990 survey took place during the late stage of a phytoplankton bloom observable from station 3 to station 9. The abundance of grazing organisms such as copepods and jellyfish was particularly notable at stations 5-7. Because the Clyde Plume is a source of nutrients and metals, it was only in the surface waters of the outer Firth that one could directly observe the manifestation of primary productivity in terms of minima in  $\text{NO}_3$ ,  $\text{PO}_4$ , Si, Fe, Zn and Cd concentrations (Fig. 5). The  $\text{O}_2$ -% vs  $p\text{CO}_2$  diagram also differed significantly from situations when photosynthesis was not a factor. As noted before,  $\text{O}_2$ -% and  $p\text{CO}_2$  were again better correlated within the Clyde Sea than within the Clyde Plume, only this time the data could be best fitted by a line passing through the equilibrium coordinate (Fig. 9c). In addition, photosynthesis appeared to be the only process resulting in significant  $\text{CO}_2$  undersaturation (Fig. 9). Further evidence for the biological alteration of chemical distributions came from the stoichiometry of the  $\Sigma\text{CO}_2$ ,  $\text{NO}_3$ ,  $\text{PO}_4$  and Si anomalies observed. We propose that in the absence of photosynthesis the inorganic carbon status of the Firth of Clyde may be given by a regression on the March 1990 ( $\Sigma\text{CO}_2$ , Alk) data,

$$\Sigma\text{CO}_2 = 0.501 (\pm 0.003) + 0.716 (\pm 0.016) \text{ Alk}$$

Regressions on the November 1989 or March 1991 would give a slightly higher intercept but the same slope, with the consequence that the final stoichiometric analysis would not be affected. Next, we define hypothetical mixing lines relating  $\text{NO}_3$ ,  $\text{PO}_4$  and Si to salinity on the basis of conservative mixing between station 2 and station 9, for the July 1990 situation. These are defined as,

$$\begin{aligned} \text{NO}_3 &= 137.6 - 3.896 \text{ S} \\ \text{PO}_4 &= 20.89 - 0.598 \text{ S} \\ \text{Si} &= 102.8 - 2.936 \text{ S} \end{aligned}$$

The anomalies  $\Delta\Sigma\text{CO}_2$ ,  $\Delta\text{NO}_3$ ,  $\Delta\text{PO}_4$  and  $\Delta\text{Si}$  are then calculated as the differences between the values observed throughout the mixed layer (stations 3-8) and those anticipated from conservative mixing. By plotting  $\Delta\Sigma\text{CO}_2$ ,  $\Delta\text{NO}_3$  and  $\Delta\text{Si}$  against  $\Delta\text{PO}_4$ , we obtain the following molar assimilation ratios:

$$\text{P:Si:N:C} = 1.0 : 5.7 : 9.2 : 68$$

Although different from recently quoted values of the Redfield ratio for oceanic plankton (Takahashi *et al.*, 1985; Hecky *et al.*, 1993), they lie within the range of values reported for other coastal areas (Brzezinski, 1985; Dauchez *et al.*, 1991). We also note that the Si:C and Si:N ratios are approximately 40% lower than those expected for uptake by diatoms (Brzezinski, 1985). This is perhaps not surprising given that diatoms tend to dominate the spring bloom (April), while in summer there are often blooms of flagellates and dinoflagellates (Gowen, 1987; Grantham and Tett, 1993). Flagellate blooms are thought to originate in the frontal zone above the Great Plateau (Jones *et al.*,

1982; Gowen, 1987). A temporary reversal of the normal estuarine circulation brought on by certain meteorological conditions (T.P. Rippeth, pers. comm.) may contribute to their subsequent transport into the Firth of Clyde.

### Principal component analysis of the data

Principal component analysis is a useful technique for reducing the dimensionality of a problem. It consists of finding an orthogonal transformation of the  $n$  original variables to a new set of  $n$  uncorrelated variables, called principal components, which are derived in decreasing order of importance in terms of their ability to depict the total variance (information) in the data (Chatfield and Collins, 1980). These components are linear combinations of the original variables. The net result of the orthogonal transformation in  $n$ -space is to construct a plot in  $n$  dimensions which optimizes the depiction of the variance in the original data set. Our objective was to see if most of the variation in the original data could be accounted for by the first two components and hence be represented in two dimensions. After substituting all missing or suspect data (6% of total) with the mean values determined from the remaining water column data, we carried out principal

component analyses on the original 28 variables of the November 1989, March 1990 and July 1990 data sets as well as the 18 variables (SPM elemental composition not analysed) of the March 1991 data set. The first two principal components accounted for 47-63% of the total variance in the 28-variable data sets and 82% in the 18-variable data set, so that a large fraction of the total information can be plotted in two dimensions. More specifically, we wish to examine the contribution that each variable makes to this variance. This contribution can be calculated from the correlation matrix of the  $n$ -dimensional ( $n = 28$  or 18) random variable and can be represented by  $n$  elements which measure the correlations between the components and the original variables. These elements are then called 'variable loadings' (Chatfield and Collins, 1980). The variable loadings on the first two components formed the basis of the two-dimensional representation given in Figure 10. It should be noted that the sign of the loadings (coordinates of the points in Fig. 10) is significant because it indicates whether the variable is positively or negatively correlated with the component of interest.

In trying to attach a meaning to these two components, we asked ourselves which variables show substantial loadings on which components, while noting the sign of the loadings (Meglen, 1992). In the March 1990 and March 1991 situa-

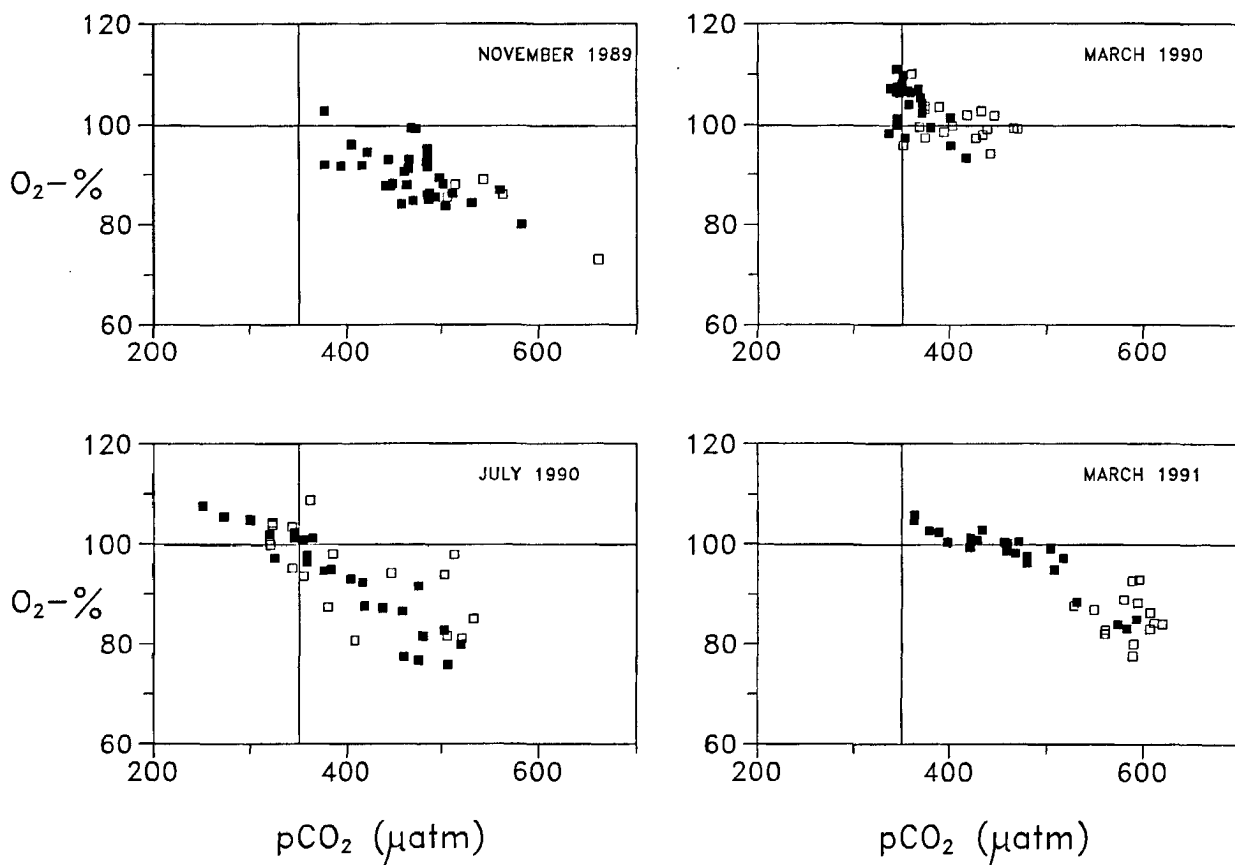


Figure 9

Percent saturation of dissolved O<sub>2</sub> versus partial pressure of CO<sub>2</sub> for the waters of the Firth of Clyde. Data are subdivided into Clyde Plume (□) and Clyde Sea (■) regions. The lines indicate the atmospheric equilibrium values for both gases.

Relation entre le pourcentage de saturation du O<sub>2</sub> et la pression partielle du CO<sub>2</sub> dans les eaux du Firth of Clyde. Les symboles □ et ■ désignent respectivement le panache estuarien (30 < S < 32) et la Mer de Clyde (32 < S < 34).

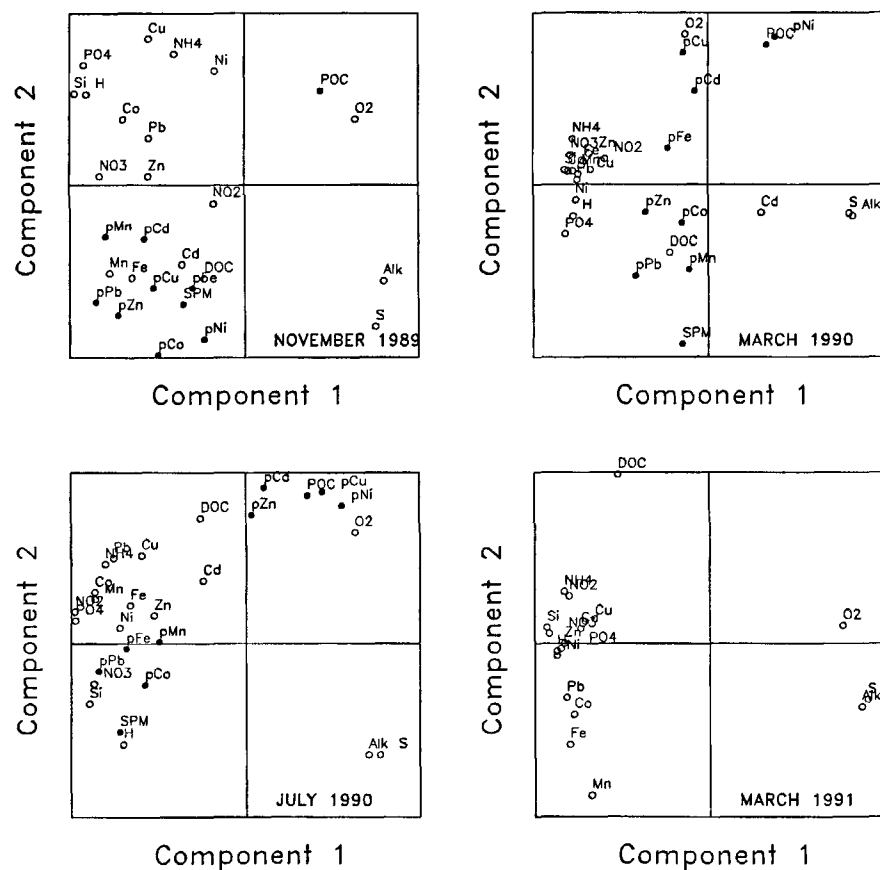


Figure 10

Representation of the first two component loadings (X and Y coordinates) for each of the 28 variables measured in this study. The first two components accounted for 47 % (November 1989), 63 % (March 1990), 62 % (July 1990) and 82 % (March 1991 — dissolved quantities only) of the total variation in the data.

Participation relative de chacune des 28 variables mesurées envers les deux premières composantes principales. Les deux premières composantes principales contribuent à expliquer 47 % (novembre 1989), 63 % (mars 1990), 62 % (juillet 1990) ou 82 % (mars 1991 — valeurs particulières exclues) des variations observées.

tions, the first principal component consists mainly of an inverse relationship to dissolved nutrients, Zn, Cd, Pb, Cu, Ni and H ( $= 10^{-pH}$ ) and a positive relationship to S (salinity) and Alk (Fig. 10). By contrast, the first principal component is not well represented by any one variable during the more stratified conditions of November 1989 and July 1990. The second principal component is associated, particularly in March 1990, with variance in  $O_2$  (positive loading) and SPM (negative loading). In addition, we note the much lower contribution of the second component where particulate constituents have been left out of the analysis (Fig. 10, March 1991). From these and other associations, it seems reasonable to interpret the first and second component as indicators of the degree of horizontal and vertical inhomogeneity, respectively.

Examination of the scatter plots for the particulate constituents reveals particularly well how each trace element is affected differently by the tendency of the processes discussed above to generate horizontal or vertical gradients in its SPM content. Figure 10 shows that the plots of particulate loadings against the first two components usually define elongated clusters between POC and SPM. That POC and SPM should oppose each other along the second axis is consistent with the results of Balls (1990) who interpreted the inverse POC-SPM relationship observed in the sea-loch system as representing mixing between the low SPM, high POC (biogenic material) surface waters and the high SPM (resuspension), low POC bottom waters. Particle reactive elements such as Fe, Mn, Pb and Co tend to plot nearer SPM while «recycled» elements (using the terminology of Whitfield and Turner, 1987) like Zn, Cd, Cu and Ni plot nearer POC. This classification is similar to that

derived by Whitfield and Turner (1987) to rationalize the involvement of these elements in the oceanic particle cycle. In the Firth of Clyde, the spatial separation of surface and near-bottom processes and the relatively long residence time of water may be instrumental in resolving the different biogeochemical behaviours of the trace elements in a way which is not always apparent in other estuarine and coastal environments (Ouddane *et al.*, 1992).

The actual distributions of the dissolved and particulate variables in the principal component plot vary greatly between the surveys (Fig. 10). The remaining discussion is aimed at showing how the main features of these distributions relate to some of the processes described earlier. In November 1989, most dissolved properties plot in the quadrant opposite to that singly occupied by S and Alk; if we consider the two remaining quadrants, we see that most particulate properties are weight contrasted with POC and  $O_2$ . In addition, we note that the clusters representing dissolved and particulate properties are rather diffuse. The first set of observations can be explained by the significance of freshwater inputs in controlling nutrient and dissolved metal distributions, as well as the relative depletion of metal contents in particles of marine origin (higher POC) at that time of year. The dispersion of both dissolved and particulate metals can be attributed to the specific sorption properties of individual metals. In effect, the combined effects of freshwater-seawater mixing and particle-solution interactions seem to have provided the main source of compositional variations in November 1989. The latter process in particular is not one which results in distributional characteristics measured exclusively by either the first or the second principal component, *i.e.*

purely horizontal or vertical gradients, so the data points fall largely between the axes. In March 1990, by contrast, all solution variables but Cd are found at the opposite end of the first axis from S and Alk, while particulate phase variables form an elongated cluster hugging the second axis. This polarisation of the scatter plot is consistent with what we know about the distributional data and the underlying processes at that time. A combination of gale force southwesterly winds and high river flows helped produce the strong horizontal gradient in dissolved properties suggested by the dense cluster of points near the first axis. Partly because of the fast mixing rates, heterogeneous reactions played a reduced role as a source of SPM compositional variation. By the same token, the resuspension of sediments took on greater significance. The solution variables of July 1990 plot in positions similar to those assumed in November 1989 (Fig. 10). In particular, and in contrast with the March 1990 situation, many solution variables now have significant loadings on both the first and second component. In fact, the July 1990 scatter plot - particulate properties excluded - may be crudely viewed as the product of a  $-30^\circ$  rotation applied to the March 1990 plot. However, the solid phase variables now show two distinct clusters. One cluster of points, in the bottom left sector, includes SPM, pFe, pMn, pPb and pCo. A second cluster, at the top right, includes POC, pZn, pCd, pCu and pNi. These groupings are consistent with the assumption that particles are of two basic types, namely crustal (dominant in resuspended material) and biological (dominant in phytoplankton-rich surface layers, especially in the outer Firth), and thus confirm that photosynthesis was a major driving force influencing chemical distributions at that time.

## CONCLUSIONS

In this study, we have endeavoured to treat the Firth of Clyde as a complete chemical system in its own right. Another important aspect of the work concerns the coupling between a major UK estuary, the Clyde, and the adjoining shelf waters of the Irish Sea and Atlantic Ocean. Although the manifestation of physical, biological and chemical processes is clearly reflected in the distributions of many chemical properties, the distributional data alone is not always sufficient to quantify these processes to the point where cycling within the system and transport across the marine boundary may be confidently predicted. For example, the interpretation of concentration-salinity relationships is complicated by the mixing time considerations leading to the differentiation between Clyde Estuary Plume ( $30 < S < 32$ ;  $4 < T \text{ (days)} < 25$ ) and Clyde Sea ( $32 < S < 34$ ;  $60 < T \text{ (days)} < 150$ ) as well as by the intrusion of considerably older water masses from the sealochs during periods of deep water renewal. These factors complicate the study of *in situ* processes in the Firth of Clyde by comparison with either the estuarine or the open shelf environment.

Apart from horizontal and vertical mixing processes, particle-solution interactions appear to be the singlemost

important process influencing trace metal distributions. It is also the least well understood. We still do not know how the rates of heterogeneous reactions compare with mixing rates. Given the much shorter flushing time of the plume, we suspect - but cannot prove - that the rates of particle-solution transformations are much higher in the plume than in the deep passages and lochs, *i.e.* comparing water bodies where such transformations have been inferred from the distributional data. There are still large gaps in our fundamental knowledge of the basic processes producing these distributions. For example, the extent to which Mn cycling influences the concentrations of dissolved trace metals is still a matter of debate. The complexity of this coastal environment will be best addressed through an iterative combination of physico-chemical experiments in the laboratory and higher resolution sampling and analysis in the field.

The summer maximum in the dissolved Mn inventory of the Firth of Clyde can only be explained by a marine, as opposed to local, source. More debatable is the significance of Mn remobilization from the sealoch sediments in the global chemical budget of this element.

One main finding concerning the remineralization of natural organic matter is that it occurs in the deepest parts of the system (*e.g.* the Bute Sound) with approximate stoichiometry  $P:N:C:-O_2 = 1:12:270:570$ . This composition suggests that an appreciable fraction of the organic matter originates from river runoff or soil leaching (Buffle, 1988). The complexing properties and other physico-chemical characteristics of the pool of natural organic matter remain to be investigated. One specific aspect that is critical to understanding the cycling of trace elements is whether specific classes of organic compounds occur in the truly dissolved form, as part of colloidal material, or as coatings on oxi-hydroxides of Mn(III), Mn(IV) and Fe(III). An important related question is whether the ubiquitous organic coatings known to control the electrokinetic properties - and hence the stability - of particles (Hunter and Liss, 1982) are removed or modified (Hunter, 1991) as the particles are remineralized in the deep layers of the Firth of Clyde.

With the notable exceptions of air-sea gas exchange and photosynthesis, this study indicates that the inner Firth of Clyde is a more active "chemical reactor" than either the Clyde Estuary or the outer Firth of Clyde in modifying the distributions of elements anticipated from simple mixing.

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