

# Annual geochemical mass balances in waters of the Firth of Clyde

Trace element fluxes  
Chemical budgets  
Mass balances  
Coastal waters  
Firth of Clyde

Flux d'éléments-traces  
Bilans chimiques  
Équilibres de masses  
Eaux côtières  
Firth of Clyde

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## ABSTRACT

A first-order mass balance of twelve minor and trace elements in the coastal sea area of the Firth of Clyde is presented for the period August 1989-July 1990. It is based on our own four sets of chemical data collected in the Clyde Estuary and Firth of Clyde over that period, complemented by independent information relating to water column hydrography, rainfall, wind speed, river discharge, as well as sewage sludge and dredged material disposed of at sea. Terrigenous inputs were measured or estimated as continuous functions of time. Mean exchange rates with the open shelf were calculated over four periods representative of 77 % of the one-year period considered here. All these fluxes were subsequently converted to monthly values to facilitate intercomparison. Sedimentation rates were estimated by difference. The trapping efficiency (%) of the system over the study period was  $80 \pm 8$  for Pb,  $75 \pm 10$  for Fe,  $70 \pm 9$  for Co,  $68 \pm 12$  for Mn,  $50 \pm 14$  for Zn,  $34 \pm 31$  for P,  $33 \pm 20$  for N,  $33 \pm 25$  for Cu,  $26 \pm 30$  for Ni,  $20 \pm 46$  for Si,  $15 \pm 16$  for Cd,  $14 \pm 26$  for organic C, and  $-14 \pm 13$  for inorganic C. Most elements exhibited a close correspondence between their annual import and export fluxes across the marine boundary. The implication is that physical transport is the dominant process in the region adjoining the North Channel, *i.e.* the outermost part of the Firth of Clyde. By extension, the inner Firth and near-shore zone must act as a trap for metal-bearing particles. Such an understanding of the present-day state of the system with regard to trace metal and nutrient cycles would enable one to predict the response of the system to any scenario of modification of the metal/nutrient inputs only to the extent that the system responds linearly to input variability.

## RÉSUMÉ

Bilans annuels des éléments géochimiques dans les eaux du Firth of Clyde.

Nous avons tenté d'établir le bilan chimique du Firth of Clyde (ouest Écosse) entre août 1989 et juillet 1990 inclus, pour les flux d'entrée et de sortie de huit éléments traces et quatre éléments nutritifs. Ce bilan annuel repose sur quatre séries de données chimiques recueillies pendant la période en question, auxquelles s'ajoutent des données auxiliaires sur les apports atmosphériques et fluviaux, les rejets en mer et les distributions de salinité permettant l'évaluation des

débits d'entrée et de sortie. Les flux de matière liés aux rejets continentaux (apports atmosphériques et fluviaux ainsi que déversement en mer de boues métalliques) sont tout d'abord évalués à l'échelle journalière, tandis que ceux qui résultent des échanges avec le large (North Channel) font l'objet d'une évaluation à une échelle de temps de l'ordre de deux à quatre mois. Ces flux sont ensuite exprimés par leurs moyennes mensuelles. A l'échelle annuelle, les pertes par sédimentation au sein du Firth of Clyde sont représentées par la différence entre les apports et les écoulements vers le large. A l'échelle globale, le système retient 80 % ( $\pm 8$  %) de l'apport total de plomb, 75 % ( $\pm 10$  %) du fer, 70 % ( $\pm 9$  %) du cobalt, 68 % ( $\pm 12$  %) du manganèse, 50 % ( $\pm 14$  %) du zinc, 34 % ( $\pm 31$  %) du phosphore dissous, 33 % ( $\pm 20$  %) de l'azote sous forme  $\text{NO}_3^-$  ou  $\text{NO}_2^-$ , 33 % ( $\pm 25$  %) du cuivre, 26 % ( $\pm 30$  %) du nickel, 20 % ( $\pm 46$  %) du silicium dissous, 15 % ( $\pm 16$  %) du cadmium, 14 % ( $\pm 26$  %) du carbone organique et -14 % ( $\pm 13$  %) du carbone inorganique. Les flux d'entrée et de sortie à l'interface Firth of Clyde-North Channel sont en général très voisins, ce qui permet d'avancer l'hypothèse selon laquelle le Firth extérieur agit essentiellement en tant que zone d'échange à deux couches tandis que le Firth intérieur, les lochs et les estuaires constituent la partie chimiquement active du système. Il est bien entendu qu'une telle description de l'état géochimique stationnaire du Firth of Clyde ne suffit pas pour prévoir l'évolution du système en réponse à une modification des apports chimiques ou un changement des conditions climatiques.

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## INTRODUCTION

The cycling of chemicals through the coastal zone has a fundamental impact on the geochemical balance of the ocean as well as on the health of our nearshore aquatic environment. A thorough understanding of the factors regulating the transfer of chemicals between different compartments (water masses, atmosphere, sediments, marine organisms etc.) is therefore needed by both the marine geochemical and environmental protection communities. Over the last 25 years, a good deal of effort has been directed to improve our knowledge of the way in which estuaries function as geochemical reaction vessels. The main focus has been on the processes occurring during the transition from freshwater to seawater, where physicochemical variables show marked changes and turbidity maxima commonly enhance the potential for particle-solution interactions. With the development of European monitoring programmes (EROS, EURO-MARGE, FLUXMANCHE, OMEX) the coupling between estuaries and shelf waters has begun to receive more attention in Europe, although the *in situ* processes modifying the flow of chemicals in estuarine plumes are still not well known. In this paper, we present a first-order attempt at a mass balance of nutrients, organic carbon and trace metals in a small coastal sea, the Firth of Clyde, following a yearlong study of their distributions (Muller *et al.*, this issue).

Knowledge of the chemical fluxes in and out of a natural reservoir is generally obtained by indirect methods. In a coastal sea such as the Firth of Clyde, chemicals enter the system in association with rainwater, aerosols, river inputs, shore erosion, inflow water of oceanic origin, or

as part of wastes dumped at sea. They leave it by being exported across the marine boundary or settling out of the water column to the seabed. Inputs from freshwater and seawater are a function of water flow and constituent concentration, both of which may vary over short time scales. For example, measured flow velocities along the main axis of the system vary on an hourly scale due to the combined effect of wind and tidal stirring (Simpson and Rippeth, 1993). Measurement methods available at present do not allow us to sample this natural variability over a long enough period of time, nor have any of these methods yet advanced to the stage of continuous *in situ* use. The best practical approach under the circumstances is to treat short term effects as statistically constant over time scales determined by variations in chemical constituent concentrations. The uncertainties introduced by the lack of spatial resolution are likely to be much less than those produced by undersampling in time. For example, the outflow from the Clyde Estuary is constrained to a relatively narrow channel, and chemical distributions near the marine limit of the system are likely to show horizontal uniformity. Indeed, the Firth of Clyde lends itself relatively well to such a crude one-box mass balance approach, in that it is a semi-enclosed basin with somewhat restricted exchange with the open shelf. What is more, the inputs of nutrients and metals are dominated by point sources of which the Clyde Estuary is the most significant.

It should be emphasized that the net river fluxes presented below represent in fact net estuarine fluxes, *i.e.* after allowance has been made for addition, removal and mixing processes within the estuary. It follows that the Clyde Estuary is not considered a part of the system studied here. Another important aspect of the present work is the incor-

poration of uncertainties into the flux estimates. These uncertainties originate from standard errors on quantities as unrelated as measured concentrations or estimated parameters which are used in the calculation of fluxes. Error estimation is a key element of a mass balance exercise in that it provides a validation – or an insight into the limits – of the approach used. For example, it is shown below that no firm conclusion can be reached regarding the carbon balance of the system.

## METHODS

Materials and methods in relation to sampling and analysis are presented elsewhere (Muller *et al.*, 1994). In this section, only the methods used to calculate fluxes of chemical constituents are presented. The waters of the Firth of Clyde are represented schematically in Figure 1 by a single box. The inventory of a given element in the box is allowed to vary seasonally, but to facilitate interpretation of the results an internal flux balance is assumed over a one-year cycle. On these assumptions, the net annual removal of an element by sedimentation may be obtained from the difference between the sum of all known inputs (Fig. 1) and the output to the North Channel. Note that phase transformations between solution and suspended solids are not considered here. Both dissolved and particulate concentrations have been measured for organic carbon and trace metals, but they have been combined to produce total flux estimates.

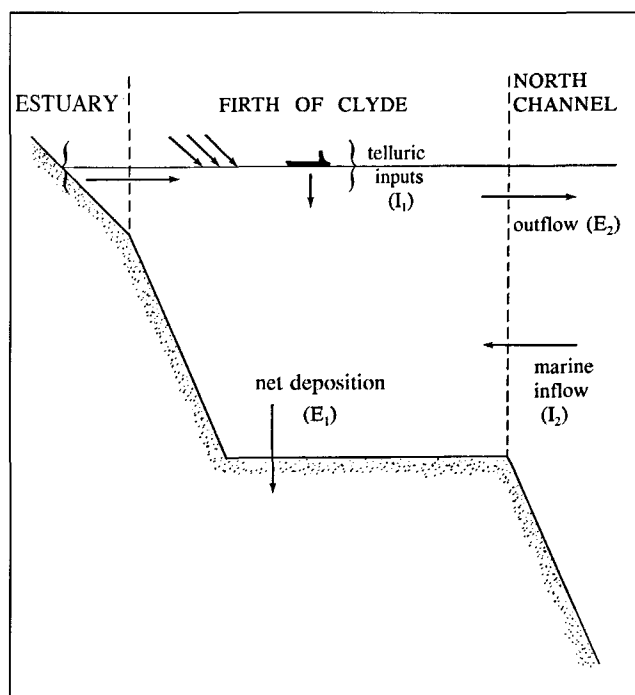


Figure 1

Pictorial representation of the mass balance exercise showing the main imports ( $I_1$ ,  $I_2$ ) to and exports ( $E_1$ ,  $E_2$ ) from the Firth of Clyde.

Représentation schématique des flux d'entrée ( $I_1$ ,  $I_2$ ) et de sortie ( $E_1$ ,  $E_2$ ) composant le bilan en matière du Firth of Clyde.

## Step 1 – Choosing the best observational period

Water samples were collected in both the Firth of Clyde and the Clyde Estuary over the following periods: 19-21 August 1989, 20-23 November 1989, 20-25 March 1990 and 2-5 July 1990. Although the final objective is the estimation of yearly mean fluxes, there are several ways in which this can be arrived at. A process-blind approach might be to calculate the annual flux as the arithmetic average of the values obtained on each of the four seasonal cruises and then scale it up to the entire August 1989-July 1990 year. However, this approach does not recognize the fact that net river fluxes are available as explicit functions of river discharge, and thus may be estimated at any time between study periods to provide a more accurate annual estimate. By contrast, marine inputs and outputs cannot be parameterized in this way and therefore can only be reliably estimated for our four snapshots during the year of interest. Another disparity lies in the times necessary to replace the freshwater of the Clyde Estuary and that of the outer Firth of Clyde, implying very different time scales of flux variations. To address these problems while allowing comparison between the seasonal fluctuations of these various fluxes, we chose to report all fluxes in the form of monthly mean values. Although months may represent slightly different lengths of time, there are obvious advantages in this presentation of the results. In addition, a one-month resolution is consistent with the approach used to calculate atmospheric as well as riverine inputs in that it integrates the short time scale “weather-related” components of the system. In this respect, it turns out to be comparable to the high frequency limit of climate variability (Hasselmann, 1976) and indeed also to the approximately 1 cycle per 45 days frequency picked out from the spectral analysis of both the rainfall and river flow three-year records (Fig. 2). The first large peak in the two frequency spectra of Figure 2 corresponds to  $\sim 1$  cycle every 365 days and is simply due to the seasonal nature of the data. The peak at the  $\sim 45$  days time scale ( $0.022$  cycle  $\text{day}^{-1}$ ) also rises above the typical random component that we expect (Hasselmann, 1976) and do get (Fig. 2) from high-frequency weather disturbances. Its existence may also be inferred from the irregular but organized pulses seen in the rainfall and river flow continuous records (Fig. 2). As noted earlier, exchanges at the marine boundary may occur not only over shorter (tides, wind) but also over longer time scales set by external factors of oceanic origin. Thus the reported monthly variations in water flow (and hence chemical fluxes) across the sill should be interpreted with caution.

## Net river fluxes

The major inflow of freshwater and associated contaminants is from the rivers discharging into the Clyde Estuary, thereafter referred to as “the Clyde rivers”. They provided  $4390 \times 10^6 \text{ m}^3$  of freshwater to the Firth of Clyde over the one-year period, against  $1880 \times 10^6 \text{ m}^3$  for the rivers of Ayrshire, Arran and the sealoch system taken together (source: Clyde River Purification Board). Net river fluxes

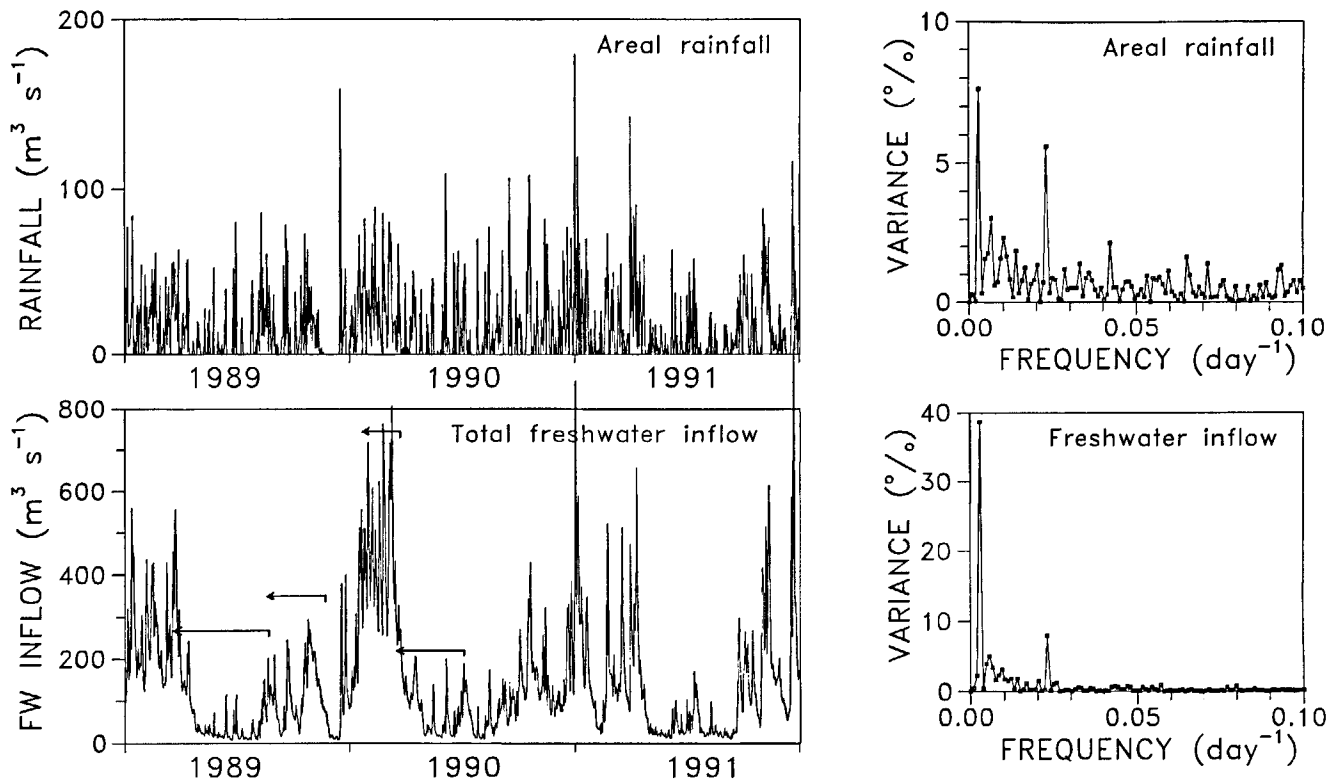


Figure 2

Rainfall over the inner Firth of Clyde (top left) and total freshwater inflow to the inner Firth (bottom left); arrows indicate the freshwater replacement time in the upper layer of the outer Firth. The variance of the data is decomposed into contributions over a range of frequencies (Chatfield, 1989); the periodograms thus obtained show significant variability on time scales of 1/365 and 1/45 cycle  $\text{day}^{-1}$ .

Séries d'observations de la pluviométrie et de l'apport des cours d'eau au Firth intérieur (à gauche) et analyses spectrales correspondantes (à droite). A la variabilité annuelle de 1/365 cycle  $\text{jour}^{-1}$  s'ajoute un pic à 1/45 cycle  $\text{jour}^{-1}$  d'origine inconnue et dont l'exploitation fiable nécessiterait une plus longue période d'observation; des harmoniques apparaissent également aux fréquences  $n/365$  cycle  $\text{jour}^{-1}$ .

of organic carbon, nutrients and trace metals contributed by the Clyde rivers were estimated from salinity relationships in the lower estuary and from a weighted average of the daily freshwater flow over a period long enough to account for most of the freshwater content of the estuary (Muller *et al.*, 1994). It was found that they could be expressed as either constants or linear functions of "effective" freshwater flow and standard errors were also calculated. One consequence of this linearity is that annual flux estimates should be independent of the observational time intervals (months selected here) used to carry out the summation. Annual estimates of net fluxes from other rivers were obtained in a similar manner, *i.e.* by summing up monthly estimates resulting from the product of effective zero salinity (EZS) concentrations and river water discharge. Daily mean discharge data were obtained from the Clyde River Purification Board; they also provided bimonthly sets of nutrient measurements taken at the mouths of the Ayrshire rivers and which enabled calculation of EZS nutrient concentrations. Fluxes were again fitted to constant (P and N) or linear functions (Si) of river flow. In a few cases (minor rivers), no information on nutrient concentration was available and so data from the geographically nearest river was used. Trace metal data for these small rivers was scarce, so that it was not possible to test for relationships between water flow and dissolved or

particulate load. However, we noted that the larger among these small rivers drain watersheds of a similar geological and climatological nature to that of the Clyde rivers; consequently, we used the same form of water flow vs metal flux relationships as for the Clyde rivers to fit what limited data was available. It should be added that while the Clyde rivers might be expected to be more contaminated than some of the smaller rivers draining Arran and the Highland region, the latter have no estuarine "filter zone" to speak of but discharge freshwater directly into the system.

#### Atmospheric deposition fluxes

Total rainfall over the area of the Firth of Clyde ( $3680 \text{ km}^2$ ) was estimated at  $5190 \times 10^6 \text{ m}^3$  for the period 1/8/89 to 31/7/90. This value was obtained by averaging the daily rainfall measurements at three well spread gauging stations: Rothesay, Isle of Bute; Carskiefy, Kintyre peninsula; Doonholm, Ayrshire coast. The location of these stations are identified by star symbols in Figure 1 of Muller *et al.* (this issue). There is no reliable data on the chemical composition of precipitation on the Firth of Clyde, particularly for trace elements. Given the large variations in reported concentrations at other west European sites, the values we selected as representative were obtained by averaging

those from at least three independent data sets. Uncertainties were represented by the standard deviations on the means which, accordingly, tended to be large (30-60 % for the most part). Representative values for organic carbon and nutrients were taken from the following sources: Hitchcock *et al.* (1990), northeastern Atlantic; Buijsman *et al.* (1991), northeastern Atlantic; Balls (1989), Scottish North Sea coast; Baeyens *et al.* (1990), North Sea. Representative values for trace metal concentrations were taken from: Buijsman *et al.* (1991), northeastern Atlantic; Lim and Jickells (1990), Ireland; Jickells *et al.* (1992), Scottish Highlands; Balls (1989), Scottish North Sea coast; Krell and Roekner (1988), North Sea; Alcamo *et al.* (1992), Europe. The selected concentrations, as stated in Table 1, were used to calculate the annual wet deposition flux of any element.

Table 1

Concentration of constituents in rainfall as selected from the literature (see text), and relative importance of dry vs wet deposition.

Valeurs moyennes des concentrations en métaux et nutriments pour l'ensemble des précipitations annuelles, et contribution du dépôt sec aux précipitations annuelles totales.

Element	Concentration	dry/(dry + wet)
Fe	600 ± 400 nmol l <sup>-1</sup>	0.20
Mn	40 ± 30 nmol l <sup>-1</sup>	0.50
Zn	110 ± 40 nmol l <sup>-1</sup>	0.20
Pb	10 ± 7 nmol l <sup>-1</sup>	0.20
Cd	1.3 ± 0.7 nmol l <sup>-1</sup>	0.20
Co	2 ± 2 nmol l <sup>-1</sup>	0.20
Ni	50 ± 50 nmol l <sup>-1</sup>	0.20
Cu	19 ± 10 nmol l <sup>-1</sup>	0.20
DOC	0.4 ± 1.0 mg l <sup>-1</sup>	—
P	1.7 ± 1.1 μmol l <sup>-1</sup>	—
N	25 ± 15 μmol l <sup>-1</sup>	—
Si	10 ± 40 μmol l <sup>-1</sup>	—

The next step was to work back the monthly wet deposition flux of each element. A first-order approach would be to consider that this flux is the same during wet and dry periods and thus to apportion the annual flux equally between the twelve months of the year. The underlying assumption would be that concentrations in precipitation are inversely proportional to rainfall volume. A more accurate description of the relationship between concentration of an element in rain and precipitation volume is (Baeyens *et al.*, 1990):

$$C = A + B/P \quad (1)$$

where C = element concentration in rain water

P = precipitation volume

A, B = hyperbolic regression coefficients.

Thus our approach was to seek A and B such that the sum of all products C<sub>i</sub>P<sub>i</sub> matched the annual value based on the literature-selected value of C:

$$\sum_{i=1}^{365} C_i P_i = C \times \sum_{i=1}^{365} P_i \quad (2)$$

A non-linear fitting procedure based on the Simplex method of Nelder and Mead (1964) was used to obtain the coefficients A and B. As pointed out by Baeyens *et al.* (1990), this model is strictly applicable to individual rain events rather than set periods of one day each. Nevertheless, we can still expect a more realistic picture of the short term variations in wet deposition fluxes than if the assumption was made of constant rainwater composition (Baeyens *et al.*, 1990). Finally, dry deposition was assumed to be constant throughout the year. Annual dry deposition was obtained from a knowledge of wet deposition together with an assessment of the relative importance of dry vs wet deposition (from 20 % for Cu up to 100 % for Mn) made possible from the following studies: Lim and Jickells (1990), northeastern Atlantic; Baeyens *et al.* (1990), North Sea; Alcamo *et al.* (1992), Europe; Galloway *et al.* (1982), world.

### Sewage and dredge spoil dumping

Maintenance dredging of the Clyde Estuary and other smaller navigation channels resulted in the introduction of approximately 103,000 tonnes (dry tonnage) of dredged material into the system over the study period (source: Department of the Environment, or DOE). In addition, a total of 63,000 tonnes (dry tonnage) of sewage sludge was dumped at Garroch Head on a daily basis throughout the period (source: Scottish Office Agriculture and Fisheries Department, or SOAFD). The disposal of these wastes was controlled by a system of licences issued by SOAFD (MAFF, 1992). The impact of unlicensed disposal was deemed to be small. The composition of the sewage sludge deposited was obtained directly from SOAFD while that of the dredged spoil was taken from MAFF (1992). Most elements were found in comparable concentrations in both types of wastes, with the following exceptions: P, N, Cu, Cd (five times higher in sewage sludge) and Fe (two times lower in sewage sludge). Metal concentrations reported for dredged material also turned out to be very close to those measured by us in the surficial sediments of the lower Clyde Estuary. We assumed that both dredged spoil and sewage sludge were deposited uniformly throughout the year.

### Air-sea exchange fluxes of inorganic carbon

The net flux of CO<sub>2</sub> across the air-sea interface was calculated according to

$$F = k \cdot s \cdot \Delta f \text{CO}_2 \quad (3)$$

where k, the transfer or piston velocity (m yr<sup>-1</sup>), was calculated from the wind speed dependent formulation proposed by Liss and Merlivat (1986) and the temperature dependence proposed by Jähne (1980). The solubility of CO<sub>2</sub> (mol m<sup>-3</sup> atm<sup>-1</sup>) was obtained from Weiss (1974) as a function of salinity and temperature. ΔfCO<sub>2</sub>, the deviation of pCO<sub>2</sub> from atmospheric equilibrium (μatm), was calculated from ΣCO<sub>2</sub> and alkalinity measurements. Monthly mean values of F were obtained by applying equation 1 to each day of the study period, and then averaging the values over

each month. Wind speed data for the outer Firth of Clyde were obtained from the Meteorological Office, and the values were scaled down by a factor of 2/3 for the inner Firth. Daily values of sea surface temperature (5 m depth measurement), salinity and  $p\text{CO}_2$  were estimated by using cubic spline functions (Hazony, 1979) to connect our four (day #, variable) data points. The uncertainty in  $F$  resulted from (1) the propagation of the standard error on temperature (affecting  $k$  and  $s$ , and estimated at  $\pm 1.5^\circ\text{C}$ ) and on wind speed (affecting  $k$ , and estimated at  $\pm 2\text{ m s}^{-1}$ ), and (2) the summation to the one-month period. When a high uncertainty in  $k$  (e.g. due to low winds) concurred with a low value of  $\Delta\text{CO}_2$  the relative uncertainty on  $F$  was accordingly large (equation 3) and the sign of the flux became uncertain.

### Inputs and outputs across the marine boundary

The intensity of the exchange with the North Channel may be related to the surface density difference across the marine boundary of the system (Edwards *et al.*, 1986; Simpson and Rippeth, 1993). In practice, however, the exchange tends to be intermittent and the wind in particular can have pronounced short-term effects on surface motions (Edwards *et al.*, 1986) to the point where these are completely decoupled from deeper motions (Rippeth, pers. comm.). Thus our approach to quantifying this exchange is based on the long-term conservation of the volume of water within the upper layers of the outer Firth, *i.e.* the geochemical box receiving all the freshwater inputs. A knowledge of its volume and mean salinity allows calculation of the time required to supply its freshwater contents. During that time, a amount of new seawater equivalent to the volume of the upper layer box must enter the system at depth. In this way, mean water fluxes across the marine boundary may be calculated for the period in question.

Unfortunately, our coverage of the outer Firth of Clyde was too sparse to allow a precise estimation of the volume and mean salinity of the upper layers. This problem was addressed by using four comprehensive salinity data sets obtained by Edwards *et al.* (1986) in January/August 1985 and by Simpson and Rippeth (1993) in June/November 1990. Each of these hydrographic studies included some stations which coincided with, or approximated, our own. The procedure for determining  $\bar{S}$ , mean salinity, and  $\bar{Z}$ , mean depth, for our surveys was as follows. An interpolation algorithm was developed to make precise estimates of  $\bar{S}$  and  $\bar{Z}$  for the four comprehensive studies (see next paragraph). It was then found that  $\bar{S}$  and  $\bar{Z}$  thus obtained could be approximated by the weighted averages of the mean value at Station 7 (weighting factor = 1.00) and that at Station 8 (weighting factor = 0.68). Using  $\bar{S} = [\bar{S}_{\text{STN7}} + 0.68 \bar{S}_{\text{STN8}}]/1.68$  thus provided a means of calculating the freshwater volume locked up under the conditions of our surveys with a relative error (based on the three point correlation) of 7% (Fig. 3).

The geographical boundaries of the box were defined by excluding the inner Firth and the sealoch system in the north (sealoch limit), and by drawing a NW-SE straight line over the area where the seabed dips gradually seawards (marine limit). In the east and west, the box was delineated by the Ayrshire coastline and the Kintyre Peninsula, respectively. A uniform grid was dropped over the survey area

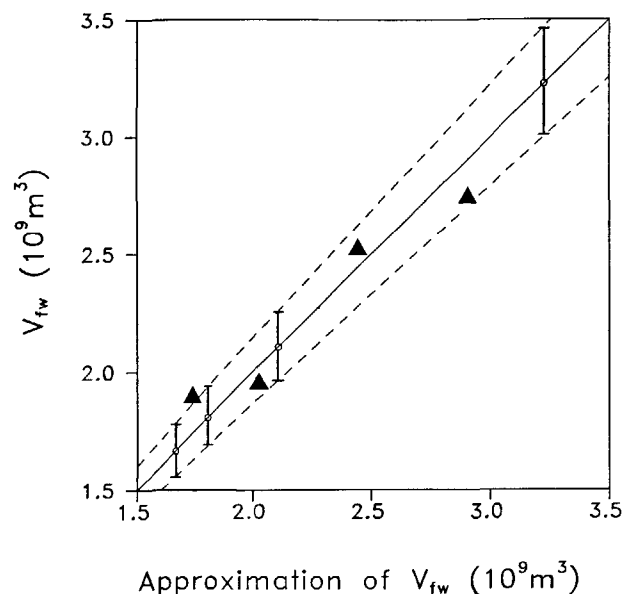


Figure 3

The four hydrographic surveys of the outer Firth of Clyde by Edwards *et al.* (1986) and Simpson and Rippeth (1993) enabled a comparison to be made (solid triangles) between the estimate of  $V_{fw}$  based on the whole box and that based on only two judiciously selected stations. Also shown are the estimates of  $V_{fw}$  on each of our surveys together with the standard errors resulting from the use of the two-station procedure.

Les quatre triangles pleins qui correspondent aux campagnes hydrographiques détaillées de Edwards *et al.* (1986) et de Simpson et Rippeth (1993) définissent une relation de travail entre la valeur précise de  $V_{fw}$  obtenue à partir de l'ensemble de leurs stations hydrographiques et celle évaluée à partir de seulement deux stations choisies par approximations successives. Cette relation (ligne continue) et le domaine d'incertitude qui l'accompagne (tirets) permet alors l'évaluation de  $V_{fw}$  correspondant à chacune de nos propres campagnes.

in order to make estimations of  $\bar{S}$  and  $\bar{Z}$  at regular intervals between the observations. Grid intersection points (nodes) were spaced every 3 km in both N-S and E-W directions and made up a total of 279 points at which  $\bar{S}$  and  $\bar{Z}$  were estimated by linearly combining some of the surrounding observed data points (30-50 in total). Shoreline points based on CRPB surveys of Ayr Bay and Irvine Bay were added to the existing observations to insure that the method was strictly based on interpolation and not extrapolation. The term "observation" denotes a ( $\bar{Z}$ ,  $\bar{S}$ ) data point produced by integrating the salinity profile over a water depth extending either to the base of the halocline/thermocline (the two usually coincided) or to the seafloor in cases where depths did not exceed 25 m. At each node, the interpolated values  $\bar{Z}$  and  $\bar{S}$  were obtained as the weighted averages of the three nearest observations. The weighting coefficient was chosen to be the inverse square of the distance so as to allow closer observations to have an even greater contribution to the estimate than if the weight was simply the inverse distance. Finally, the ( $\bar{Z}$ ,  $\bar{S}$ ) values were averaged over the whole grid to produce the final estimates required in the calculation of freshwater volume. The mapping/interpolation algorithm described above was implemented by a QBasic program to which sets of observations stored in sequential files were supplied.

Once the freshwater volume,  $V_{fw}$ , corresponding to one of our surveys has been calculated, the residence time,  $T$ , can be obtained by summing up all freshwater inputs back through time from the date of the survey ( $t = 0$ ) until the volume  $V_{fw}$  has been accounted for:

$$V_{fw} = \sum_{t=0}^T [R_A(t) + R_C(t-T_0) + 0.15 P(t)] \quad (4)$$

with  $R_A(t)$  = daily freshwater input from Ayrshire, Arran and the sealochs

$R_C(t)$  = daily freshwater input from the Clyde rivers

$P(t)$  = daily rainfall

$T_0$  = flushing time of water in the Clyde plume (time delay)

Equation 4 allows for a time lag of 4-25 days (Muller *et al.*, this issue) between recording of freshwater flow at the gauging stations on the Clyde rivers and discharge into the outer Firth. The term  $0.15 P(t)$  is based on an estimated difference between precipitation and evaporation of  $200 \text{ kg m}^{-2} \text{ yr}^{-1}$  (Gill, 1982). Equation 4 led to freshwater replacement times of 150 days (August 1989), 94 days (November 1989), 62 days (March 1990) and 107 days (July 1990). These values are comparable to estimates based on long-term variations in  $^{137}\text{Cs}$  concentrations (Baxter *et al.*, 1981), water balance in the outer Firth (Edwards *et al.*, 1986) and exchange rate inferred from the density structure (Simpson and Rippeth, 1993). In turn, these values led to estimates of new water inflow of  $0.444$ ,  $0.599$ ,  $0.938$  and  $0.648 \times 10^9 \text{ m}^3 \text{ day}^{-1}$ , with corresponding estimates of outflow of  $0.457$ ,  $0.614$ ,  $0.985$  and  $0.663 \times 10^9 \text{ m}^3 \text{ day}^{-1}$ . Since the residence time and box volume are related *via*  $V_{fw}$  (which is known to within 7 %, as illustrated in Figure 3) an uncertainty of 7 % on the box volume seemed appropriate. It is worth noting that the difference between water outflow and inflow is also known to within 7 % since  $E_2 - I_2 = V_{fw}/T$ . It is for this reason that  $E_2$  and  $I_2$  are reported with an uncertainty of 0.1-0.2 % ( $\pm 0.001$ ): taken individually they should be expressed with a relative error of 7 %, but because they are tied together through the conservation equation ( $E_2 - I_2 = V_{fw}/T$ ) their errors are not independent. To smooth the exchange flow data and express the variations with time mathematically, a cubic spline function was fitted through the data points after these had been shifted back in time so as to lie at the centre of the time intervals shown in Figure 2. The reason for this correction is that water flows reported here are not instantaneous values but are representative of a period running up to the date of the survey.

The last step was to multiply the monthly mean flow values by the corresponding constituent concentrations in the outflowing and inflowing water bodies in order to provide estimates of chemical fluxes. Concentrations measured at the outermost station (Station 9) were used for this purpose. The 5-20 m and 40-55 m depth ranges were taken to represent the composition of the outflowing water and inflowing water, respectively. In both cases, cubic-spline interpolating functions were used to connect the four data points and thus allow estimation of monthly mean concentrations. The standard error on this esti-

mation was taken to be half the standard deviation among the four observations.

## RESULTS

The simulated variations of the monthly inputs (marine and non-marine) and outputs for all 12 elements are shown in Figure 4. A general trend is that outputs as well as land-derived (river/estuarine + aeolian + dumping at sea) inputs are highest in some of the winter months. With the notable exceptions of Mn, Zn and Pb, marine inputs (Fig. 4, positive differences between connected and unconnected points) show variations which are generally in phase with this trend. Manganese shows a uniquely different pattern in that both its inputs and outputs across the marine boundary peak in the summer months while its land-derived inputs show slightly elevated values in the winter. Inorganic carbon has been left out of Figure 4 for two reasons. Firstly,  $\Sigma\text{CO}_2$  was always oversaturated in the inner Firth but undersaturated (except in November) in the outer Firth with respect to atmospheric equilibrium of  $\text{pCO}_2$ , with the consequence that — from January to August — the inner Firth acted as a source to the atmosphere while the outer Firth acted as a sink. On a global scale, the system took up  $\text{CO}_2$  from the atmosphere in January-August and released  $\text{CO}_2$  in September-December. Secondly,  $\Sigma\text{CO}_2$  exchange fluxes across the marine boundary were some two orders of magnitude greater than either the air-sea exchange flux or the river input, which would have made a graphical representation inappropriate.

The annual contribution of each source to the total input of each element is given in Table 2. Marine inputs are significant for all elements and dominate all other inputs by one order of magnitude for Cd, Ni, Cu, and two orders of magnitude for OC (organic carbon) and IC (inorganic carbon). This is because the net volumes of water transported across the sill are so large. The contribution of rivers is particularly significant for Fe, Mn, Pb, Co, P, N and Si. Inputs from dredge spoil are important for Fe, Pb and Co. Atmospheric inputs as well as inputs from sewage sludge dumping are important for Pb. For each element, it is instructive to examine the proportion of the total annual input that escapes to the offshore marine environment ( $\text{Output}/\Sigma\text{inputs}$ ) as well as the relative contribution of the marine source ( $\text{Marine input}/\Sigma\text{inputs}$ ). Particle-reactive elements such as Fe, Mn, Pb and Co show greater than 50 % removal through the system. At the opposite end of the spectrum, Si and C appear to pass through the system unaffected by any net sedimentation process. What is more, there is remarkable numerical correspondence between the two ratios ( $\text{Output}/\Sigma\text{inputs}$ ) and ( $\text{Marine input}/\Sigma\text{inputs}$ ) over the whole suite of elements (Tab. 2). Uncertainties in the two ratios are relatively large due to error propagation but do not invalidate the conclusion that the two ratios are closely correlated ( $r^2 = 0.962$ ;  $n = 12$ ).

## DISCUSSION

It is important to note from the outset that the errors associated with the evaluation of fluxes (Tab. 2) may have been

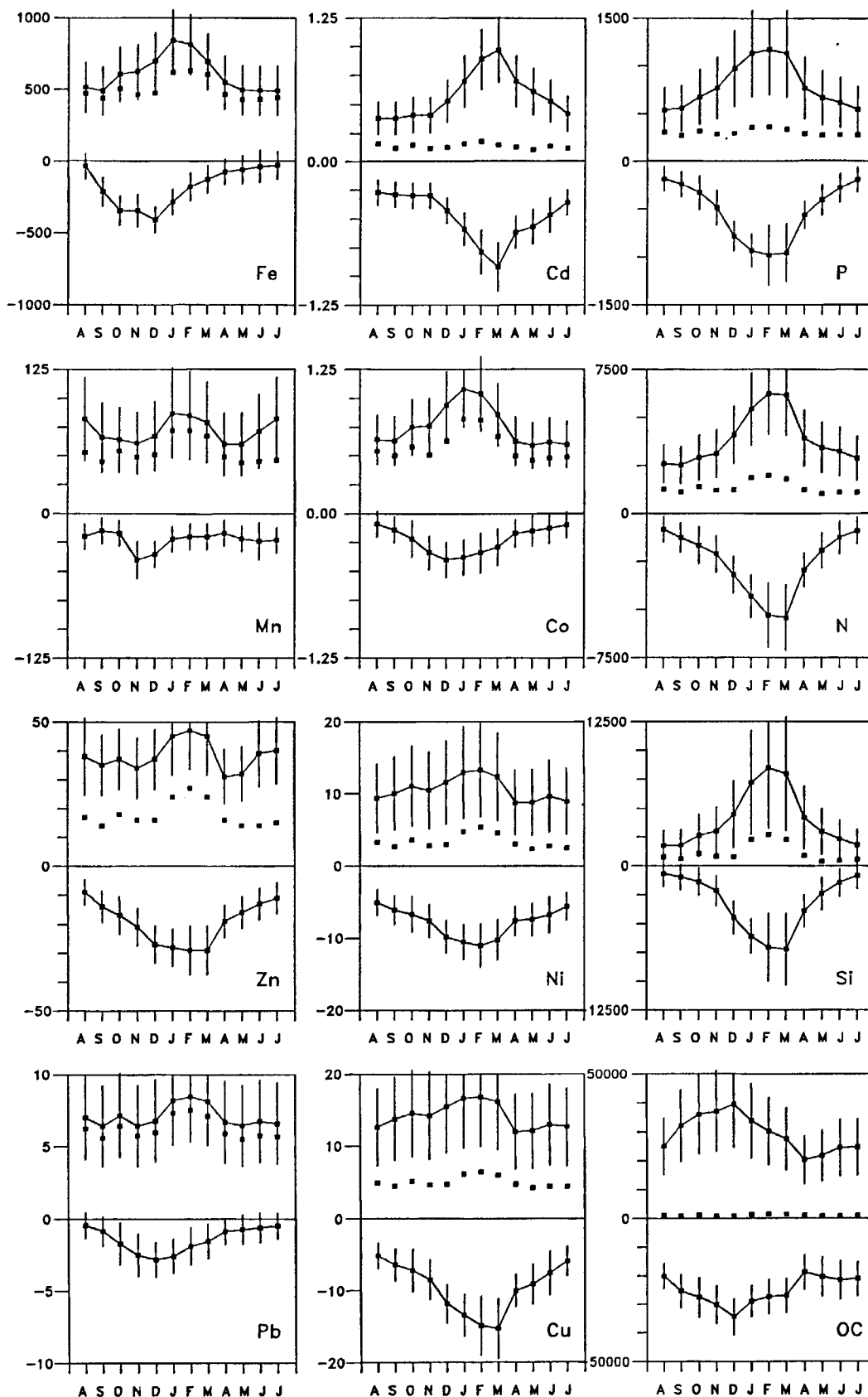


Figure 4

Monthly variations in the imports (positive) and exports (negative) of trace metals, nutrients and organic carbon, in tonnes month<sup>-1</sup>; a) unconnected points: terrigenous inputs; b) top line; total inputs; c) bottom line: seaward flux. Vertical lines show standard error.

Évolution, entre août 1989 et juillet 1990, des flux mensuels d'entrée (positifs) et de sortie (négatifs) exprimés en tonnes mois<sup>-1</sup>; a) points non raccordés : apports continentaux (cours d'eau, ruissellements, déversements urbains) ; b) courbe supérieure : apport total (continentaux et marins) ; c) courbe inférieure : sorties vers le large. Les traits verticaux correspondent à l'écart-type.



Table 2

Export to the open sea (column 2) and known imports (columns 3-8) of 12 elements, in tonnes per year, percentage lost to the open sea (column 9) and percentage of inputs from the open sea (column 10).

Flux élémentaires vers le large (colonne 2) et en provenance de sources connues (colonnes 3-8), exprimés en tonnes par an, fraction des apports exportée vers le large (colonne 9) et fraction des apports d'origine marine (colonne 10).

Element	Export to North Channel (E <sub>2</sub> )	Atmosphere	Sewage	Dredged spoil	Rivers	North Channel (I <sub>2</sub> )	Inputs	E <sub>2</sub> × 100 / inputs	I <sub>2</sub> × 100 / inputs
Fe	1840 ± 480	213 ± 110	849	2781 ± 260	2132 ± 789	1335 ± 440	7310 ± 946	25 ± 10	18 ± 8
Mn	276 ± 49	23 ± 8	28	41 ± 10	557 ± 178	219 ± 48	868 ± 185	32 ± 12	25 ± 10
Zn	234 ± 37	47 ± 14	48	34 ± 8	87 ± 16	247 ± 53	463 ± 58	50 ± 14	53 ± 18
Pb	16.7 ± 4.7	13.4 ± 7.5	23.6	21.0 ± 0.4	16.8 ± 7.6	10.3 ± 3.6	85 ± 11	20 ± 8	12 ± 5
Cd	5.89 ± 0.46	0.95 ± 0.40	0.38	0.12 ± 0.04	0.24 ± 0.11	5.25 ± 0.68	6.9 ± 0.8	85 ± 16	12 ± 5
Co	2.76 ± 0.50	0.76 ± 0.61	1.25	3.0 ± 0.6	1.97 ± 0.60	2.17 ± 0.47	9.1 ± 1.1	30 ± 9	24 ± 8
Ni	94 ± 19	19 ± 15	3	5.0 ± 1.0	14 ± 2	87 ± 21	128 ± 27	74 ± 30	68 ± 31
Cu	115 ± 23	9 ± 3	28	9 ± 5	16 ± 4	110 ± 27	171 ± 30	67 ± 25	64 ± 27
P	6350 ± 1520	280 ± 160	1380	—	2060 ± 515	5850 ± 1600	9570 ± 1690	66 ± 31	61 ± 27
N	31100 ± 4900	1800 ± 1000	2760	—	11640 ± 1510	30300 ± 5150	46500 ± 5460	67 ± 20	65 ± 19
Si	38700 ± 11500	1400 ± 5800	—	—	12100 ± 2070	35100 ± 12200	48600 ± 13700	80 ± 46	72 ± 45
OC	303000 ± 41900	2000 ± 5000	1150	4100 ± 500	5750 ± 980	339000 ± 57600	353000 ± 57800	86 ± 26	96 ± 32
IC	6783000 ± 686000	-40000 ± 25000	—	—	67000 ± 26800	5913000 ± 330000	5940000 ± 332000	114 ± 13	100 ± 11

overestimated. This is because the calculation of fluxes involved addition and multiplication of variables which were treated as independent but may in fact have had some degree of interaction between them. Typical pairs of such variables may have included (water flow – concentration), (dissolved fraction – particulate fraction), (wind speed – temperature), (surface layer salinity – surface layer depth) etc. Consequently, the numerical values of the two ratios listed in Table 2 are likely to be more significant than might at first appear.

It is surely not surprising that the greatest percentage of retention is found for elements that occur predominantly in the particulate phase throughout the system, particularly since sewage sludge and dredged wastes also tend to have high contents of these elements. Similarly if an element exhibit a rather high concentration in seawater relative to its crustal and freshwater abundance, as for Cd, this indicates weak interactions with the solid phase and long residence times and hence mixing is likely to dominate. The results of Table 2 must reflect particle association above all else. Thus sedimentation alone largely explains why large amounts of Fe, Pb and Mn are held back in the Firth of Clyde. By contrast Cd inflows and outflows, which are dominated by the dissolved fraction, are in approximate balance. A crude verification of this idea is given in Figure 5 which shows a reasonably good relationship (open circles:  $r^2 = 0.71$ ) between the observed export fluxes of eleven elements and those estimated indirectly by assuming that all solid phases entering the system are subsequently trapped. This is not to say, however, that initial solid-solution partitioning is the only factor controlling the fate of chemical elements in this system. In particular, the differing physico-chemical conditions and residence times of the inner and outer Firth must surely play a role. Indeed assuming that all terrigenous inputs, dissolved and particulate alike, become trapped within the system results in an even higher degree of correlation (full circles in Figure 5:  $r^2 = 0.95$ ) between the observed and estimated export

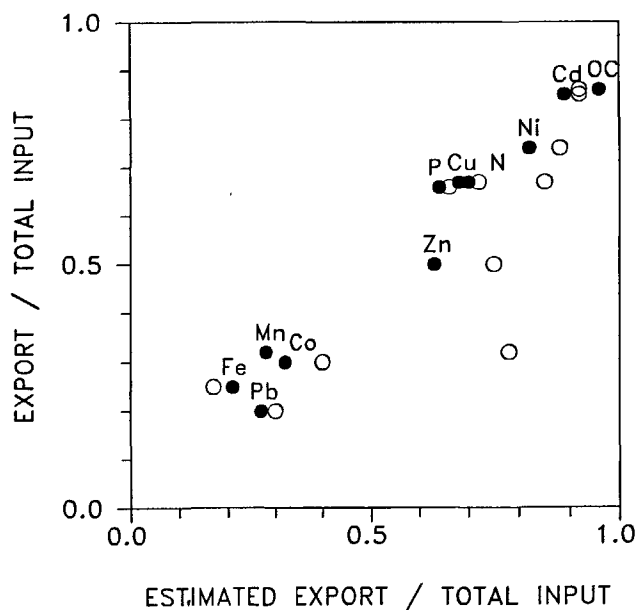


Figure 5

For each element, the proportion of the total input which escapes to the open shelf is plotted versus the value estimated on the assumption that (a) all particulate inputs and none of the dissolved inputs are removed within the system (open circles), (b) all terrigenous inputs dissolved and particulates, are removed within the system (full circles).

Comparaison entre la fraction des apports évacuée vers le large et la valeur à laquelle on s'attendrait dans deux cas de figures extrêmes : (○) tous les apports particulaires sont piégés et tous les apports dissous s'écoulent sans modification, (●) les apports continentaux uniquement se retrouvent piégés.

fluxes! Unfortunately, the relative weight of terrigenous vs marine inputs for these chemical elements is also inextricably linked to their solid-solution partitioning so that the separation between fundamental element properties and characteristics of the system remains indeterminate.

The relationship (Output/ $\Sigma$ inputs) vs (Marine input/ $\Sigma$ inputs) across our suite of twelve elements (Fig. 6) may help to understand the functioning of the Firth of Clyde as a geochemical system over a one-year time scale. It is hard to imagine a geochemical process that would result in such a tight interdependency between, effectively, the export and import fluxes of twelve unrelated elements. One way to describe Figure 6 is to say that elements supplied mostly from land based sources (Fe, Mn, Pb, Co) appear to be scavenged from the water column of the Firth of Clyde while elements of predominantly marine origin (Cd, Si, OC) appear to be exported back to the open sea. To a first order approximation, the Firth of Clyde would appear to function as a linear process whose net result is the accumulation within the system of a large fraction of the land based inputs but a very small fraction of the marine inputs of any given element. Based on this simple model, the removal efficiency towards the two types of inputs may be quantified by performing a multi-linear regression of  $E_2$  on  $I_1$  and  $I_2$  (Fig. 1) after division of all the terms by the normalizing factor  $[I_1 + I_2]$ ,

$$E_2 = (0.90 \pm 0.03) I_1 + (0.02 \pm 0.03) I_2 \quad (5)$$

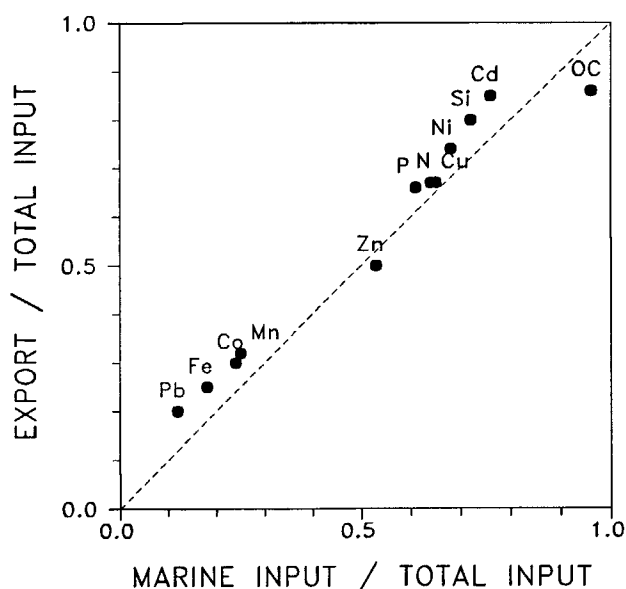


Figure 6

For each element, the proportion of the total input which escapes to the open shelf is plotted versus the marine contribution to that total input.

Comparaison entre la fraction des apports évacuée vers le large et la fraction des apports en provenance du large.

which gives 90 % removal of all land based inputs and only 2 % removal of marine inputs. Although these results point to a fine balance between imports and exports across the marine boundary, they do not rule out the possibility of significant imbalances during the course of the study period. The latter is indeed observed for several elements such as Fe, Pb and Zn (Fig. 4). Similarly, the mass balance model gives an indirect estimate of the net burial flux,  $E_1$ , but does not reveal any information about the dynamics of recycling between the sediments and the water

column. This would require direct determinations of diffusive fluxes from sediments using benthic chambers. The diagenetic release of Fe and Mn from sealoch sediments was observed throughout the period (Muller *et al.*, this issue) but its global significance is still a matter of debate. The remineralization of particulate Si in the deeper parts of the system throughout the autumn of 1990 has been reported by Grantham and Tett (1993), but annual fluxes for the system as a whole are not available. Another approach to assessing the dynamics of the release/deposition internal cycle for each element would be to calculate its residence time, *e.g.* from a knowledge of water column inventory and total input or output. However, our survey sampling resolution was not sufficient to accurately measure elemental inventories. Moreover, it has been shown that, for many elements, marine inputs make a very large contribution to the mass balance (Tab. 2) and their seasonal variations are likely to exert a large influence over the water column inventory (Fig. 4). This means that a higher resolution in both time and space would be needed for the purpose of characterizing the reactivity of the elements within the system on the basis of their residence time at steady state.

Despite its crude nature, the single box model presented here is able to quantify with reasonable precision the main sources and sinks for organic carbon, nutrients and trace metals. It is also compatible with the hypothesis that the inner Firth, which receives a large fraction of the land based inputs, acts as the main chemical reactor of the system (Muller *et al.*, this issue) while the outer Firth functions more like a two-layered mixing reservoir. By using new, automated methods of chemical sensing it might become possible to collect a sufficient number of measurements to address the main limitations of the present model. The "black box" approach would then give way to a proper transport model of water quality with a resolution commensurate with the characteristic scales of processes that define the system. Coupling the better-known inputs and chemical distributions to a model of the water circulation and of the suspended particulate transport in the Firth of Clyde could be the next logical step towards simulating field conditions (Paulson *et al.*, 1993).

## CONCLUSIONS

A first-order mass balance of organic carbon, nutrients and trace metals in the waters of the Firth of Clyde is presented. A single box model based on the assumption of steady state over a one-year period allowed quantification of the net sedimentation fluxes from a calculation of the input fluxes and the net export fluxes across the marine boundary. Although significant imbalances show up during the course of the year, a composite plot including all the elements considered (Fig. 6) shows an approximate balance between import and export across the marine boundary. The simplest and most plausible explanation is that marine inputs are exported back to the North Channel with little modification, while terrigenous inputs are lost to the

sediments in some large measure. Where marine inputs dominate (Cd, OC), the assessment of the removal of terrigenous inputs becomes more uncertain. The importance of marine versus telluric inputs increases in the order: Pb < Fe < Co < Mn < Zn < P < N < Cu < Ni < Si < Cd < OC.

During October-December the exchange across the marine boundary entails a net loss of trace metals. At least for the more particle reactive elements such as Pb, removal onto the suspended solids generated by the highly turbulent conditions of the North Channel may be a factor (Balls, 1987). During January-March the nutrients transported out to the North Channel also exceed their marine influx. It can be inferred from Figure 4 that the difference between  $\Sigma$ inputs ( $I_1 + I_2$ ) and marine output ( $E_2$ ) is rather uniform for Cd, Ni, Cu, P, N, Si and OC, but peaks in the summer months for Fe, Mn, Pb, Zn and Co. However, these do not necessarily represent the trends followed by net sedimentation fluxes ( $E_1$ ), since the water column

inventory of these elements can – and does – fluctuate over a one-year period.

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