Nutrient behaviour in two contrasting Scottish estuaries, the Forth and Tay

Nutrients
Estuaries

Nutriments
Estuaires

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ABSTRACT

The distribution and behaviour of nutrients (nitrate, nitrite, ammonia, silicate and phosphate) have been examined over the course of a year in two major Scottish estuaries, the Forth and Tay.

Maximum concentrations of nitrate and silicate in both estuaries occur in winter, when mixing is conservative. By contrast maximum phosphate, ammonia and nitrite concentrations (notably in the Forth) are observed in summer, these are related to lower oxygen concentrations both within the water column and sediments. Phosphate, ammonia and nitrite concentrations are high in the Forth relative to the Tay.

Phosphate behaviour in plots for both estuaries show some common features including removal at low salinity, mid estuary inputs and simple dilution at high salinity. The results are interpreted on the basis of removal onto particles at low salinity followed by desorption at higher salinity together with an input from sediment porewaters. In the Forth the phosphate flux from sediments during the summer is estimated to be 1.98 ± 1.25 mmol m^{-2} day^{-1}. At this time the river input of phosphorus is only 10-14 % of the mid estuary input.

Under low river flow conditions in summer a large turbidity maximum (400-500 mg l^{-1} suspended solids) develops in the Forth estuary and this results in removal of phosphate. Removal is less dramatic in the Tay estuary as the turbidity is wind generated and therefore rarely exceeds 100 mg l^{-1}. Water quality in the Forth (as defined by the occurrence of low dissolved oxygen concentrations and the presence of species such as ammonia and nitrite) is inferior to that of the Tay. Relative to contaminated estuaries however concentrations in both estuaries are low. By virtue of its high fresh water discharge the Tay is a more significant source of nitrate to the North Sea during the winter than is the Forth.

In the Forth bacterial mineralisation and nitrification of organic nitrogen occurs in the upper estuary, this results in an input of nitrate and consumption of dissolved oxygen. Further downstream broad mid estuarine peaks of nitrite and ammonia are observed indicative of a benthic source. Estimates of this source for ammonia and nitrite are 19-44 and 3.9-8.1 mmol m^{-2} day^{-1} respectively. In winter the main source of nitrogen to the Forth is from the river but in summer mid estuarine sources dominate.

In the outer Tay a peak in dissolved ammonia is estimated to represent an input of 0.5-1.1 tonnes N day^{-1}, this is attributed to sewer inputs from Dundee.

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RÉSUMÉ

Nutriments dans l'estuaire du Forth et du Tay

La répartition et le comportement de certains nutriments (nitrate, nitrite, ammoniaque, silicate et phosphate) ont été examinés au cours d'une année dans deux estuaires importants de l'Écosse, faisant partie du Forth et du Tay.

Les teneurs maximales en nitrate et silicate dans les deux estuaires se produisent en hiver, période caractérisée par un mélange modéré. Par contraste, on observe les teneurs maximales en phosphate, ammoniaque et nitrite (notamment dans le Forth) en été, phénomène mis en corrélation avec les teneurs abaissées en oxygène enregistrées dans la colonne d'eau, ainsi que dans les sédiments. Les teneurs en phosphate, ammoniaque et nitrite constatées dans le Forth sont élevées par rapport à celles du Tay.

Le comportement du phosphate dans les graphiques tracés pour les deux estuaires manifeste quelques traits communs, tels que le déplacement à un faible taux de salinité, l'introduction au milieu de l'estuaire et la dilution simple quand la salinité est élevée. Les résultats semblent indiquer un déplacement sur les particules à un faible taux de salinité, suivi de la désorption à un taux plus élevé, ainsi qu'un apport provenant des eaux de pore sédimentaires. Dans le Forth, le flux de phosphate provenant des sédiments est évalué à 1,98 ± 1,25 mmol m^{-2} $jour^{-1}$ pendant l'été. A cette époque, l'apport fluvial de phosphore n'atteint que 10 à 14 % de la quantité introduite au milieu de l'estuaire.

Sous les conditions de débit fluvial abaissé en été, un maximum important de turbidité (400-500 mg l^{-1} de solides en suspension) se produit dans l'estuaire du Forth, ce qui provoque un déplacement du phosphate. Ce déplacement est moins spectaculaire dans l'estuaire du Tay parce que la turbidité est engendrée par le vent, et par conséquent dépasse rarement 100 mg l^{-1}. La qualité de l'eau dans le Forth (définie par l'existence de basses teneurs en oxygène dissous et la présence d'espèces telles que l'ammoniaque et le nitrite) se montre inférieure à celle du Tay. Cependant, par rapport aux estuaires contaminés, les niveaux déterminés dans ces deux estuaires sont bas. Le Tay, en raison de la décharge élevée d'eau douce, apporte significativement plus de nitrate dans la Mer du Nord pendant l'hiver que le Forth.

Dans le Forth, la minéralisation bactérienne et la nitrification de l'azote organique qui se produisent dans la partie supérieure de l'estuaire entraînent l'introduction de nitrate et la consommation d'oxygène dissous. Plus en aval, le nitrite et l'ammoniaque présentent une pointe large au milieu de l'estuaire, ce qui indique une source benthique. On évalue cette source d'ammoniaque et de nitrite à 19-44 et 3,9-8,1 mmol m^{-2} $jour^{-1}$. En hiver, l'azote est principalement d'origine fluviale dans le Forth, tandis que les sources dominantes en été se trouvent au milieu de l'estuaire.

Dans le Tay extérieur, l'ammoniaque dissoute atteint une valeur de pointe qui devrait représenter l'introduction de 0,5-1,1 tonnes N $jour^{-1}$, phénomène attribué à l'entrée d'eaux d'égout provenant de Dundee.

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INTRODUCTION

Estuaries are a major source of nutrients to coastal zones and for this reason their behaviour has been extensively studied. The contrasting nature of river catchment areas, population densities and the flushing characteristics of individual estuaries mean that results obtained from one estuary cannot be generally applied to others.

Recent studies have implicated anthropogenic nutrient inputs from estuaries with the increased occurrence of nuisance plankton blooms in coastal waters (Brockmann *et al.*, 1988). For some coastal areas the variability in the plankton community has been successfully linked to the increased input of nutrients from estuaries following rainfall events (Gieskes and Schaub, 1990; Garcia-Soto *et al.*, 1990).

The extent to which nutrient exports from estuaries can be estimated is limited. This is a consequence of our lack of understanding of source and sinks within estuaries and the extent to which nutrient elements are cycled between different forms. Nitrogen, for example, exists in a range of oxidation states in estuaries from ammonia up to nitrate which coexist with intermediate species such as nitrite and gaseous forms including nitrous oxide and nitrogen. The behaviour of nitrogen within estuaries and coastal areas together with the processes responsible for conversion between forms, *e. g.* nitrification and denitrification have been the subject of many studies (*e. g.* Billen, 1975; Billen *et al.*, 1985; Helder and de Vries, 1983; Owens, 1986; Law and Owens, 1990). These studies have highlighted the inherent variability within and between individual estuaries (Jensen *et al.*, 1984; Jorgensen and Sorensen, 1985; Jensen *et al.*, 1990).

Internal cycling can make it difficult to assess whether or not the estuary is acting as a source or a sink for nitrogen. In pristine estuaries nitrate, the most highly oxidised species, is dominant. At the other extreme estuaries such as the Scheldt, which is characterised by extensive areas of anoxia, reduced forms such as ammonia dominate (Billen, 1975). Some estuaries are well oxygenated in the winter when river flows are high but show an oxygen minimum in the summer when reduced river flows are insufficient to replace oxygen consumed within the estuary, an example is the Tamar estuary (Owens, 1986). In such an estuary several nitrogen species coexist (nitrate, nitrite and ammonia).

Phosphate exhibits a wide range of behaviour both between estuaries and also within the same estuary. Simple conservative mixing is reported in the Rhine (van Bennekom and Wetsteijn, 1990) and Rhône (Denant and Saliot, 1990) estuaries while in systems not significantly influenced by man, addition generally occurs *e. g.* Amazon (Fox *et al.*, 1986). Removal is observed in the Clyde estuary (Mackay and Leatherland, 1976) while in the Yarra, both addition and removal has been reported. This has been attributed to variations in river flow (Smith and Longmore, 1980). In extensively studied systems such as the Tamar, a range of behaviour is also exhibited, on some occasions addition is observed while on others concentration is practically invariant throughout the estuary (Morris *et al.*, 1981). Estuarine mixing has been simulated in the laboratory by Bale and Morris (1981) who were able to demonstrate both removal and addition processes. It is evident from the above that the interpretation of phosphate behaviour is complex and dependent not only on the particular estuary but also on the hydrodynamics of the system.

Phosphate is a particle reactive species and it has long been recognised that concentrations within estuaries are controlled to some extent by interaction with sediment or suspended material (Pomeroy *et al.*, 1965). The concept that phosphate partitions between solid and dissolved phases has come to be known as the "phosphate buffer mechanism" and has recently been discussed by Froelich (1988). The ability of sediments to release phosphate to water has been established (Chase and Sayles, 1980; Fox *et al.*, 1986).

The present study examines nutrient behaviour in two contrasting Scottish estuaries, the turbid, industrialised Forth and the relatively clear, non-industrialised Tay. The purpose of the study was to examine behaviour over an annual cycle and under a range of river discharge conditions. While little is known about the chemistry of the Tay, earlier work has demonstrated simultaneous phosphate removal and addition in different parts of the Forth estuary (Toole *et al.*, 1987; Griffiths, 1987).

Description of the study areas

The study areas are indicated in Figure 1 together with more detailed insets of the estuaries indicating sampling locations. The combined catchment area of the Tay and Earn is *ca.* 6,000 km^2 and together these two rivers provide 96 % of the fresh water input to the Tay estuary. The River Tay has a catchment area of *ca.* 5,000 km^2 and by flow is the largest in Great Britain (Maitland and Smith, 1987). The catchment is characterised by extensive areas of rough grazing and forest with agricultural land exceeding 20 % by area only in the lower part of the system. Population is low, the two major settlements being Perth at the tidal limit and Dundee at the seaward end. Fresh water inputs have been described by Pontin and Reid (1975), the long term daily average flows of the Tay and Earn are 167 and 31 m^3 s^{-1} respectively. The discharge of the Tay rarely drops below 40 m^3 s^{-1} but regularly exceeds 1,000 m^3 s^{-1} under

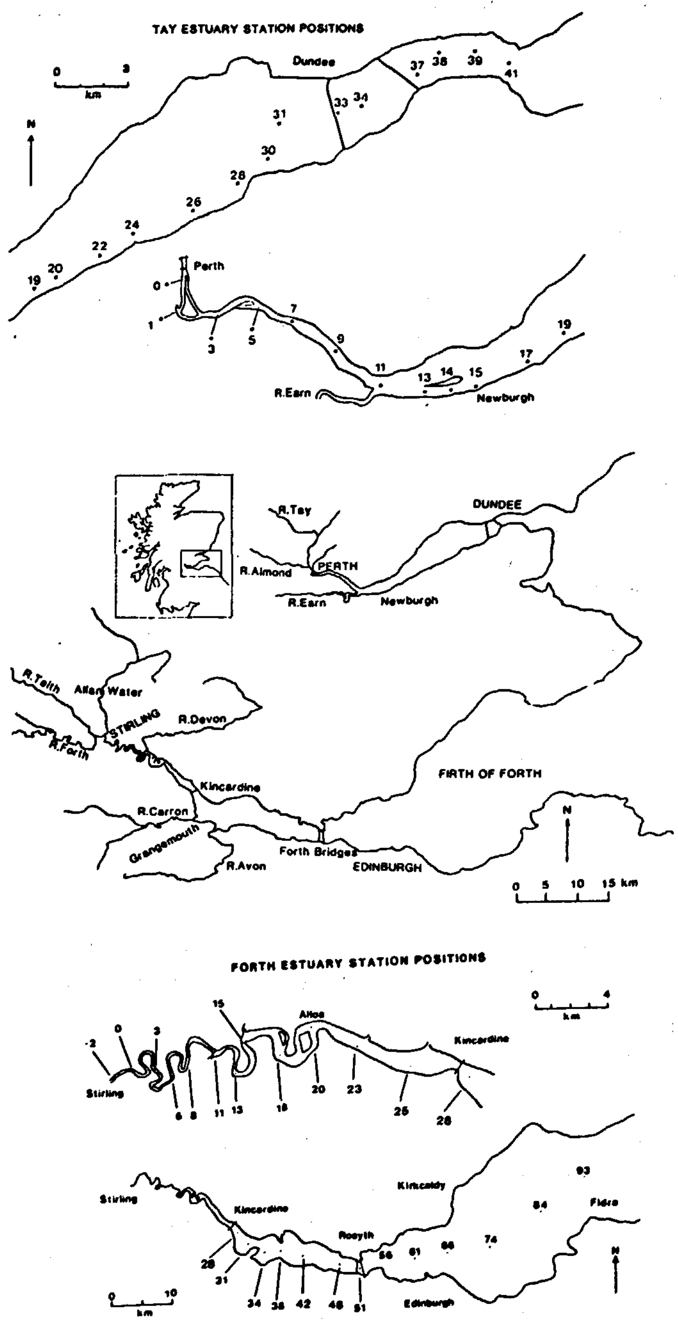
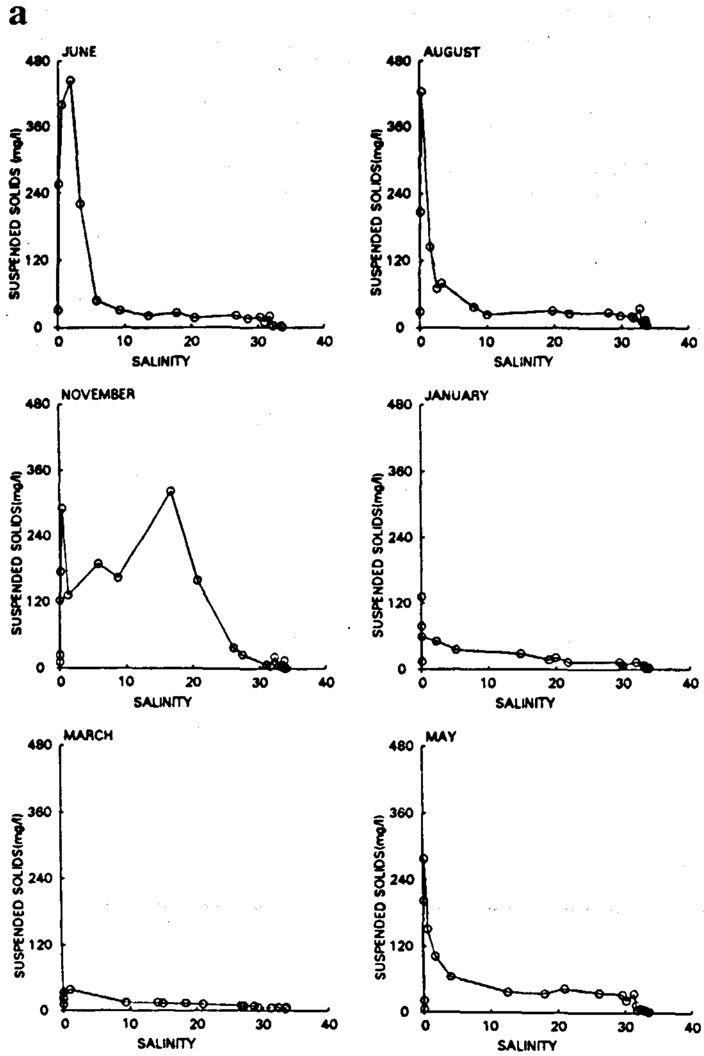


Figure 1

Map of study area with detailed insets indicating the sampling positions. Numbers refer to distance in kilometres below Stirling (Forth) and Perth.

Carte de la région étudiée avec des papillons détaillés indiquant les endroits où le prélèvement d'échantillons a été réalisé. Les numéros se réfèrent à la distance en kilomètres en aval de Stirling (Forth) et de Perth (Tay).



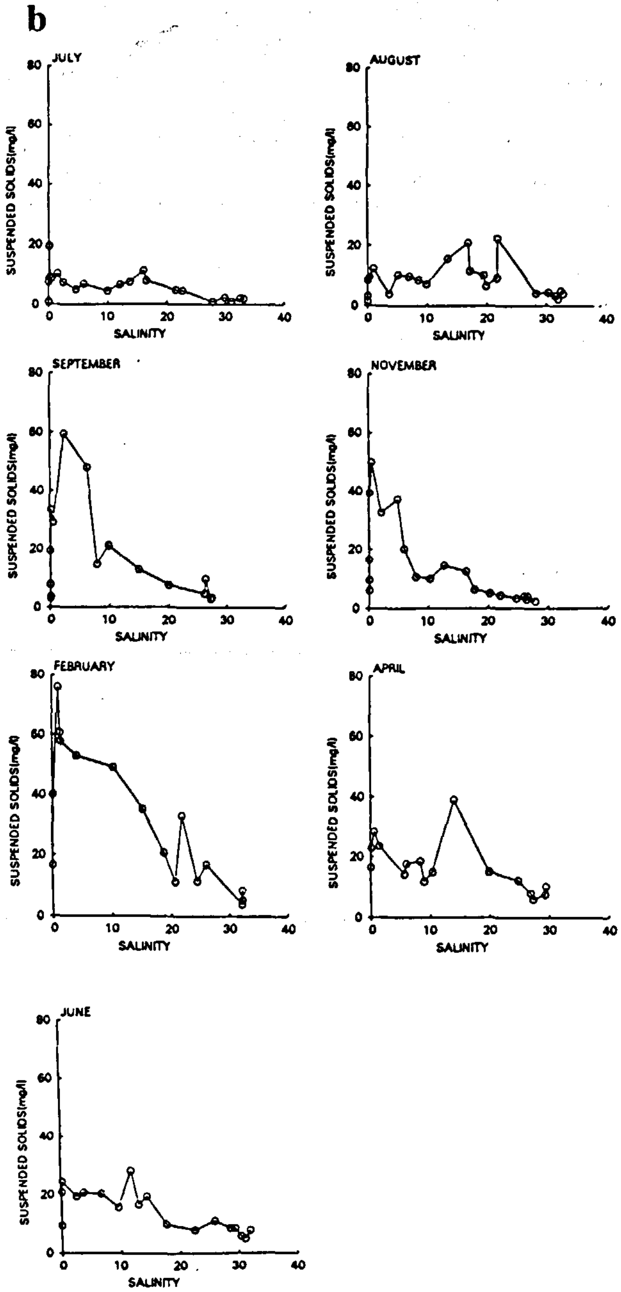


Figure 2

SPM/salinity plots for: a) the Forth estuary (June 1989 to May 1990); and b) the Tay estuary (July 1989 to June 1990).

Tracés de MPS/salinité pour : a) l'estuaire du Forth (juin 1989 à mai 1990); et b) l'estuaire du Tay (juillet 1989 à juin 1990).

winter spate conditions. The estuary is shallow with extensive tidal mud flats along the northern shore, it varies from being partially mixed to well mixed. The high river flow and low population have led to the Tay estuary being described as "one of the least contaminated in Europe" (Sholkovitz, 1979).

The catchment area of the Forth estuary and Firth of Forth is *ca.* 4,700 km^2, it contains approximately a quarter of the population of Scotland (*ca.* 1.3 million) and a significant proportion of its industry. The tidal limit of the Forth estuary is close to Stirling and fresh water enters from several major rivers. The rivers Forth, Teith and Allan which enter at the head of the estuary contribute on average 75 % of the total fresh water flux to the estuary (Webb and Metcalfe, 1987). Smaller but significant contributions are made by the Devon, Avon and Carron. The average long term flow of fresh water to the estuary is 63 $m^3\ s^{-1}$ (Leatherland, 1987); low discharge conditions can result in flows less than 10 $m^3\ s^{-1}$ while in winter they can exceed 300 $m^3\ s^{-1}$.

The main inputs to the estuary are related to domestic sewage but some major industrial inputs also enter the system. Low fresh water flow conditions associated with summer can lead to a pronounced oxygen minimum in the upper estuary (Griffiths, 1987). The Forth estuary is considerably more turbid than the Tay with a well developed turbidity maximum in the summer months. The contrasting nature of the two estuaries makes a comparison of the behaviour of chemical elements and species particularly attractive.

Sampling and analysis

The survey period extended from June 1989 to June 1990, the Forth estuary was sampled in June, August, November, January, March and May, the Tay in July, August, September, November, February, April and June. A small fast boat was used for sampling in the Tay estuary and for the Forth estuary west of the road and rail bridges, in the

Firth of Forth a larger vessel was used (RS Forth Ranger). All surveys were undertaken at high water on spring tides. In addition to nutrients trace metal samples were taken and these will be the subject of subsequent publications.

Samples were collected from a depth of one metre using the clean sampler described by Balls and Laslett (1991). This sampler fills six bottles simultaneously thus avoiding the necessity of subsampling. Samples for phosphate, nitrate, nitrite and ammonia analysis were filtered on the day of collection through glass fibre filters (Whatman GF/C), silicate samples were filtered through cellulose nitrate membranes (Sartorius). Prior to analysis samples were stored deep frozen in polythene bottles except those for phosphate which were stored in glass bottles and preserved by the addition of chloroform. Due to the high turbidity in the Forth it was sometimes also necessary to filter salinity samples; salinity was determined in the laboratory with an inductively coupled salinometer (Autosal).

Phosphate was determined by a method based on that of Murphy and Riley (1962) with turbidity correction. Nitrate and nitrite were determined by an autoanalyser technique based on that of Stanton (1974). The manual method for ammonia was based on that of Solorzano (1969) and that for silicate on Strickland and Parsons (1972).

Suspended loads were obtained by filerting a known volume of water through a pre-weighed Nuclepore membrane (polycarbonate 0.4 µm pore size), salt was removed by washing with distilled water. Particulate organic nitrogen samples were obtained by filtering a known volume of water through a preheated GFF (Whatman) filter. Carbonate was removed by exposing the filter paper to HCl fumes after which it was combusted in a CHN analyser (Perkin-Elmer 240B).

Surveys proceeded sufficiently far upstream to reach fresh water. In summer surveys went to Stirling and Perth but in winter with high river discharges it was necessary only to proceed to eight kilometres below Stirling in the Forth and to Newburgh in the Tay.

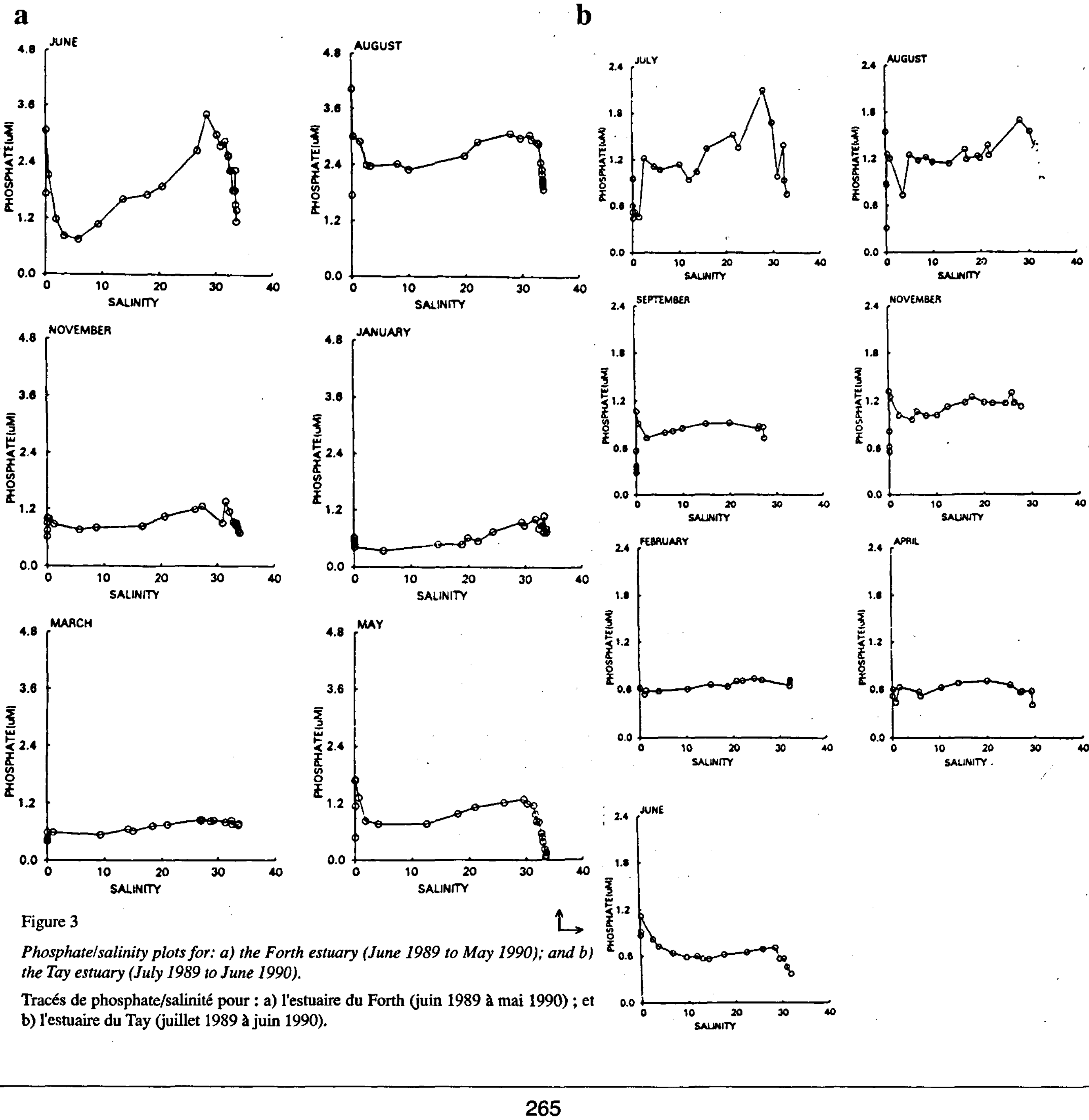


Figure 3

Phosphate/salinity plots for: a) the Forth estuary (June 1989 to May 1990); and b) the Tay estuary (July 1989 to June 1990).

Tracés de phosphate/salinité pour : a) l'estuaire du Forth (juin 1989 à mai 1990) ; et b) l'estuaire du Tay (juillet 1989 à juin 1990).

RESULTS

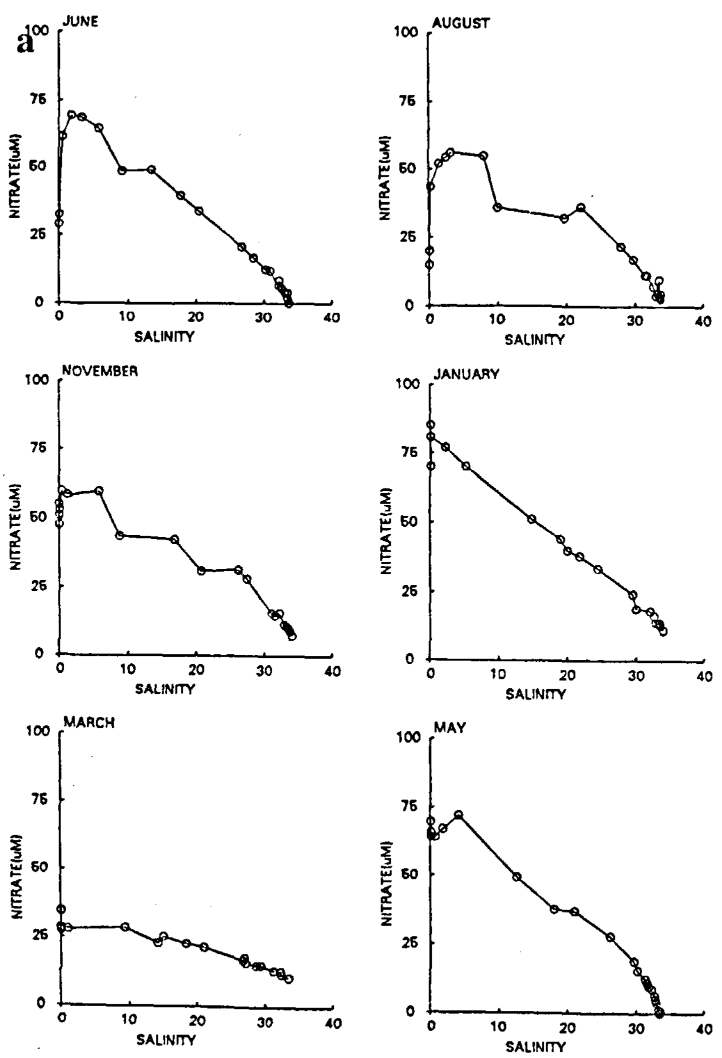
Suspended particular matter (SPM) salinity plots for the Forth and Tay are given in Figures 2 *a* and 2 *b* respectively. In the Forth the SPM loading exhibits a seasonal cycle with maximum concentrations in the summer approaching 500 mg l^{-1}, winter concentrations are 5-10 times lower. By comparison with the Forth the Tay has relatively low SPM loadings with minimum concentrations in the summer, maximum levels are associated with winter but do not exceed 100 mg l^{-1}.

Phosphate-salinity plots for the Forth and Tay estuaries are shown in Figures 3 *a* and 3 *b* respectively. In both estuaries the highest concentrations occur in the summer, maximum levels being higher in the Forth (*ca.* 3 µM) than is the Tay (*ca.* 2 µM). Winter concentrations by contrast are very similar in both estuaries (0.5-0.8 µM) and vary little over the salinity gradient. Many of the surveys exhibit an increase in phosphate concentration in the mid salinity (5-25) range, this is particularly evident for the Forth. At low salinities there is some evidence of phosphate removal. In the outer parts of the estuaries the inverse relationship between concentration and salinity is indicative of simple dilution.

For the Forth estuary nitrate, ammonia and nitrite-salinity plots are shown in Figures 4 *a*, 5 *a* and *b* respectively. In the Tay estuary nitrite was never present at significant concentrations (*i. e.* >1 µM), for this reason it has not been plotted but nitrate and ammonia data are presented in Figures 4 *b* and 5 *b* respectively.

River water nitrate concentrations are greatest in the winter (Fig. 4 *a* and 4 *b*) and of similar magnitude in both estuaries, 80-100 µM. In winter dilution behaviour is conservative. Summer concentrations are lower and a rapid increase is apparent at the very low salinity end of both estuaries indicating on additional source of nitrate.

Ammonia concentrations in the Tay (up to 5 µM) are low relative to those in the Forth (up to 30 µM). In the Tay maximum concentrations are often observed in the outer



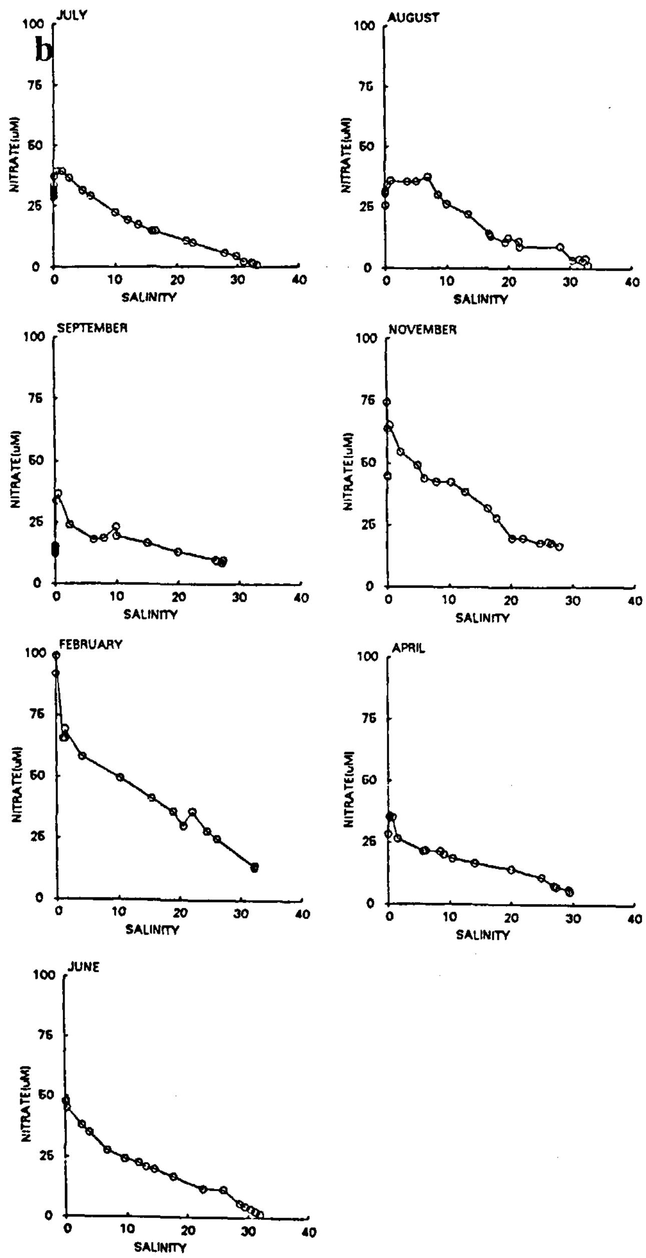


Figure 4

Nitrate/salinity plots for: a) the Forth estuary (June 1989 to May 1990); and b) the Tay estuary (July 1989 to June 1990).

Tracés de nitrate/salinité pour : a) l'estuaire du Forth (juin 1989 à mai 1990) ; et b) l'estuaire du Tay (juillet 1990 à juin 1990).

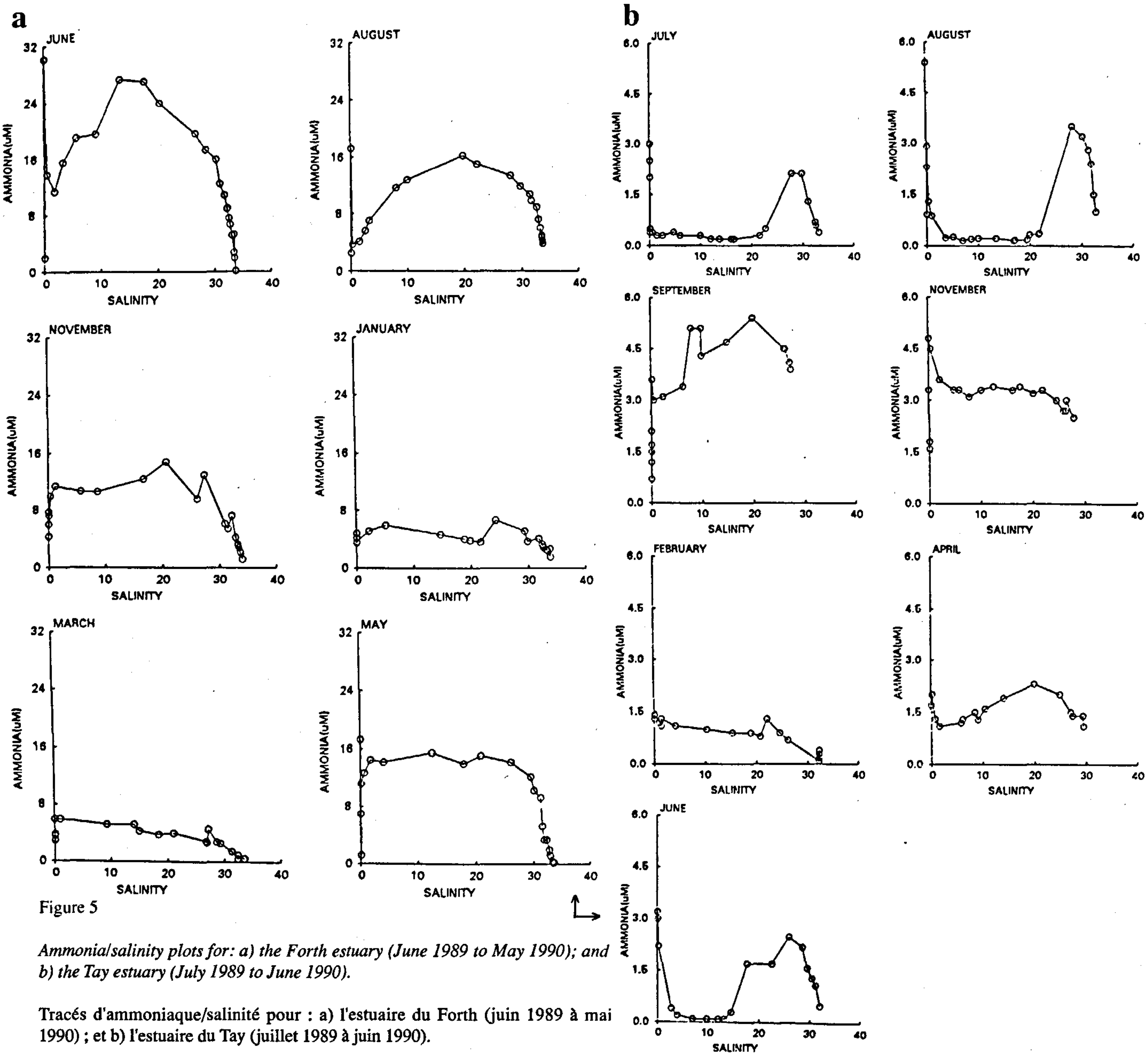


Figure 5

Ammonia/salinity plots for: a) the Forth estuary (June 1989 to May 1990); and b) the Tay estuary (July 1989 to June 1990).

Tracés d'ammoniaque/salinité pour : a) l'estuaire du Forth (juin 1989 à mai 1990) ; et b) l'estuaire du Tay (juillet 1989 à juin 1990).

part of the estuary in the vicinity of Dundee (Fig. 5 *b*). In the Forth a broad mid estuarine peak is evident with maximum concentrations associated with summer (Fig. 5 *a*). Nitrite distributions in the Forth (Fig. 6) follow a similar pattern to those of ammonia.

In both estuaries maximum silicate concentrations occur in the autumn/winter period (80-100 µM) when mixing is conservative. Summer concentrations are lower, in the Tay there is evidence that removal is occurring over long stretches of the estuary. In the Forth other than at low salinity, mixing tends to be conservative for all of the year (Fig. 7 *a*, *b*).

DISCUSSION

SPM loading

The possibility of nutrient cycling between dissolved and particulate forms and also sorption reactions at the surface of particles necessitates a brief discussion of SPM distributions. The factors controlling SPM loading include tidal range, river discharge and wind. In the present study all surveys were undertaken on spring tides, consequently tidal range should not be a major factor in accounting for seasonal variations.

The discharge data for the rivers Forth and Tay are plotted for the study period in Figure 8, survey dates are indicated. It is evident that minimum flows are associated with summer while in winter the flow is persistently higher. Low river discharges in summer allow sea water to penetrate further up the estuary and in the case of the Forth to enter a part of the system with a small volume where resuspension of material results in a very high turbidity. In winter high discharge conditions push the tidal limit further downstream where the estuary volume is greater, resuspension here results in a relatively low SPM loading. This process is well documented in other macrotidal estuaries of similar shape (*i. e.* rapid narrowing towards the head) such as the Tamar (Morris *et al.*, 1986).

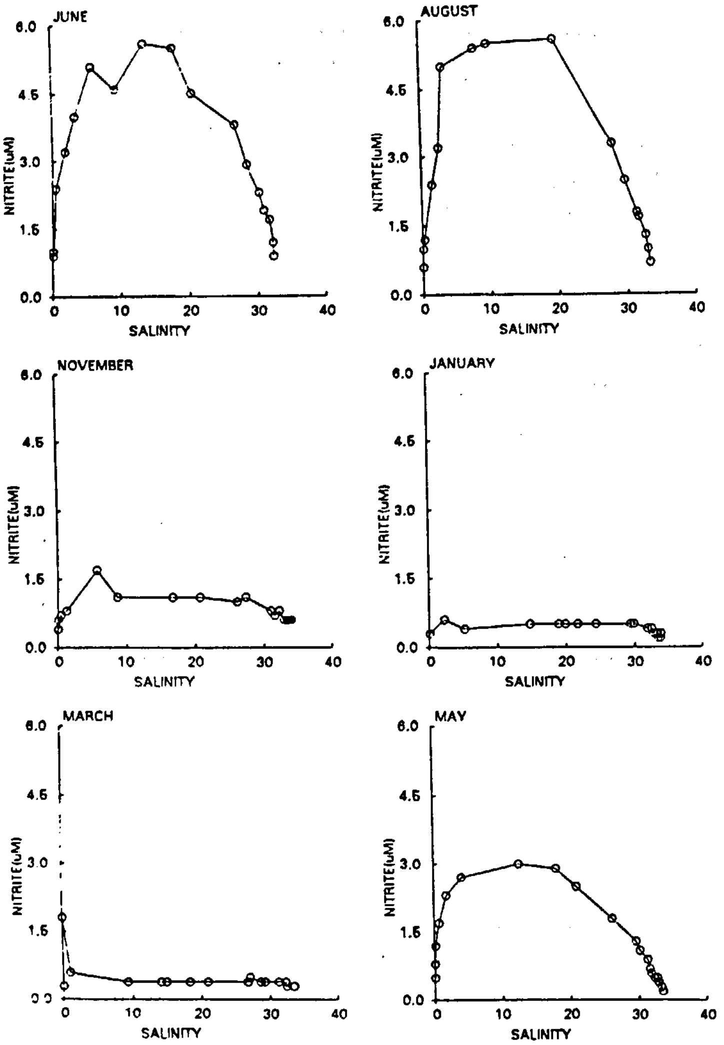


Figure 6

Nitrite/salinity plots for the Forth estuary (June 1989 to May 1990).

Tracés de nitrite/salinité pour l'estuaire du Forth (juin 1989 à mai 1990).

In the Tay, turbidity is essentially controlled by the wind (Weir and McManus, 1987), but under spate conditions considerable quantities of sediment are transported into the estuary. The highest SPM loadings were observed in February 1990, a survey preceded by two days of severe gales.

Phosphate

The three dominant features of the phosphate/salinity plots are removal in the low salinity/high turbidity area, addition in the middle part of the estuary and simple dilution in the outer part of the estuary. In the following discussion these features are examined separately and an explanation sought as to why all these features are observed in some surveys (Forth, summer) while in winter concentrations are practically constant within both estuaries.

Removal at low salinity

Phosphate removal in the low salinity region of estuaries could occur by two mechanisms, flocculation and precipitation or uptake by particles. It has been demonstrated that removal can occur in the absence of particles when filtered river and sea water are mixed, this is attributed to flocculation and precipitation (Sholkovitz, 1976). This removal is almost certainly linked to the precipitation of iron, an apparently ubiquitous process in estuaries (Church, 1986). Were this to be the dominant mechanism removal should be a persistent feature of all profiles. There is however, little evidence of removal in the winter data and this is taken as evidence that flocculation is not the dominant removal mechanism.

In the Tamar estuary Morris *et al.* (1981) concluded that removal by particles was the dominant sink in the low salinity region. This also appears to be the case in the Forth where the most dramatic removal is observed in association with the highest SPM concentrations (*i. e.* summer). In a laboratory simulation Bale and Morris (1981) demonstrated this removal and also its temperature dependence. Removal was observed to increase at higher temperatures and this favours greater removal in the summer months. In the present study removal is more dramatic in the Forth than in the Tay, this is attributed to the greater concentration of particles.

Inputs to the middle estuary

Both estuaries exhibit a general increase in phosphate concentration in the middle estuary. In the Forth it is tempting to attribute this to waste inputs, since however the same behaviour is observed in the Tay, where such inputs are insignificant, an alternative explanation must be sought. While it is not possible to attribute the input to a single mechanism, possible sources include desorption from SPM and a benthic flux from porewaters. Phosphate release from resuspended sediment has been demonstrated in laboratory trials to be sufficient to account for the typical concentrations at which phosphate appears to be buffered in estuaries (Fox *et al.*, 1986; Chase and Sayles, 1980). Increasing pH and ionic strength with distance down the estuary favour desorption processes as sea water anions, *e. g.* sulphate compete for ads-rption sites, relative to adsorption however desorption is a slow process (Froelich, 1988). Following work in the Ems estuary an alternative mechanism by which phosphorous can be released to estuarine waters has recently been proposed (de Jonge and Villerius, 1989). They suggested that calcite formed at sea adsorbs phosphate as it is transported up the estuary during summer, on encountering the reduced pH associated with low salinity part of the calcite dissolves releasing phosphate. The release of phosphate from sediments via porewaters is recognised as a widespread process and in some locations is a major influence on water column concentrations *e. g.* Naragansett Bay (Pilson, 1985).

Both of the processes outlined above are slow and only approach equilibrium on the time scale of days and weeks. Since this is similar to the flushing times of many estuaries some consideration must be given to the dynamics of the Forth and Tay estuaries. It is to be anticipated that the detection of any signal (reflected in phosphate water column concentrations) would be most likely under conditions of long water residence times, *i. e.* slow flushing. The approximate age of fresh water in different parts of the Forth and Tay estuaries have been calculated, details of the technique used are given in the *Appendix* and results in Figure 9.

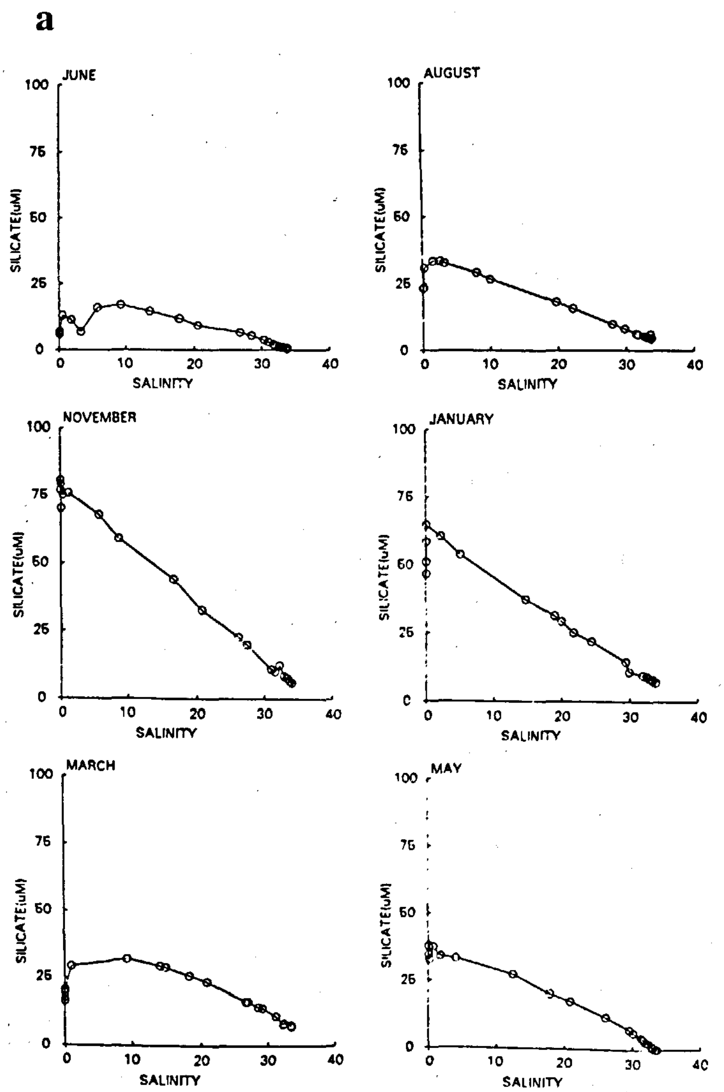
It is evident that variations of almost an order of magnitude exist in both estuaries for surveys completed under high and low discharge conditions. It is further apparent that the Tay estuary is flushed *ca.* three-four times more rapidly than the Forth. Conceptually this result is not unexpected but the simple model is able to quantify the difference between the two systems.

The mid estuary input of phosphate is least pronounced under fast flushing conditions (*e. g.* February-Tay, March-Forth; *see* Fig. 2 and 3). This is consistent with the idea that desorption processes and/or benthic inputs are slow relative to the flushing time of the estuary.

The kinetics of phosphate sorption behaviour have been examined in the laboratory. Phosphate uptake onto mineral phases although initially fast (hours) is subsequently controlled by slow diffusion into the particles (Chen *et al.*, 1973) with a time scale of days to weeks. Desorption is a considerably slower process and equilibrium is not likely to be reached in estuaries where residence times are relatively short. Long resuspension times of particulate material have been demonstrated to result in greater desorption of phosphate (Chase and Sayles, 1980).

In experiments examining the release of phosphate from resuspended sediments Fox *et al.* (1986) observed a maximum release in the salinity range 20-28, this range is similar to that at which the mid estuarine maxima appear in the Forth and Tay estuaries. The release of phosphate from resuspended material is likely therefore to be contributing to the mid estuarine input.

The magnitude of the phosphate input to the mid estuary region of the Forth has been estimated for two surveys in



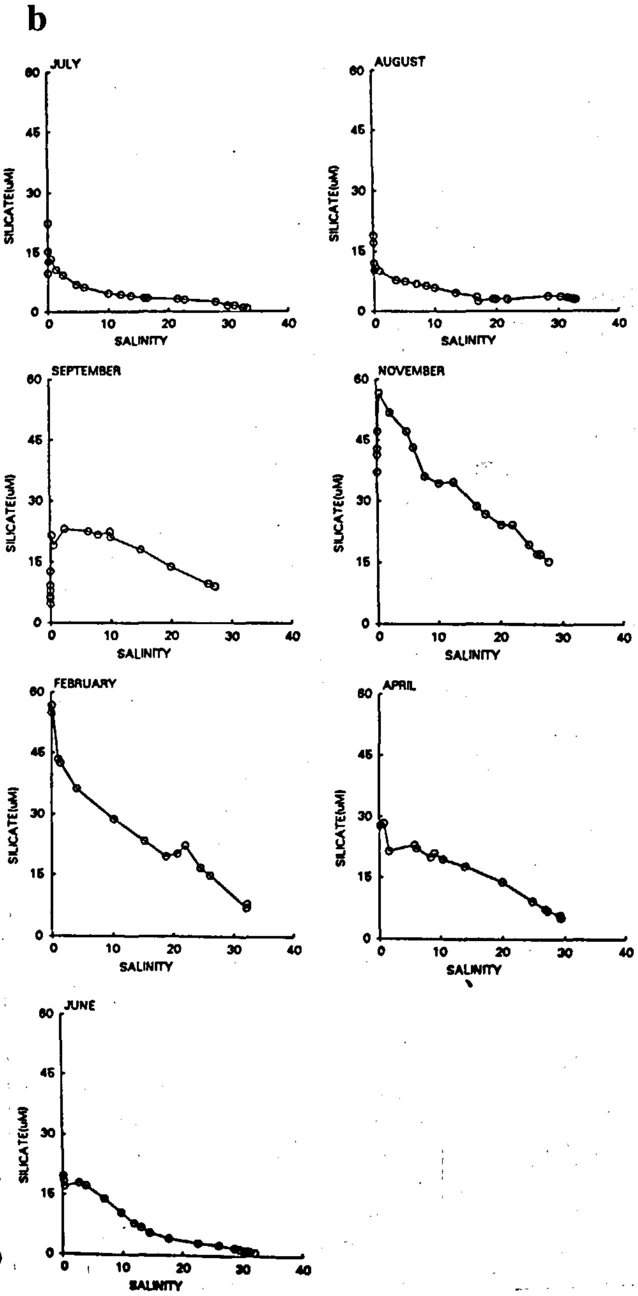


Figure 7

Silicate/salinity plots for: a) the Forth estuary (June 1989 to May 1990); and b) the Tay estuary (July 1989 to June 1990).

Tracés de silicate/salinité pour : a) l'estuaire du Forth (juin 1989 à mai 1990) ; et b) l'estuaire du Tay (juillet 1989 à juin 1990).

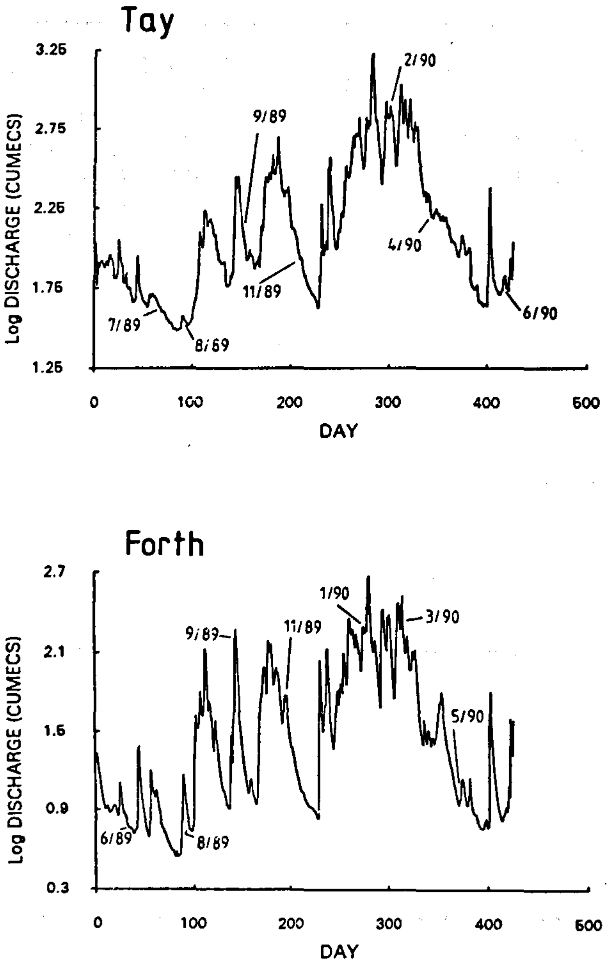


Figure 8

Discharge data for the rivers Forth and Tay for the period May 1989 to June 1990.

Données relatives à la décharge des deux fleuves, le Forth et le Tay, pendant la période de mai 1989 à juin 1990.

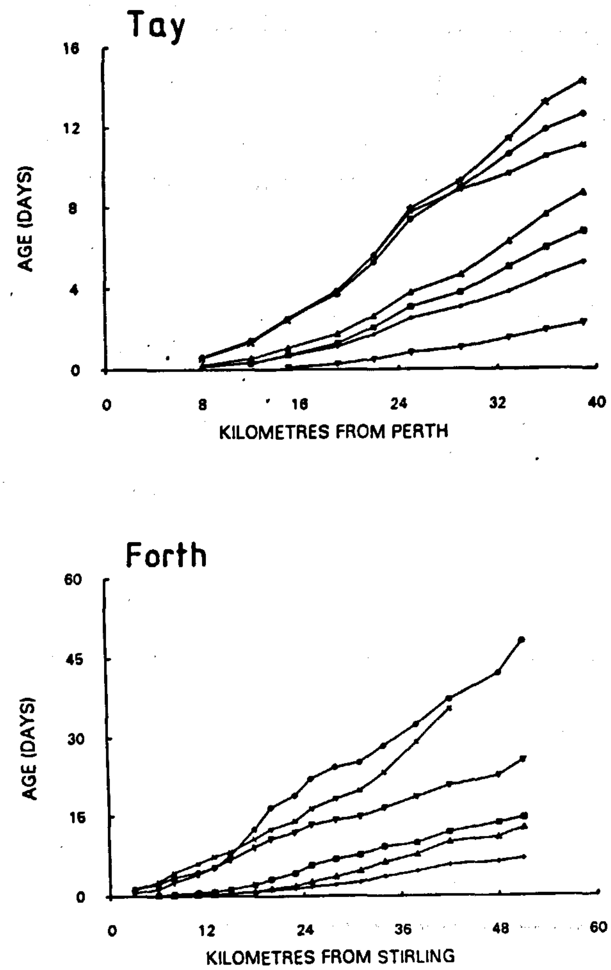


Figure 9

Plots of fresh water age for each survey in the Forth and Tay, see the Appendix for details of the calculation.

Tracés montrant l'âge de l'eau douce pour chaque enquête dans le Forth et le Tay ; détails du calcul dans l'Annexe.

which it was particularly evident, June 1989 and May 1990. This was undertaken by considering that portion of the phosphate-salinity plot where there is a nett input, *i. e.* from the minimum (prior to which removal is dominant) up to the maximum concentration (after which dilution dominates). Excess phosphate concentration in each box(*see* Appendix) are calculated by assuming conservative mixing between the phosphate concentrations at the minimum and that at the outermost station. Combining this with box volume, surface area of sediment and flushing time permits a flux to be calculated for each box. Values range from 0.67-4.40 mmol m^{-2} day^{-1} for June 1989 and 0.22-2.36 mmol m^{-2} day^{-1} for May 1990. Combining all data gives a mean and standard deviation of 1.98 and 1.25 mmol m^{-2} day^{-1} respectively.

These estimates must be regarded as approximate only since they represent a nett input and attribute it solely to a benthic source whereas in reality there are other contributory factors *e. g.* desorption from particles and wastewater inputs. Limited data exist with which to compare these values but for the Ems-Dollard estuary Rutgers van der Loeff *et al.* (1981) give a figure of 1 mmol m^{-2} day^{-1}, this is of similar magnitude to the present estimates. The fluxes calculated here are for late spring and early summer, at such times benthic fluxes are likely to be at their greatest. High productivity in the water column provides a high input rate of organic material to the sediments and can lead to reducing conditions there (Jensen *et al.*, 1990).

From laboratory experiments it is established that phosphate is released at a greater rate from anoxic than from oxic sediments (Sundby *et al.*, 1986). The Forth estuary has areas of anoxic sediments especially in summer when dissolved oxygen concentration in the water column regularly fall below 50 % saturation.

It is instructive to compare the magnitude of the mid estuarine input to that from the river end. When this is done the river contributes 177 kg P day^{-1} in June 1989 and 120 kg P day^{-1} in May 1990, 14 and 10 % respectively of the mid estuarine input. The important conclusion is therefore reached that internal cycling dominates the river input at this time of year.

Similar estimates for the Tay have not been made. Reasons for this include the lack of reliable data for sediment surface areas, the weak input signal and wastewater inputs in the vicinity of Dundee.

Mixing in the outer estuary

At high salinity in the outer estuary, simple conservative mixing generally holds. The best examples are in summer when reduced river discharges result in high salinity water extending over long stretches of the estuary. High water discharges in winter can result in the plumes being swept out beyond the sampling grid especially in the Tay. In the Forth simple mixing begins to dominate in the stretch between Kincardine Bridge and the Forth road and rail bridges. It is in this region that suspended loads decrease as the volume of the estuary increases dramatically (Fig. 10).

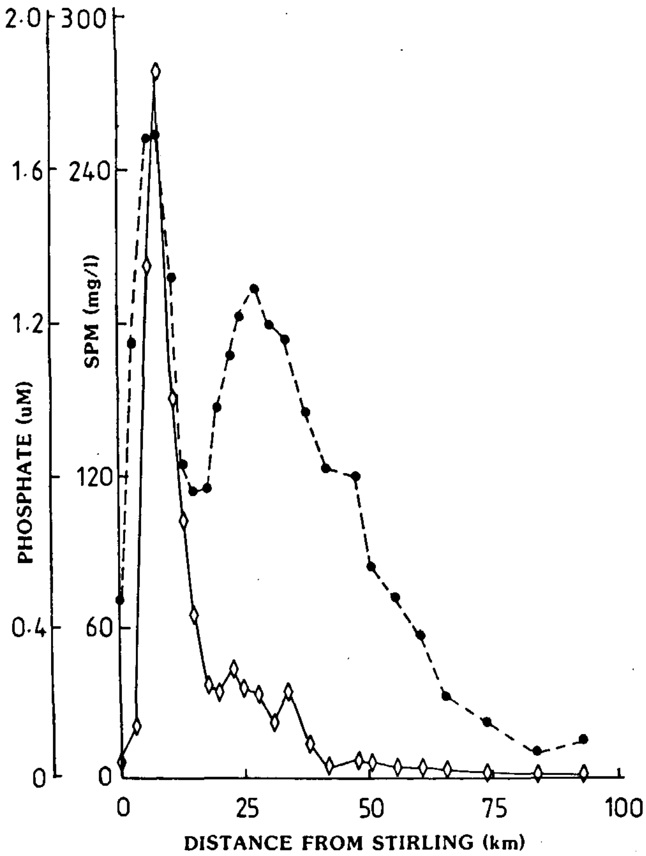


Figure 10

SPM (—◇—) and phosphate (--•--) concentrations as a function of distance for the outer Forth estuary, May 1990.

Teneurs en MPS (—◇—) et phosphate (--•--) en fonction de la distance dans l'estuaire extérieur du Forth en mai 1990.

In the Tay, simple mixing is also apparent but the surveys generally do not proceed sufficiently seaward to encounter truly coastal water. Here the situation is complicated by the main sewer inputs being in the outer estuary, their presence is most obvious in the summer under low flow conditions.

As previously discussed phosphate in estuaries exhibits a wide range of behaviour at low and intermediate salinity. At high salinity, however, simple mixing appears to adequately describe the behaviour, Mississippi (Fox *et al.*, 1985), Amazon (Fox *et al.*, 1986), Rhine, Scheldt (van Bennekom and Wetsteijn, 1990), Tamar (Morris *et al.*, 1981) and Clyde (Mackay and Leatherland, 1976). Such a unifying feature is attributed to low particle concentration, greater estuarine volume (less intimate contact with sediments) and only slowly changing physico-chemical conditions (pH/salinity).

Nitrogen species

The nitrate concentrations reported here for the Forth and Tay (up to 100 μM) are not high relative to those of contaminated rivers and estuaries. For example river water concentrations of 450 and 600 μM respectively have been reported for the Rhine and Scheldt estuaries (van Bennekom and Wetsteijn, 1990). In the UK the intensively agricultural catchment of the river Ouse results in river water nitrate concentrations of 380 μM (Morris, 1988). A simple consideration of concentrations is of limited value however since what is of greater relevance to coastal waters is the flux of material through the estuary. Small rivers may have high concentrations merely because fresh water flow is insufficient to dilute the inputs, *e. g.* the river Ythan (Scotland; Rafaelli *et al.*, 1989). By contrast a similar input into a large system like the Tay with its high dilution capacity would not be reflected in measurably enhanced concentrations.

The estimation of fluxes through estuaries has received considerable attention yet it remains an essentially unresolved problem (GESAMP, 1987). Although it is simple to multiply river discharge by river water concentration this assumes conservative mixing behaviour throughout the estuary, it also assumes that there are no further inputs along the estuary. From the data presented here (Fig. 4) it is apparent that conservative mixing is only approximated to during winter. Since both river flow and concentration are greatest at this time of year any flux estimate, although appropriate for winter, will represent an overestimate for other seasons. The difficulties of estimating realistic fluxes are exacerbated by the fact that major runoff events occur-

Table 1

Nitrate nitrogen fluxes from some major European estuaries.

Flux d'azote et de nitrate provenant de quelques estuaires importants de l'Europe.

River	Flux (tonnes/day)	Reference
Rhine	1120	Brockmann *et al.* (1988)
Rhine	1150	DOE (1987)
Elbe	685	Brockmann *et al.* (1988)
Elbe	410	DOE (1987)
Scheldt	74	Brockmann *et al.* (1988)
Weser	115	Brockmann *et al.* (1988)
	238	DOE (1987)
Humber	114	DOE (1987)
Thames	86	DOE (1987)
Tay*	60	This study
Forth#	16	This study

* 2/90
# 1/90

ring on the timescale of days can account for the majority of the annual input of material through an estuary (Schubel and Pritchard, 1986).

Given these limitations, estimates of fluxes based on winter data can at least give a useful indication of the relative importance of individual estuaries as nutrient sources to coastal waters. The results of such an exercise are presented in Table 1 for some important North Sea estuaries. The difference between estimates for the same estuary are likely to result from variations in river discharge data rather than from those in river water nitrate concentrations. It is evident that although the Forth and Tay represent relatively small sources compared to major estuaries such as the Rhine, they are important from a UK point of view. It is also apparent that the Tay represents a more important source to the North Sea than the Forth. In view of our conception of the Tay as an uncontaminated system this is possibly surprising, it is principally due however to the exceptionally high fresh water input from the river.

The simple approach used above cannot be used at other times of year when non conservative behaviour is evident and, notably in the Forth, other nitrogen species (NH_4^+, NO_2^-) make important contributions to the total dissolved nitrogen concentration.

The role of the nitrogen cycle in estuaries has been the subject of several studies *e. g.* Scheldt (Billen, 1975; Billen *et al.*, 1985), Ems-Dollard (Helder and de Vries, 1983) and Tamar (Owens, 1986). Such is the complexity of the subject that such studies have tended to concentrate on one of the processes, *e. g.* mineralisation, nitrification, denitrification, responsible for converting nitrogen from one form into another. Such conversions complicate the interpretation of data. In the present study for example the mid estuary nitrite peak in the Forth could be the consequence of denitrification and/or nitrification processes. Since no determinations were made of the rates of such processes their presence can therefore only be inferred from the distributions of individual nitrogen species against salinity.

A persistent feature of the summer nitrate distributions is a rapid increase in concentration at the very low salinity end of the estuaries *e. g.* June and August in the Forth and July and August in the Tay. The estuary flushing time associated with these summer surveys are long (Fig. 9). It is possible that nitrate distributions are influenced by variations in river water concentration which occur on time scales short relative to estuary flushing (Loder and Reichard, 1981). Any variations in concentration are likely to be related to flow.

No suitable data set exists for either the Forth or Tay with which to test the concentration/flow relationship but reference can be made to studies in other rivers. Work in lowland areas with intense agriculture suggests that species with a diffuse source, *e. g.* nitrate from agriculture, increase in concentration when flow increases whereas those coming from point sources, *e. g.* ammonia and phosphate from sewage treatment works, decrease (Edwards, 1973). For nitrate however there appears to be a seasonal difference in behaviour since Webb and Walling (1985) report an increase in concentrations after summer rainfall events but a decrease after winter rainfall. Schemel and Hager (1986) studied the effect of the Sacramento river on Northern San Francisco Bay and observed that nitrate concentrations in river water increased during the early part of rainfall events but subsequently decreased.

From the above it is evident that variations in the river water concentration may be responsible at least in part for the decrease in nitrate levels at the head of the estuaries in summer. This does not however provide a full explanation since the decrease is large relative to the magnitude of typical river water concentrations.

The probable source of nitrate in the upper estuaries is derived from the mineralisation of particulate organic nitrogen (PON) which is either produced in the water column or supplied by the river. The transformation of PON to ammonia and subsequently to nitrate (nitrification) is catalysed by bacteria and is accompanied by the consumption of oxygen (Richards, 1984), it can be approximated by the equation

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2$$
$$= 106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 236\ H_2O.$$

It must be stressed that this equation represents an oversimplification of the process since it assumes a constant composition of organic material and that mineralisation proceeds to completion. If it is assumed that mineralisation is the only process occurring and that PON is fully converted to nitrate then the oxygen consumption can be estimated from the increase in nitrate concentration. Taking the June survey in the Forth as an example the increase in nitrate

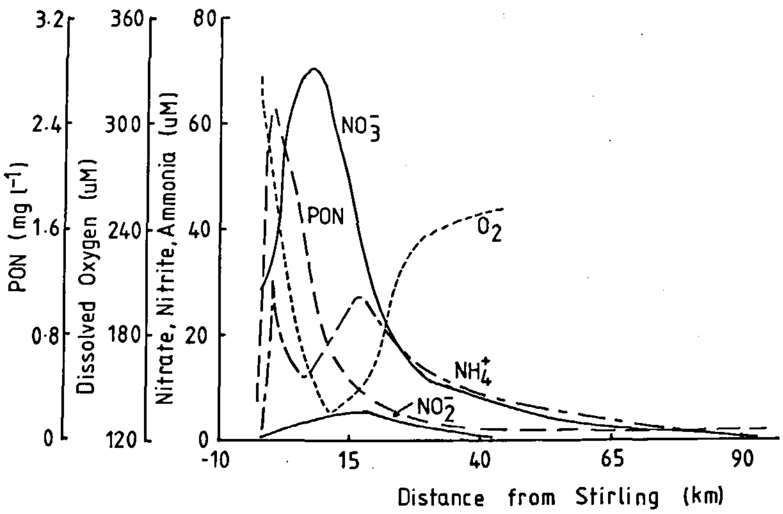


Figure 11

PON, dissolved oxygen, nitrate, nitrite and ammonia distributions as a function of distance for the Forth estuary in June 1989.

Distribution de NOP, oxygène dissous, nitrate, nitrite et ammoniaque en fonction de la distance dans l'estuaire du Forth en juin 1989.

Table 2

Estimated benthic inputs of ammonia and nitrite for individual surveys in the Forth estuary (mmol m^{-2} day^{-1}).

Estimation des apports benthiques d'ammoniaque et de nitrite relatifs aux enquêtes individuelles réalisées dans l'estuaire du Forth.

Survey	Ammonia			Nitrite		
	n	Mean	SD	n	Mean	SD
June 1989	15	44	25	15	8.1	5.6
August 1989	16	20	13	16	6.6	7.1
March 1990	11	19	10	-	-	-
May 1990	15	40	17	15	3.9	2.3

n corresponds to the number of boxes from which an estimate was obtained.
No estimate of the nitrite flux was made for March 1990 since the signal was very small.

concentration is *ca.* 40 µM indicating the consumption of *ca.* 340 µM of dissolved oxygen. The observed decrease in dissolved oxygen is *ca.* 200 µM, considering the approximations and assumptions made in this estimate the agreement is considered reasonable. In the present study the low level of mineralisation in winter is evidenced by conservative mixing in both estuaries.

Since bacteria are generally attached to particles (Owens, 1986) high turbidity should be associated with higher bacterial numbers. The data appear to support this idea since the input of nitrate is much greater in the turbid Forth (up to 600 mg/l in the turbidity maximum in summer) than in the relatively clear Tay (less than 100 mg/l). Previous work in the upper Forth estuary has demonstrated that the Biological Oxygen Demand (BOD) attributable to particles is a linear function of the SPM loading transformed to the power two thirds (Forth River Purification Board, 1983). This suggests a surface area dependency and supports the idea that bacteria on particles are responsible for mineralisation and oxygen consumption.

In the Forth high turbidities result from low river flows, these are generally associated with summer and coupled with higher temperatures will favour mineralisation. In the Tay high turbidity is generally produced by wind rather than by river discharge effects. For this estuary then temperature and turbidity are not generally coupled to reinforce mineralisation, nonetheless there is evidence that it is significant in the summer.

Figure 11 shows the nitrogen species data for the Forth in June 1989, also that for dissolved oxygen and PON. Abundant PON and dissolved oxygen (also higher water temperatures) provide ideal conditions for mineralisation and this is evidenced in increasing nitrate concentrations downstream as oxygen is consumed. Further downstream PON and dissolved oxygen concentrations are depleted favouring denitrifying bacteria (probably in the sediments) which produce nitrite and ammonia.

Maximum ammonia concentrations in the Forth estuary were observed in the summer months in association with low river discharges and long residence times. The mid estuarine maximum is characteristic of a species with a dominant benthic source, Knox *et al.* (1981). The high concentrations at low salinity (June, August and May) are a consequence of sampling close to the Stirling sewage treatment works. This was necessary since on these surveys river discharge was low and to reach fresh water it was necessary to proceed further up the estuary.

An alternative explanation for the mid estuarine maxima in ammonia concentrations is that wastewater inputs are responsible. 78-80 % of the total ammonia inputs from such sources are located at distances greater than 30 km downstream from Stirling (FRPB, pers. comm.). The peak in ammonia concentration however is generally located 15-18 km from Stirling. As all surveys were completed around high water it is possible that the tidal excursion could be responsible for shifting the apparent input to the middle estuary. Although this possibility cannot be eliminated other evidence indicates that the sediments are the most important source. The peaks in dissolved nitrite (Fig. 6) and dissolved manganese (unpublished data) are in the same location as that of ammonia. Manganese is not associated with wastewater inputs of ammonia and its source can only be from the sediments. Since peak concentrations occur in the same area this strongly suggests that the dominant source of ammonia is also within the sediments.

Ammonia is a product of excretion and decay, it is released during the breakdown of dead organic material, it is also produced during the denitrification which converts oxidised nitrogen species *e. g.* nitrate, nitrite ultimately to nitrogen. The magnitude of the flux is dependent on several factors including the redox state of the sediments and bacterial populations, the latter are also influenced by temperature.

If in the Forth estuary the source of ammonia is assumed to be entirely of benthic origin it is possible to estimate a flux in the following way. The excess ammonia concentration in each box (*see* Appendix) is estimated from the ammonia/salinity plot assuming conservative mixing between river and seawater. This is multiplied by the box volume and divided by the surface area of the bottom sediment and the flushing time to produce a flux. The same exercise can be undertaken with the nitrite data and the results of these calculations are summarised in Table 2. The most appropriate data with which to compare these estimates is that from a similar environment. In the Tamar

Table 3

Inputs of soluble inorganic nitrogen to the Forth estuary (tonnes N day^{-1}).

L'azote inorganique soluble introduit dans l'estuaire du Forth (tonnes N $jour^{-1}$).

Survey	River	Ammonia[a]	Nitrate[b]	Nitrite	Total
June 1989	0.23	2.02	1.30	0.16	3.71
August 1989	0.12	1.51	1.12	0.13	2.88
March 1990	6.43	1.98	-	-	8.41
May 1990	1.13	2.26	-	0.14	3.53

a) The ammonia input is attributed to a benthic and/or wastewater source (see discussion).
b) The nitrate input is due to mineralisation/nitrification in the upper estuary.

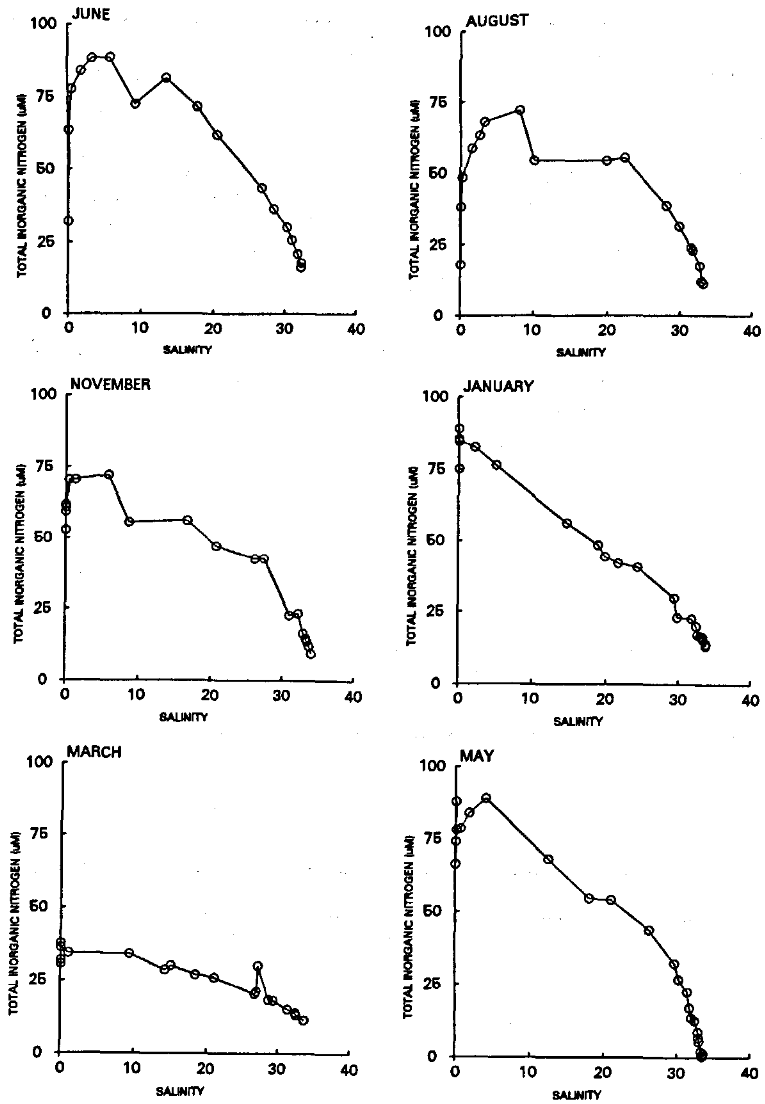


Figure 12

Total inorganic nitrogen/salinity plots for the Forth estuary (June 1989 to May 1990).

Tracés d'azote inorganique total/salinité pour l'estuaire du Forth (juin 1989 à mai 1990).

estuary Knox *et al.* (1981) estimated ammonia fluxes of 12-41 mmol m^{-2} day^{-1} in general agreement with the data presented here.

It is also possible to calculate the magnitude of the nitrogen input for these surveys attributable to the sources of ammonia and nitrite. The dissolved nitrogen input due to mineralisation can also be estimated by the same method if conservative mixing of nitrate is assumed between river and seawater. The results of these calculations are given in Table 3 where such inputs are compared to those from the river and from wastewater inputs (FRPB, pers. comm.). The results indicate that in winter (March) the dominant source of dissolved nitrogen is from the river while at other seasons it is from internal cycling processes within the estuary.

If this cycling were entirely between dissolved inorganic species then a plot of total inorganic nitrogen against salinity would be linear for all seasons. Such plots are shown in Figure 12 from which it is evident that this is not the case. For the Scheldt estuary Billen *et al.* (1985) observed linearity in such plots at high salinity and although this is apparent for winter surveys in the Forth it does not hold at other times. Figure 12 indicates an additional source of dissolved inorganic average and this is attributable to production from particulate material *via* mineralisation.

Ammonia and nitrite concentrations in the Tay estuary are much lower than those in the Forth and profiles do not exhibit mid estuary maxima. It is not appropriate therefore to treat the data in the same way as that for the Forth. One feature worthwhile of more detailed investigation however is the dissolved ammonia peak which is apparent in the vicinity of Dundee under slow flushing conditions. The magnitude of this input has been estimated for July and August 1989 using the technique described previously. The ammonia inputs for these two surveys is 0.52 and 1.12 tonne N day^{-1} respectively. These estimates are in reasonable agreement with discharge data from Dundee sources of 1.5 tons N day^{-1}(pers. comm., Tay River Purification Board).

Silicate

While silica is not considered to be a contaminant its geochemical importance in weathering processes and its role as a plant nutrient have led to a widespread interest in its distribution and behaviour in estuaries. River water concentrations from the Forth and Tay are compared to those from other UK rivers in Table 4. While the concentrations in the Forth and Tay are slightly lower than those in other rivers they are by no means exceptional.

In many estuaries conservative mixing is reported at times of low biological productivity, *e. g.* Rhine and Western Scheldt (van Bennekom and Wetsteijn, 1990), Rhone (Denant and Saliot, 1990). In the present study essentially conservative behaviour is also apparent during winter for both the Forth and Tay estuaries, at other seasons however this simple behaviour breaks down. An overall feature of the seasonal distributions is that those from the Forth are smoother than those from the Tay. A contributory factor is

Table 4

Silicate concentrations in UK rivers.

Teneurs en silicate dans les fleuves du Royaume-Uni.

River	Si (µM)	Reference
Alde	116	Liss and Pointon (1973)
Southampton Water	166	Burton *et al.* (1970)
Conway	50	Liss and Spencer (1970)
Clyde	100-130	Mackay and Leatherland (1976)
Tamar	107-125	Morris *et al.* (1981)
Forth	60-80	This study
Tay	45-60	This study

that flushing times are longer in the Forth and these result in better mixed, more stable conditions. In consequence the Tay estuary is characterised by fronts and local patches of high turbidity whereas the Forth is more homogeneous both laterally and longitudinally.

As for nitrate (Fig. 4 *b*) summer distributions of silicate in the Tay (Fig. 7 *b*) are characterised by removal, in other estuaries this has been attributed to biological uptake. In the Yaquina estuary for example it was concluded that non conservative behaviour was a function of high insolation and that residence time was the primary controlling factor (Calloway and Specht, 1982), stable conditions favouring phytoplankton growth. By contrast in the Forth estuary (Fig. 7 *a*), even in the summer, mixing is generally conservative above *ca.* 10 ppt. The reason for this difference between the two estuaries is unclear but is possibly associated with their contrasting turbidities. High turbidity in the Forth may result in a poor light regime relative to the Tay with a consequent inhibition of phytoplankton growth, such an effect has been reported in the Delaware estuary (Pennock, 1985).

The abiological removal of silicate during estuarine mixing has also been reported (Liss and Spencer, 1970; Morris *et al.*, 1981). Liss and Spencer concluded that the removal was due to suspended particulate material (SPM) and that the extent of removal increased with both increasing SPM loading and salinity. Morris *et al.* attempted to quantify the degree of removal and correlate it with environmental properties (salinity, SPM loading, pH, chlorophyll fluorescence, fresh water composition). Their results however were inconclusive and this was attributed to short term fluctuations in river concentrations of silicate and to turbidity changes associated with tidal resuspension and deposition of sediment. In the present study the highest particle loadings were observed in the upper Forth estuary during summer and at such times there is some evidence of removal occurring.

Variations in silicate concentration associated with flow have been reported and as previously discussed for nitrate these may influence the shapes of estuarine profiles. An inverse relationship between flow and concentration has been reported for the Sacramento river (Schemel and Hager, 1986) For lowland rivers of East Anglia (UK) however concentrations were insensitive to flow except following dry periods when rainfall events resulted in high silicate levels (Edwards, 1973).

The complexity of interpreting individual estuarine profiles is well demonstrated by the surveys in the Forth from January through to May. In January, a winter survey under high flow conditions, mixing is conservative. In March concentrations in the outer stations are characteristic of winter while at the river end removal is occurring, in May the outer stations have low (summer) concentrations but river water levels have increased (Fig. 7 *a*). A similar pattern is observed for nitrate (Fig. 4 *a*). Such striking contrasts highlight the caution which should be exercised in explaining the estuarine behaviour of a species or element (Church, 1986).

In summary silicate distributions are controlled by:

a) biological removal both in the river and estuary;

b) possible removal in the turbidity maximum (Forth estuary);

c)variations in the river water end member associated with changes in flow.

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Appendix

The flushing characteristics of the estuary were examined using the approach of Kaul and Froelich (1984). This consists of dividing the estuary into a series of boxes straddling sample positions. A knowledge of the volume of each box together with the salinity allows the fresh water volume in each box to be calculated. Commencing with the topmost box (*i. e.* nearest the river) and starting with the day preceding the survey river discharge data is used to calculate the time required to provide this volume of water. Each box is considered sequentially until they have all been provided with the requisite volume of water. This simple model is unlikely to give precise values of fresh water age since it neglects lateral and depth variations of salinity. Since, however, it uses actual discharge data and not some long term average it is superior to the tidal prism method and other basic models. The results should give a realistic estimate of the relative flushing times for individual surveys.

The volume of each box in the Forth was extracted from the data of Webb and Metcalfe (1987) while for the Tay it was estimated from the Admiralty Chart and bathymetric data provided by the Tay Estuary Research Centre. River discharge data for the Forth, Allan, Devon, Carron and Avon was provided by the Forth River Purification Board. Tay, Almond and Earn discharge data were provided by the Tay River Purification Board.

For the Tay estuary the calculation is relatively simple since the dominant input of fresh water is at the head of the estuary. In the Forth estuary however, rivers such as the Avon and Carron enter further downstream. In the programme used this is accounted for by only using such discharge data for boxes downstream of the point of entry.

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