Coastal Zone Topics: Process, Ecology & Management

3. The estuaries of Central Scotland

Edited by D.S. McLusky

Contents

Conservation and management

Preface

The estuaries of Central Scotland have long been a focus of the life of Scotland. There are three principal estuaries - the Clyde, the Forth and the Tay, as well as several smaller estuaries, such as the Garnock and the Eden.

In their various ways these estuaries have been, and remain, at the commercial heart of Scotland. Glasgow, one of the principal industrial cities of the British Empire, lies at the head of the Clyde Estuary, and the banks of the estuary were at one time lined by the world famous shipyards. Today the Forth, from Stirling to Edinburgh, has the greatest tonnage of shipping of any port authority in Britain, as well as the only oil refinery in Scotland on its shores, at Grangemouth. The Tay Estuary, from Perth to Dundee, receives the largest river flow from any British river.

Each estuary is also a principal focus for nature conservation, with large sections of all the estuaries designated as Sites of Special Scientific Interest, or internationally important nature reserves.

In all these estuaries, therefore, the problems of controlling and managing industrial development in harmony with nature conservation is the major task of the agencies charged with the duties of environmental management of the coastal zone. A study of these estuaries is, however, of interest not only to local organisations. The resolution and management of the conflicts which occur form valuable case studies for all whose task is to understand and manage the estuaries and coastal zones of the world.

The meeting, for which the present volume provides a permanent record, to discuss the current state of the estuaries of Central Scotland was held at Heriot-Watt University, Edinburgh on 6-8th April 1995, under the local meetings programme of the Estuarine and Coastal Sciences Association (ECSA). Joint support for the meeting was also given by the Scottish Association for Marine Science (SAMS).

The meeting was intended to be a successor to the Royal Society of Edinburgh Symposia on the subjects of the Clyde, Tay and Forth estuaries held in the 1980s. Each of these were published as follows:

J.A. Allen *et al.*, *eds.* 1986. The environment of the Estuary and Firth of Clyde. *Proceedings of the Royal Society of Edinburgh, Volume 90B.*

J. McManus, *ed.* 1987. The environment of the Tay Estuary. *Proceedings of the Royal Society of Edinburgh, Volume 92B.*

D.S. McLusky, *ed.* 1987. The environment of the Estuary and Firth of Forth. *Proceedings of the Royal Society of Edinburgh, Volume 93B.*

The authors of the present symposium were asked to regard the PRSE volumes as an agreed starting point, and were invited to provide information on progress and developments in our scientific understanding of the estuaries and firths of Central Scotland since these earlier publications.

In this volume, the papers are divided for convenience. After consideration of water movements and quality, attention is focused on contaminants which have been measured, especially heavy metals. Within the biological group of papers, there is a range from the primary producers, through the primary consumers (mainly benthic), and on to consider the secondary consumers (including shrimps, fish and birds). Finally, attention is given to the developing role of conservation and environmental management.

Acknowledgements

Donald S. McLusky

Modelling the Forth Estuary with MIKE11

S.G. Wallis & N.J.W. Brockie

The paper describes current progress on a project which aims to apply the MIKE11 mathematical model to the Forth Estuary. The project is a joint venture between the Forth River Purification Board and Heriot-Watt University, Edinburgh. MIKE11 is a one-dimensional modelling system, which is capable of simulating the hydrodynamic response and the water quality characteristics of an estuary under the influence of tidal forcing, fluvial discharges and contaminant loadings. The hydrodynamic model of the Forth Estuary has been validated throughout the length of the estuary, and it replicates all the important features of the tidal response of the estuary. For example, tidal amplitudes, phase lags and double high and double low waters are faithfully reproduced. The water quality model has not been validated to the same extent, nor does it presently reproduce observed water quality parameters to the same degree of accuracy as achieved for the hydrodynamics. Nevertheless, the model reproduces the key features of the salt transport in the estuary. Further work will be aimed at improving the calibre of the water quality model as a tool to help maintain recent improvements to the water quality environment of the estuary and to support future water quality management decisions.

S.G. Wallis, Department of Civil and Offshore Engineering, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS, UK.

N.J.W. Brockie*, Forth River Purification Board, Clearwater House, Avenue North, Heriot-Watt Research Park, Riccarton, Edinburgh, EH14 4AP, UK.

*To whom correspondence should be addressed

Introduction

The Forth River Purification Board (FRPB) is the regulatory authority responsible for licensing and monitoring discharges to the Forth catchment including the Estuary and Firth of Forth (see Figure 1). FRPB also has a statutory responsibility to monitor these controlled waters and seeks to maintain water quality where this is good and to improve water quality where it is unsatisfactory. In the past the assessment of the impact of discharges on water quality, particularly on dissolved oxygen (DO), in the Forth Estuary was based on the use of a one-dimensional, tidally averaged, water quality model (FRPB 1986; Webb & Metcalfe 1987). In recent years, as improvements in estuary water quality were achieved and discharged loads reduced (Griffiths 1995) the limitations of this model reduced its effectiveness as a water quality management tool. Potential changes in water quality due to changes in discharged loads became difficult to distinguish against the uncertainties in the tidally averaged predictions. Therefore it was decided to upgrade to a fully dynamic water quality model.

This paper discusses the calibration and validation of the MIKE11 hydrodynamic and advection-dispersion modules and briefly describes the progress to date with calibrating the water quality module. The work has been done jointly by FRPB and the Department of Civil and Offshore Engineering, Heriot-Watt University. The aim of the project is to provide FRPB with a predictive capability enabling water quality management decisions to be based on sound scientific information. The model will also be a powerful research tool enabling further investigation and understanding of the processes controlling tidal dynamics and water quality in the Forth Estuary.

The Forth Estuary

The Forth Estuary is defined as extending from the Stirling Old Bridge, the upstream limit of saline intrusion, to a line just east of the Forth Bridge (see Figure 1). Eastward of this boundary the waters of the Firth of Forth are classified as coastal. A full description of the physical dimensions and hydrography of the Forth Estuary is given in Webb & Metcalfe (1987).

The major freshwater input at the head of the estuary comes from the combined flows of the Rivers Forth and Teith and the Allan Water (see Figure 1). The long-term (14-year) mean annual flow recorded for these rivers is 58 m^3 s^{-1} (FRPB 1995). The mean winter flow (December, January, February) is 93 m^3 s^{-1} and the mean summer flow (June, July, August) is 24 m^3 s^{-1} for the same period. Further significant freshwater inputs come from the Bannock Burn and the Rivers Devon, Black Devon,
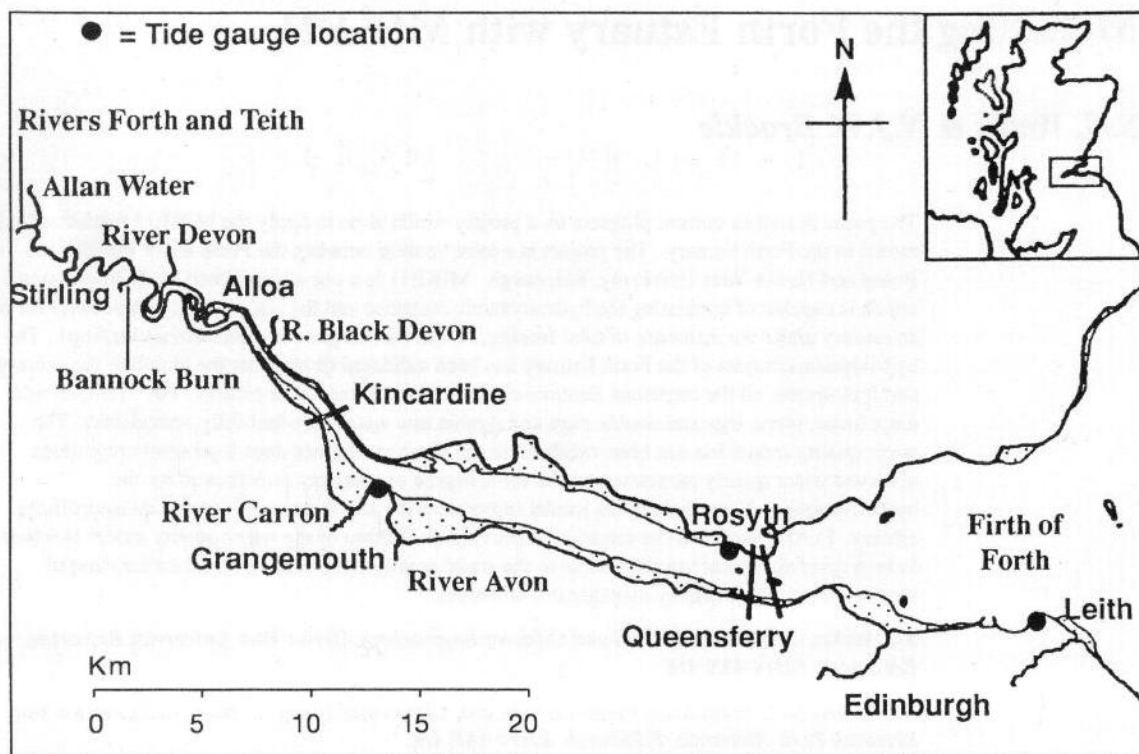
Figure 1. The Forth Estuary and the Firth of Forth.

Carron, Avon, and Almond. In total these contribute a mean annual flow of 21 m³ s⁻¹ or just over 36% of the input from the Forth, Teith and Allan.

The tidal regime in the Firth of Forth and Forth Estuary is predominantly semi-diurnal. At Leith the mean spring tidal range is 4.8 m and the mean neap range is 2.4 m. These ranges are amplified by approximately 20 cm and 40 cm at Rosyth and Grangemouth respectively. At Rosyth the flood period is longer than the ebb with a pronounced stand at low water. The average spring tidal velocities in the lower estuary are of the order of 1 m s⁻¹. Further upstream at Grangemouth double high and double low waters are observed. The extent of the distortion of the semi-diurnal tide varies through the spring neap cycle. It is considered that these features are caused by reflections of the semi-diurnal tide at Queensferry and at Kincardine where the estuary narrows significantly (HR Wallingford 1994).

Between Alloa and Stirling the estuary consists of a series of large meanders and the width and depth continue to decrease. The distortion of the tidal regime becomes increasingly influenced by shallow water effects and the ebb period is longer than the flood, significantly so at Stirling where conditions are dominated by fluvial rather than tidal action. The onset of the flood tide is very rapid and on occasions a bore has been observed upstream of the confluence with the Bannock Burn. Zidan (1978)

attributed the distortion of the tidal curve to amplification of the higher harmonics of the diurnal constituents. The double low water becomes attenuated in the upper estuary due to increasing bed elevation but the double high water persists as far up estuary as Stirling (Webb & Metcalfe 1987).

The estuary varies from a vertically well-mixed condition to a partially mixed condition depending on the tidal range and the freshwater flow. Greatest vertical stratification is observed on neap tides during a period of high freshwater flow. A typical two-layer gravitational circulation exists in the lower estuary with a seaward residual flow in the upper waters and a landward residual flow in the lower waters. Wind-induced mixing also plays a significant part in controlling the vertical structure of the water column in the wider reaches of the lower estuary.

The major sewage discharges to the estuary are from treatment works at Stirling, Alloa, Falkirk, Grangemouth and Dunfermline (see Figure 1). The major industrial discharges are located at Alloa and Grangemouth. In total these discharges contribute a mean annual flow of 3.3 m³ s⁻¹ (1994, unpublished data), approximately 4% of the total annual freshwater flow to the estuary.

The Upper Forth Estuary experiences a seasonal dissolved oxygen (DO) minimum which has resulted in a water quality classification of C (Poor) from the River Black Devon to Long Reach for 1994. Water

quality improvements have continued over the past decade (Griffiths 1995). However during periods of low flow during summer severe DO depletion can still cause a barrier to migratory fish species and occasional fish kills have been reported. The high degree of sediment resuspension during spring tides results in a pronounced turbidity maximum in the upper estuary with the associated BOD exerting a significant oxygen demand (Dobson 1995). In warmer weather oxygen consumption is higher and if the resupply of oxygen is reduced by low freshwater flows then dissolved oxygen depletion can reach critically low levels. There is also a significant oxygen demand in the upper estuary owing to nitrification (Balls *et al.* 1995). Over the last decade the input of BOD to the estuary has reduced considerably and there is some evidence to suggest that the internal production of nitrate in the estuary is increasing owing to the greater availability of dissolved oxygen.

In the light of this a realistic model of estuary water quality is required so that the processes resulting in DO depletion can be further understood. FRPB, as the regulatory authority, can then act to protect the water quality improvements already achieved and take further steps to attain the environmental quality objective of class B (Fair) for the estuary. For dissolved oxygen this translates to a 95 percentile environmental quality standard of 4.5 mg l^{-1}, allowing the passage of migratory fish at all times.

The application of MIKE11

MIKE11 is one of a number of well-founded numerical modelling software tools currently used within the UK water industry. It simulates rainfall run-off, channel hydraulics, solute transport, sediment transport and water quality in river and estuary systems using standard finite difference techniques to solve the one-dimensional unsteady flow, advection-dispersion and reaction kinetic equations (DHI 1992). The one-dimensional approach implies the use of cross-sectionally averaged parameter values, and therefore, strictly speaking, the model is suitable only for well-mixed flows. Although for estuaries there is weak feedback from the solute transport and water quality equations to the hydrodynamic equations (through the water density), the standard MIKE11 software does not cater for this. Hence, the calculations proceed in a serial fashion, i.e. hydrodynamic calculations precede solute transport calculations which precede water quality calculations.

In this work, the package has been used to simulate the hydrodynamic response and water quality characteristics of the Forth Estuary under the influence of tidal forcing from the North Sea, fluvial discharges, wastewater discharges and effluent loadings. Initial development of the model used MIKE11 Version 2.12 running under MS-DOS, but following software upgrades the original model was successfully transported to Version 3.11 running under MS-Windows.

The Forth Estuary is represented by 70 cross-sections (taken off Admiralty Charts) between the seaward boundary of the model at Leith and the landward boundary at the tidal limit (Craigforth, 4 km upstream of Stirling Bridge). These data are of good quality between Leith and Alloa, but between Alloa and the tidal limit the resolution of the shape of the channel cross-section progressively reduces. There are also some doubts on the accuracy of chart datum in this part of the estuary.

The model is driven by information provided at its boundaries: at Leith, water levels at 15 minute intervals were obtained from an automatic tide gauge operated by the British Oceanographic Data Centre (BODC); flows from the rivers at the tidal limit, in the tributaries and in the wastewater discharges were provided by the FRPB; other necessary data (salinity and water quality parameters at both boundaries and in the tributaries and wastewater discharges) were also provided by the FRPB. Supplementary calibration and validation data (water levels, salinity and water quality) were supplied by the FRPB and HWU. Further details are given in Nilssen (1994).

The hydrodynamic model

Calibration of the hydrodynamic module consisted of adjusting Manning's 'n' friction coefficients such that the model reproduced the observed tidal response of the estuary. Water levels from the model were compared with measured water levels at several sites along the estuary during one day in May 1991, and excellent agreement was obtained at all locations except Stirling. The difficulties at Stirling were attributed to the particularly poor cross-sectional data in the uppermost 10 km of the estuary, which resulted in the model under-predicting water levels at low water. Following Zidan (1978), who reported the existence of a step-like feature in the bed at Stirling, the cross-sections in the uppermost 4 km of the model were adjusted to reduce the depth of flow. Minor adjustments were also made to the friction coefficients at these cross-sections. These changes had no effect on the model results in the lower and middle reaches of the estuary, but dramatically improved the results at Stirling. The friction coefficient values finally adopted are shown in Table 1. Supplementary

investigations showed that i) the time step in the model should not exceed 15 minutes, with a time step of 5 minutes being necessary for full resolution of the tidal response in the upper estuary and, ii) the model results were not particularly sensitive to the resolution of the river flow data used and, hence, daily mean flows were adopted for subsequent runs.

Validation of the model was performed by running it for periods in 1993 and 1994, with no further changes to cross-sections or friction coefficients. Predicted water levels were compared against observations at four sites along the estuary in 1993 and at three sites in 1994. Results from these runs are shown in Figures 3, 4 and 5 (see Figures 1 and 2 for locations). Figure 3 shows predicted and observed water levels at four locations on the 18th August 1993, Figure 4 shows water levels at three locations during the first week in September 1994 and Figure 5 shows predicted cross-sectional mean velocities and observed depth mean channel centre-line velocities at two locations in the upper estuary on the 18th August 1993, and at two nearby locations on the following day.

In general the model reproduces satisfactorily all the main features of tides in the estuary. Of particular note is the reproduction of both spring and neap tides and the faithful representation of double high and double low waters. Clearly, the model agrees very well with the data at Rosyth and Grangemouth. The disagreement shown in Figure 3 at the two stations in the upper estuary (Broom and Cambuskenneth) can be attributed to offset errors in the observations since the shapes of the tide curves are so strikingly similar and also because the agreement at Stirling is good (see Figure 4). The velocity results show that the model correctly reproduces the rates of water movement, an essential

Table 1. Friction coefficients.

Section number	Distance from tidal limit (km)	Resistance Coefficient Manning's 'n'
1-39	68.8-25.0	0.022
40-44	24.0-20.3	0.024
45-49	19.4-16.0	0.026
50-54	15.3-12.4	0.028
55-58	11.6-9.1	0.030
59-62	8.4-6.2	0.035
63-64	5.4- 4.7	0.038
65-70	3.9- 0.0	0.050

aspect for the water quality modelling. The minor disagreements between predicted and observed velocities can be attributed to the complex channel geometry and small aspect ratio of the channel in the upper estuary which are likely to cause cross-sectional and depth mean velocities to be somewhat different.

The transport model

In a one-dimensional estuary model, solute transport is represented in terms of two longitudinal processes: advection and dispersion. The former describes solute movement at the cross-sectional mean velocity of the water (calculated in the hydrodynamic model); the latter describes longitudinal spreading of solute by the aggregated effect of a host of mixing mechanisms, and is quantified by the longitudinal dispersion coefficient. Appropriate values of this coefficient are notoriously difficult to determine because of the complexity of mixing processes in estuaries and the lumped nature of the coefficient. Not only is it likely to vary along
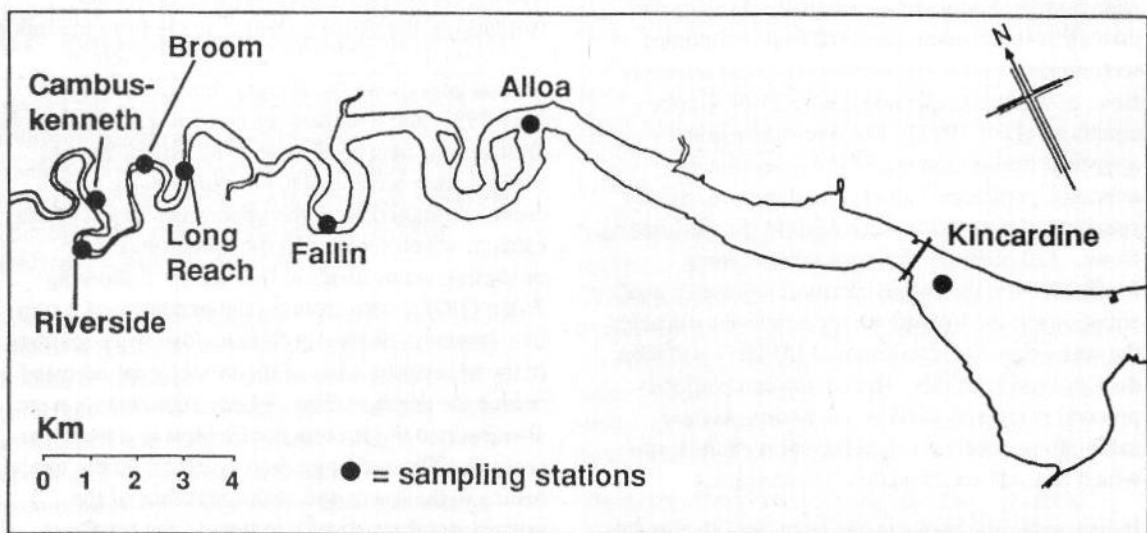
Figure 2. The Upper Forth Estuary showing sampling stations.
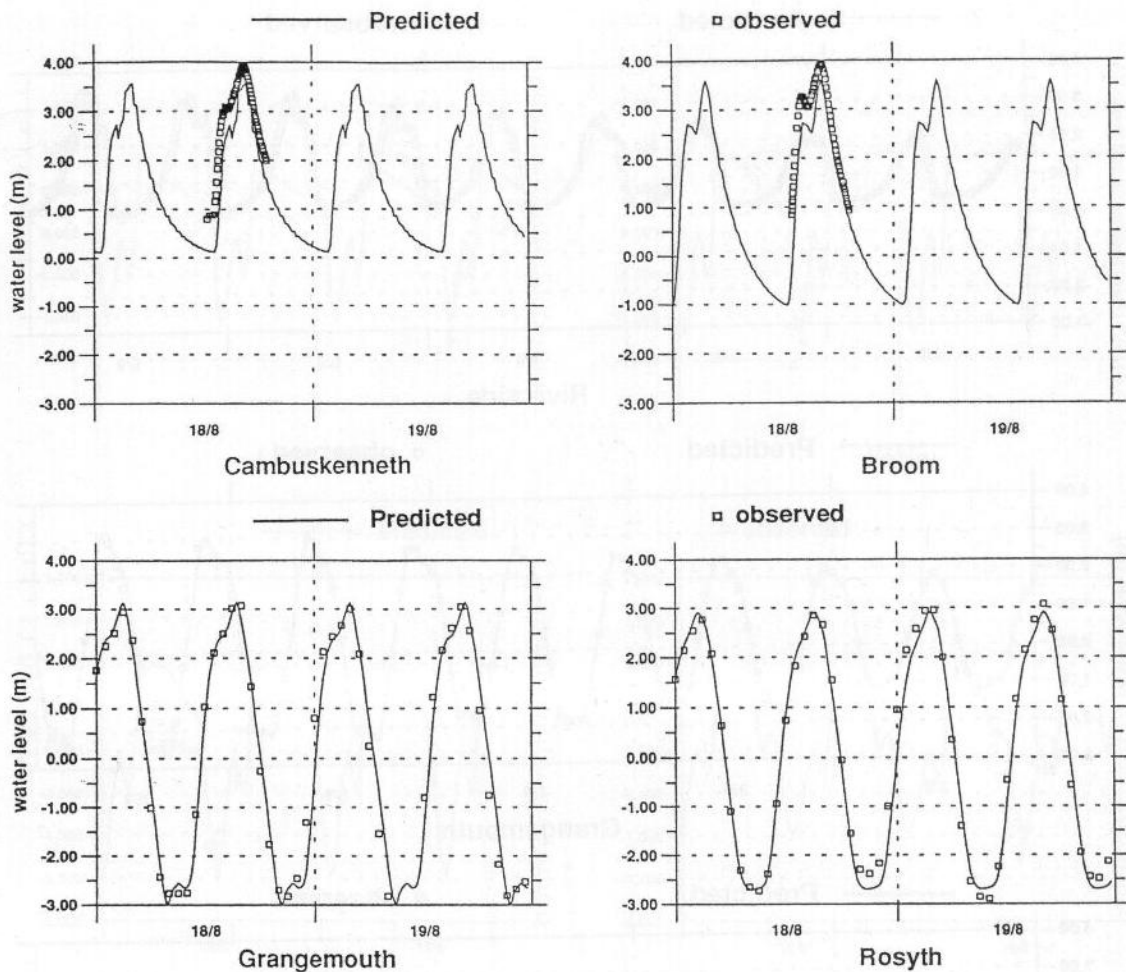
Figure 3. Predicted and observed water levels at Cambuskenneth, Broom, Grangemouth and Rosyth for 18th and 19th August 1993.

the estuary, but variations during a tidal cycle are also likely as the flow structure adapts in response to changes in the tidally driven flow.

The presence of salinity in estuaries is a great boon to modellers, since it provides a ready-made solute for validating transport models. Also, the required boundary values for it are simple: zero at the tidal limit and in any inflows; 34, the salinity of sea water at the mouth. Hence, the transport model was calibrated by adjusting dispersion coefficient values until the best agreement was obtained with continuous salinity measurements from a water quality monitoring system operated by FRPB at Alloa.

In contrast to hydrodynamic models, in which the choice of initial conditions is not critical, when modelling salinity the provision of appropriate initial values of salinity along the estuary is crucial, because flushing times can be very long. In the present study estimates of the initial conditions were available from routine longitudinal estuary surveys undertaken by FRPB. The seaward boundary was simulated with an open boundary condition. This

enabled the model to calculate the boundary salinity value during an ebb tide and to use an imposed value during the flood tide, with a rapid transition at low water. This configuration allowed the salinity at Leith to remain almost constant during a simulation. It was found that a time step of 2 minutes was necessary to ensure accurate resolution of salinity variations.

A number of calibration runs were undertaken, each of which started with a series of repeating boundary conditions, so that at the beginning of the calibration period the salinity distribution had reached a dynamic equilibrium state for the specified dispersion coefficients. Typically, 20 tidal cycles of repeating boundary conditions were necessary to achieve equilibrium.

The estuary was divided (on physical grounds) into four reaches and dispersion coefficients were held constant in each reach. The overall trend was that of decreasing coefficients from mouth to head, which is consistent with other estuaries (West & Broyd 1981) and with steady state models of the Forth Estuary (Wallis & Graasvoll 1995). It was found necessary
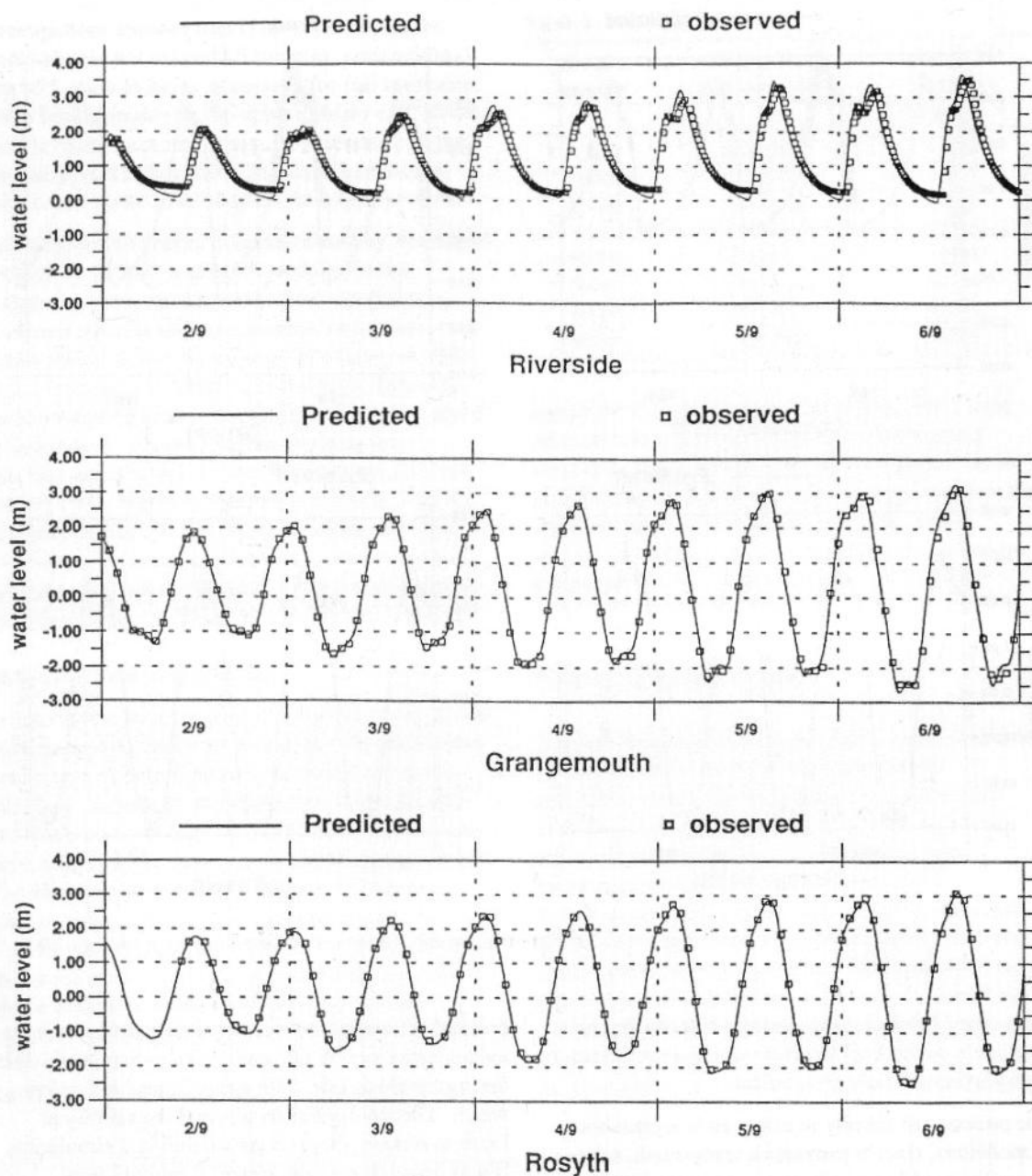
Figure 4. Predicted and observed water levels at Riverside, Grangemouth and Rosyth for 2nd-6th September 1994.

Table 2. Dispersion coefficients.

Section number	Distance from tidal limit (km)	Dispersion Coefficient ($m^2 s^{-1}$)	
		Neap	Spring
1-9	68.8-55.3	300	500
10-27	54.4-35.4	200	400
28-62	34.8-6.2	30	60
63-70	5.4-0.0	20	40

to use different sets of dispersion coefficients for spring and neap tides (Table 2). Since the use of velocity-dependent dispersion coefficients made little difference to the results, the coefficients were

held constant in time. Results from two calibration runs are presented (May 1991 and August 1993). For the first of these dates a spring-neap cycle of boundary conditions was imposed during the calibration period. Figure 6 shows predicted and observed salinities at Alloa for neap tides during this period. For the second date, the repeating spring tide boundary conditions for 18th August 1993 were continued into the calibration period (18th-19th August). Figure 7 shows predicted salinities with those observed at the four upper estuary locations considered in the previous section.

In general the agreement is good and the model reproduces the full extent of the penetration of salt
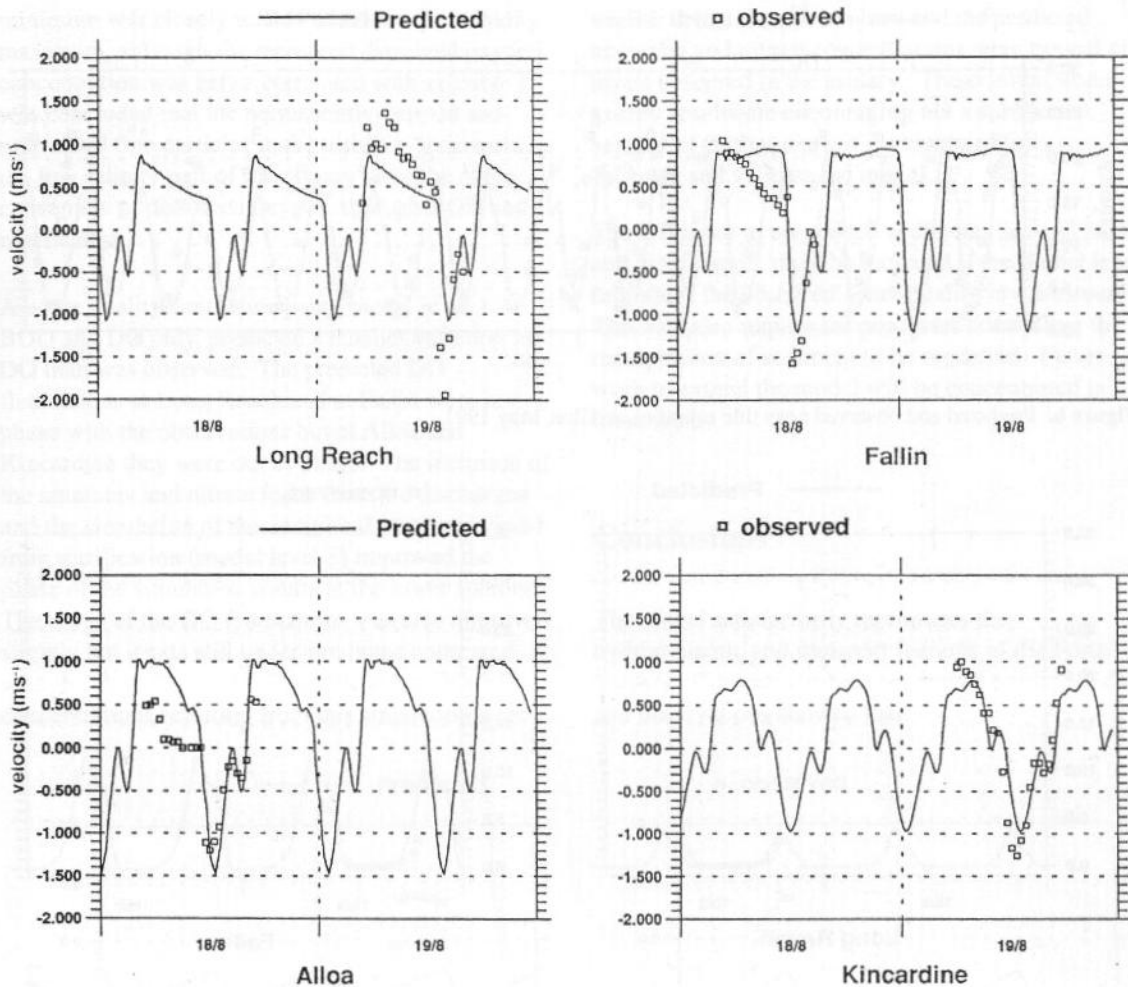
Figure 5. Predicted and observed velocities at Long Reach, Fallin, Alloa and Kincardine for August 18th and 19th August 1993.

water and the fluctuations in salinity in response to the distortions in the tidal regime. Figure 6 shows some of the difficulty found in matching predicted and observed salinities at Alloa. Typically, the salinity at high water or low water could be reproduced, but not both, and phase errors were present. The dispersion coefficients finally adopted were chosen to give the best overall agreement during a period of neap or spring tides. The agreement between predicted and observed salinities shown in Figure 7 is better than that at Alloa, although the comparison extends for only about 12 hours of a spring tide. Clearly, further work is required to fully calibrate and validate the transport model.

The water quality model

MIKE11 offers the user a choice of six levels of water quality model varying from a simple dissolved BOD and DO simulation to the inclusion of dissolved and particulate BOD, DO, bed/sediment

interactions and nitrogen processes. The ultimate aim of this project is to implement a water quality model simulating all these processes and including the advanced cohesive sediment transport module of MIKE11. However this is a very complex model requiring a considerable quantity of calibration and validation data. Early work to implement the water quality model has been focused on the lower model levels to assess the sensitivity of the results to the model's complexity and the associated user inputs.

In the water quality model dissolved oxygen is produced by photosynthesis of algae and plants. An additional source of oxygen is reaeration through the air/water interface. Oxygen consumption in the model is due to respiration, BOD (the degradation of organic matter), sediment oxygen demand and nitrification (the oxidation of nitrogen compounds). The oxygen balance is represented by a differential equation describing these processes. The reaction rates and temperature coefficients controlling the relation can be input by the user. In the model the water temperature is controlled by a balance between absorbed solar radiation and emitted heat radiation.
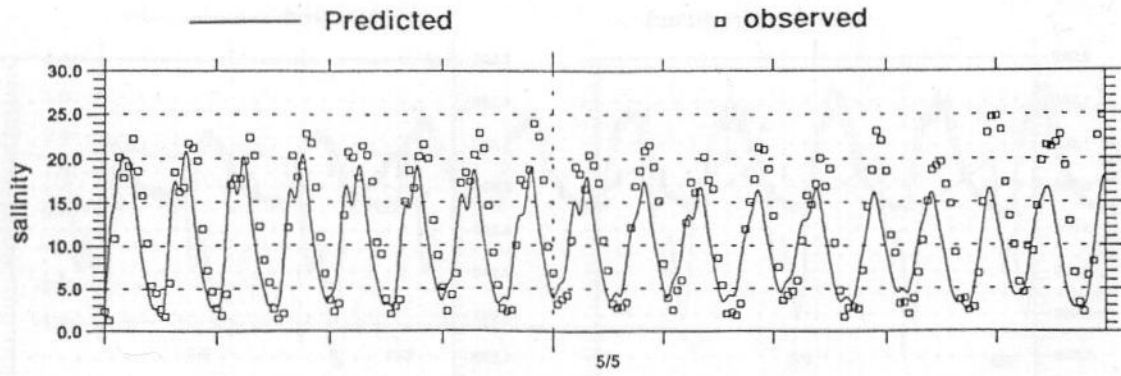
Figure 6. Predicted and observed neap tide salinities at Alloa, May 1991.
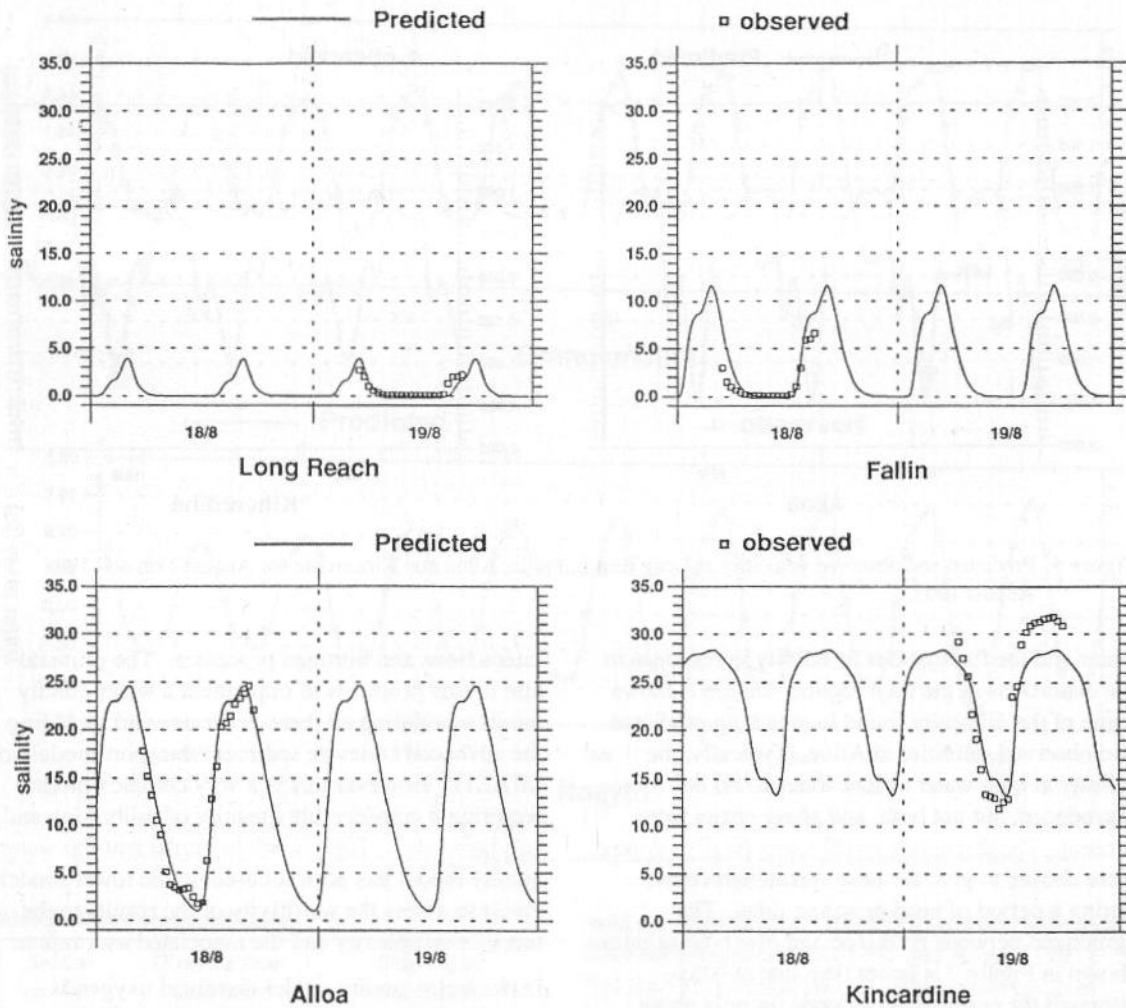
Figure 7. Predicted and observed spring tide salinities at Long Reach, Fallin, Alloa and Kincardine for 18th and 19th August 1993.

Calibration of the water quality module has been undertaken using the repeating spring tide simulation described in the previous section. The 1993 mean annual loads for all tributaries and significant discharges were input to the model. Predictions were compared with observations from four stations in the upper estuary on 18th and 19th

August 1993 (as for the velocity and salinity data already discussed). Predictions were also compared with data from the continuous water quality monitoring system at Alloa.

A discussion of aspects of the water quality data used for calibration is given in Dobson (1995). The extent and location of the dissolved oxygen

minimum was closely related to that of the turbidity maximum, although the measured dissolved oxygen concentration was better correlated with salinity. It was concluded that the permanently trapped and suspended fine particles in the turbidity maximum in the low salinity part of the estuary were the major consumers of dissolved oxygen, through BOD and nitrification.

A water quality simulation using model level 1, BOD and DO only, predicted a smaller variation in DO than was observed. The predicted DO fluctuations at Long Reach and at Fallin were in phase with the observations but at Alloa and Kincardine they were out of phase. The inclusion of the ammonia and nitrate loads from the discharges and the simulation of the additional oxygen demand from nitrification (model level 3) improved the phase of the simulation results at the lower stations. The range of the DO fluctuations was also improved slightly but it was still under-predicted compared with the data (Figure 8). The tidal mean DO concentrations resulting from this simulation were

similar to the observed values and the predicted ammonia and nitrate concentrations were typical of levels observed in the estuary. These initial water quality results are encouraging but a substantial amount of further work is necessary to fully calibrate and validate the model.

The influence of suspended sediment, through BOD and nitrification, must be included if the model is to reproduce the observed water quality in the estuary. This will also require the processes controlling the resuspension of sediment to be modelled. Future work to extend the model will be concentrated in these areas.

Conclusions

The model satisfactorily reproduces the hydrodynamic and transport features of the Forth Estuary. Comparison between model predictions and observations showed that:
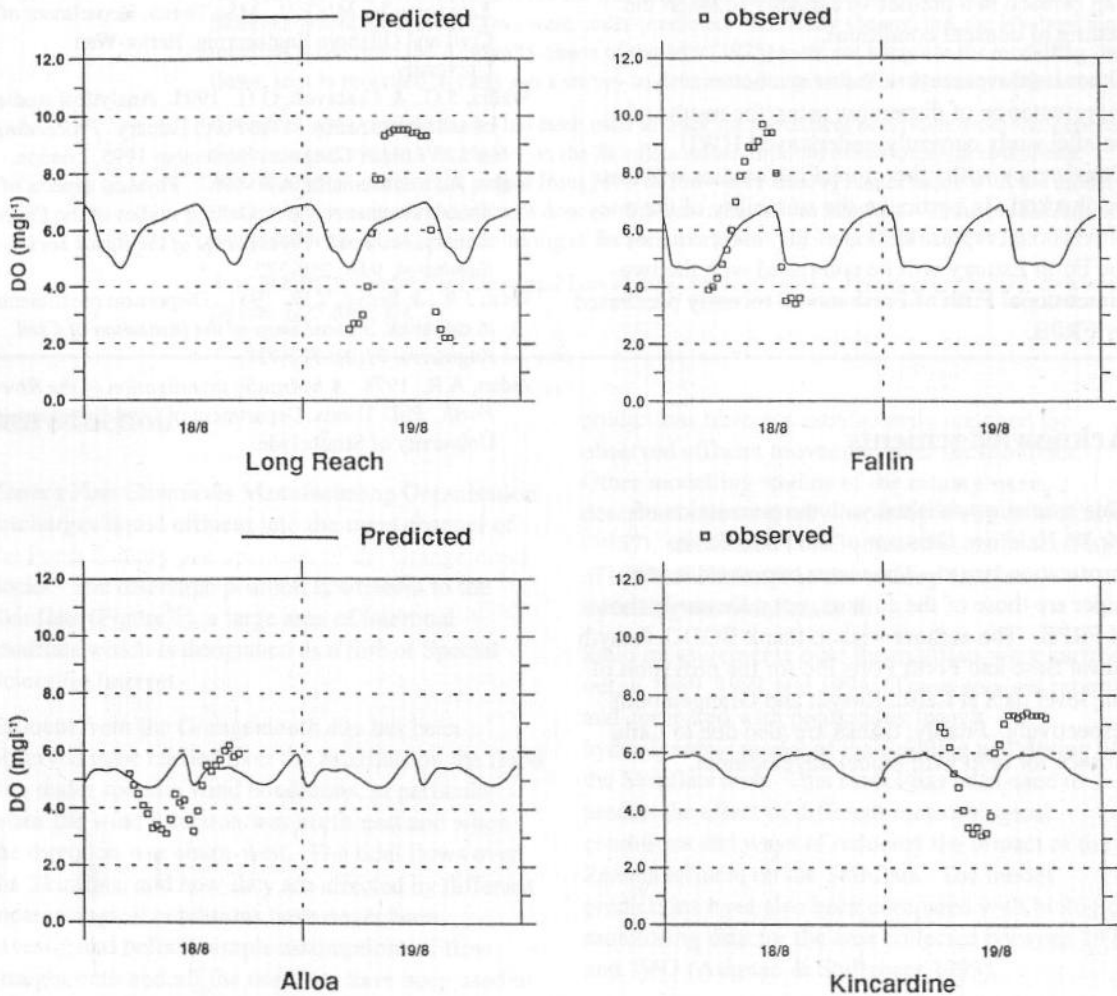
Figure 8. Predicted and observed dissolved oxygen at Long Reach, Fallin, Alloa and Kincardine on 18th and 19th August 1993.

- the predicted water levels reproduced the tidal response throughout the estuary, particularly in the upper reaches where distortion of the tidal curve is significant;

- the predicted velocities in the upper estuary agreed well with the magnitude and phase of the observed tidal velocity fluctuations;

- the predicted tidal variation of salinity gave good agreement with observations and demonstrated that the simulation of solute transport by the model was good;

- further work is required to improve the accuracy of the water quality predictions, particularly to simulate the effect of suspended sediments.

Further work

Further work will be directed at establishing a model suitable to FRPB for water quality management purposes. The ultimate aim is to obtain representative spring and neap tide simulations that can be used in a predictive capacity to assist the setting of consent conditions.

Other improvements will aim at a better representation of dispersion using the results of a parallel study currently underway at HWU. Consistency with other modelling studies will also be checked. In particular the suitability of the one-dimensional representation of the lower reaches of the Forth Estuary will be compared with the two-dimensional Firth of Forth model recently purchased by FRPB.

Acknowledgements

References

Balls, P.W., Brockie, N.J.W., Dobson, J.E., & Johnston, W. 1996. Dissolved oxygen and nitrification in the upper Forth Estuary during summer (1982-1992): patterns and trends. *Estuarine and Coastal Shelf Science, 42(1):* 117-134.

Danish Hydraulics Institute. 1992. *MIKE11 Reference Manual.* Danish Hydraulics Institute.

Dobson, J.E. 1997. The role of suspended solids in the dissolved oxygen budget of the Forth Estuary. *Coastal Zone Topics, 3: The estuaries of central Scotland,* 38-45.

FRPB. 1986. *A 1-D tidally-averaged water quality model for the Forth estuary.* Edinburgh, Forth River Purification Board.

FRPB. 1995. *River gauging stations annual data summary, 1994.* Edinburgh, Forth River Purification Board.

Griffiths, A.H. 1997. An overview of the quality status of the Forth estuary. *Coastal Zone Topics, 3: The estuaries of central Scotland,* 20-27.

HR Wallingford. 1994. *Firth of Forth water quality model - assessment of field data.* Oxford, HR Wallingford. (Report EX2950).

Nilssen, L. 1994. *Water quality modelling of the Forth Estuary using MIKE11.* MSc Thesis, Department of Civil and Offshore Engineering, Heriot-Watt University.

Wallis, S.G., & Graasvoll, O.H. 1995. Analytical studies of salinity intrusion in the Forth Estuary. *Proceedings of XXVI IAHR Congress,* September 1995, London.

Webb, A.J., & Metcalfe, A.P. 1987. Physical aspects of water movements and modelling studies of the Forth Estuary, Scotland. *Proceedings of the Royal Society of Edinburgh, 93B:* 259-272.

West, J.R., & Broyd, T.W. 1981. Dispersion coefficients in estuaries. *Proceedings of the Institution of Civil Engineers, 71(2):* 721-737.

Zidan, A.R. 1978. *A hydraulic investigation of the River Forth.* PhD Thesis, Department of Civil Engineering, University of Strathclyde.

Modelling tidal flows in the Forth Estuary and over the intertidal mudflats at Grangemouth

A.M. Riddle

A mathematical model has been developed to compute tidal flows in the Forth Estuary and in particular over the Skinflats, an area of intertidal mudflats. The model is based on the work of Leendertse (1967) with the addition of routines for the drying and wetting of the intertidal areas as described by Falconer & Chen (1991). The model covers the area from Rosyth upstream to Alloa and uses harmonic constants from the Admiralty tide tables to define the variation in surface height at these two positions. The surface height data are used as boundary condition data to run the model.

The model has been used to investigate the effect of different winds on the flows in the estuary and over the Skinflats. The results show a clockwise flow on the Skinflats when there is no wind or a wind with an easterly component, but an anti-clockwise circulation when the wind has a westerly component. In the main channel of the estuary the tidal flow is dominant and the wind has little influence on the water movement.

Field surveys over the Skinflats area were carried out by Brixham Environmental Laboratory in 1989, 1991 and 1994; data were collected using recording current meters, tracer dye, drogues and position fixing of the water front as it advanced over the Skinflats on the flood tide. The accuracy of the model was assessed by comparisons with these survey data. The results have shown that the model gives a good simulation of the measurements except at the landward edge of the Skinflats where the current flows were under-predicted. The study showed that the levels of the mudflats taken from the Admiralty charts of the area (1975) were not adequate for modelling the flows, so it is proposed to carry out a survey to determine an up to date bathymetry of the area.

A random walk particle model has been used to track the movement of effluent from the Zeneca discharge and to assess its impact on the Skinflats under different meteorological conditions. Meteorological data for the period from 1975 to 1984 were used in combination with the model predictions to estimate the effluent dose on different areas of the Skinflats. These predictions are compared with ecological monitoring of the area carried out between 1975 and 1992.

A.M. Riddle, Brixham Environmental Laboratory, Zeneca Limited, Freshwater Quarry, Brixham, Devon, TQ5 8BA, UK.

Introduction

Zeneca Fine Chemicals Manufacturing Organisation discharges liquid effluent into the main channel of the Forth Estuary just upstream of the Grangemouth docks. The discharge position is adjacent to the Skinflats (Figure 1), a large area of intertidal mudflats which is designated as a Site of Special Scientific Interest.

Effluent from the Grangemouth site has been observed to be carried over the mudflats on the flood tide under specific wind conditions, in particular when the wind direction was north-east and when the direction was south-west. The tidal flows over the Skinflats, and how they are affected by different meteorological conditions have never been investigated before; simple assumptions of flow straight onto and off the mudflats have been used in previous modelling studies (Riddle 1991) but

predictions have not satisfactorily matched the observed effluent movement over the mudflats. Other modelling studies of the estuary were described in a summary paper by Webb & Metcalfe (1987), and Clarke (1993) describes the modelling of sediment balance in the estuary and firth, including the Skinflats area.

Field measurements over the mudflats were carried out in 1989, 1991 and 1994. These data are reported and compared with predictions from a hydrodynamic model of the flooding and drying of the Skinflats area. This model has been used to predict the effect of different meteorological conditions and ways of reducing the impact of the Zeneca effluent on the Skinflats. The model predictions have also been compared with biological monitoring data for the area collected between 1975 and 1992 (Ashman & Shillabeer 1993).

Field survey measurements

In 1989 Recording Current Meter (RCM) measurements were carried out between 10th and 14th July at four positions as shown on Figure 1; these measurements were made with Valeport 208 RCMs which had been modified by the addition of a braking system to stop the rotor revolving when the area was dry. One meter failed but the other three operated successfully. Dye tracking using Rhodamine B, a red fluorescent dye, was carried out on 11th July in the area shown on Figure 1.
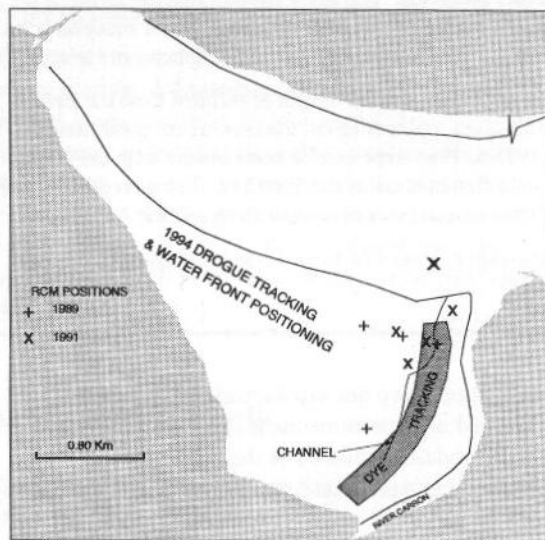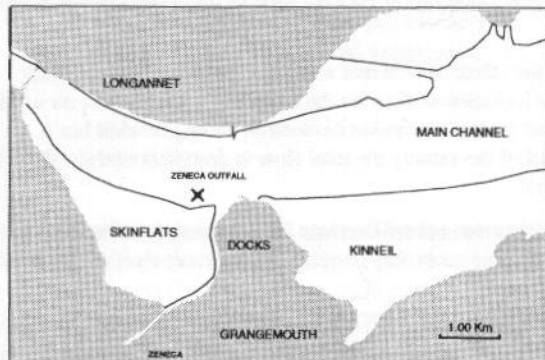
Figure 1. Skinflats area of the Forth Estuary. Location of field survey work.

On 31st July and 1st August 1991 further RCM measurements were carried out at an additional four positions as shown on Figure 1.

In 1994 drogue tracking was carried out over the Skinflats on the flood and ebb tides. This work was carried out on 25th, 26th and 27th June. In addition positioning of the water front over the Skinflats was carried out between 10:48 and 15:00 BST on the flood tide of 25th June. A Navstar XR4-G mobile differential global position fixing system operated from a hovercraft was used in tracking the water front positions; the accuracy of the position fixing was within ± 10 m.

Description of the hydrodynamic model

A two-dimensional (horizontal grid) model has been used to compute depth-averaged tidal and residual currents and water surface elevations for the Forth Estuary from Alloa downstream to the Forth road bridges (Figure 2). Output from the hydrodynamic model was used to set up datafiles for a water quality model covering the same geographical area.
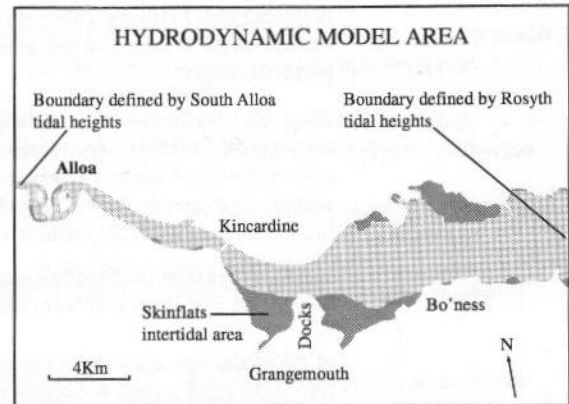
Figure 2. Modelled area.

To perform the calculations, data are required on the water depth and bottom friction over the whole of the model area and on the rise and fall of the water surface along the boundaries of the model (Alloa and Rosyth). In order to define these data, a grid (50 m square) was placed over the area of interest and the information prepared for each grid intersection. The water depth data were obtained from Admiralty charts of the area and the boundary data were predicted from data on the harmonic constants for Rosyth and Alloa published in the Admiralty tide tables (Hydrographer of the Navy 1992); an example of the water surface variations is shown on Figure 3. The predicted levels at Alloa do not accurately reproduce observed water levels; this has been confirmed by comparison with a short-term tide gauge record from South Alloa (Figure 3). Improved harmonic constants or a tide gauge record from Alloa would be needed to give a better specification of the model boundary conditions, however, the water level differences are significant only at low water, and so do not affect the flooding of the Skinflats area, which occurs only after half flood.

The water movement is described by the equations of momentum and continuity given below which are taken from the model documentation (Leendertse 1967).

ROSYTH TIDAL HEIGHTS

SOUTH ALLOA TIDAL HEIGHTS (PREDICTED)

SOUTH ALLOA TIDAL HEIGHTS (TIDE GAUGE DATA 1988)
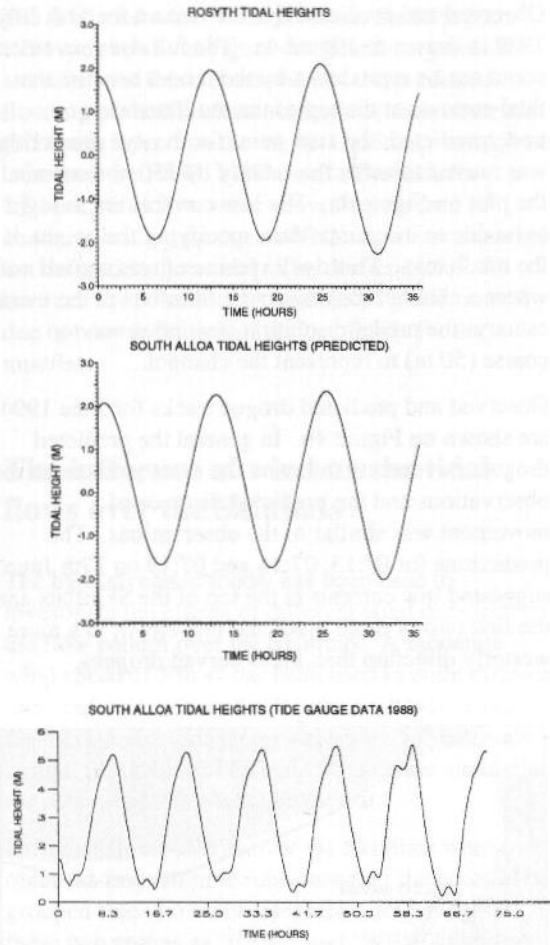
Figure 3. Water surface elevations at Alloa and Rosyth.

$$\frac{\partial U}{\partial t} + U.\frac{\partial U}{\partial x} + V.\frac{\partial U}{\partial y} - f.V + g.\frac{\partial \zeta}{\partial x} + \frac{g.U.\sqrt{U^2+V^2}}{C^2.(h+\zeta)} = F_x$$

$$\frac{\partial V}{\partial t} + U.\frac{\partial V}{\partial x} + V.\frac{\partial V}{\partial y} + f.U + g.\frac{\partial \zeta}{\partial y} + \frac{g.V.\sqrt{U^2+V^2}}{C^2.(h+\zeta)} = F_y$$

$$\frac{\partial \zeta}{\partial t} + \frac{\partial[(h+\zeta).U]}{\partial x} + \frac{\partial[(h+\zeta).V]}{\partial y} = 0$$

where x, y and t are the co-ordinate directions east/west, north/south and time respectively, with U and V the currents in the x and y directions. The water depth, h, is measured relative to mean tide level and the water surface elevation above or

below mean tide. The friction is parameterised in terms of the Chezy coefficient, C, and external stresses are introduced through the Fx and Fy terms. Parameters f and g are the Coriolis coefficient and the acceleration due to gravity.

The external stress terms are used to introduce the effect of wind on the water movement, using the method described by Falconer (1986):

$$F_x = \frac{k.W_e.W}{(h+\zeta)} \quad ; \quad F_y = \frac{k.W_n.W}{(h+\zeta)}$$

where k is the wind friction factor, We the wind speed (m s^{-1} and Wn are the east and north components of the wind speed (m s^{-1}).

These equations cannot be solved analytically so a numerical technique is used: the equations are rewritten in finite difference form for solution. Full details of the development of the finite difference equations are given by Leendertse (1967) together with information on the approximations used, the stability of the numerical scheme and full details of the computational formulae. These finite difference equations are then solved in a time-stepping manner to calculate new values for U, V and ζ.

A drying/wetting routine has been added to simulate flows in areas where mudbanks are exposed for a portion of the tide. The method used to determine whether a grid cell is dry or wet is given by Falconer & Chen (1991).

Model predictions of survey conditions

The hydrodynamic model was used to compute the tidal flows in a section of the Forth Estuary from Rosyth to Alloa (Figure 2). Table 1 shows the measured and predicted peak current speeds (m s^{-1}) and duration of wetting (h) at the 1989 and 1991 RCM survey positions. These positions were on the lower portion of the Skinflats and show a good agreement between the observed and predicted currents, but also indicate that the wetting time is generally overpredicted.

Table 1. Measured and predicted current speeds and duration of wetting at recorded current meter survey positions in 1989 and 1991.

Year Position		1989			1991			
		P1	P3	P4	P1	P2	P3	P4
Peak current (m s^{-1})	Measured	0.25	0.32	0.15	0.44	0.38	0.40	0.30
	Predicted	0.30	0.35	0.18	0.44	0.34	0.22	0.25
Duration of wetting (h)	Measured	4.2	4.5	2.0	3.5	3.3	2.7	2.3
	Predicted	5.4	4.5	3.0	4.4	3.8	3.2	3.3

Figure 4. Comparisons between measured and predicted data: (a) dye tracking, (b) drogue tracking, (c) water front positions.

(a) Observed and predicted dye tracks
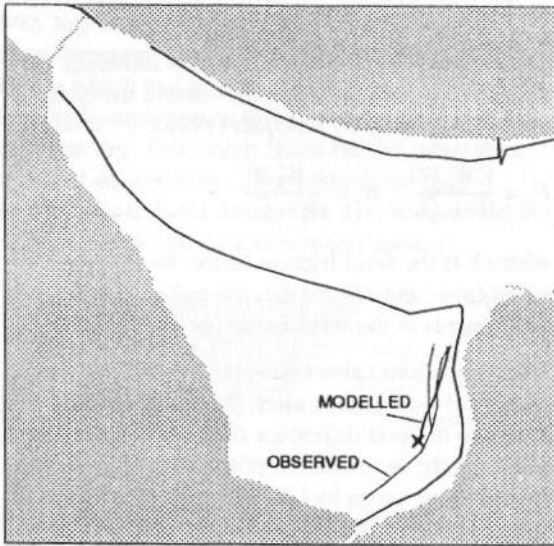
Observed and predicted dye movement for 11th July 1989 is shown on Figure 4a. The full dye movement could not be reproduced by the model because the tidal currents at the top of the mudflats were underpredicted; the start point for the dye prediction was moved towards the estuary by 150 m to obtain the plot on Figure 4a. The low currents are thought to be due to inaccurate data specifying the height of the mudbanks. This dye experiment was carried out where a channel runs down the Skinflats to the main estuary; the model resolution was, however, too coarse (50 m) to represent the channel.
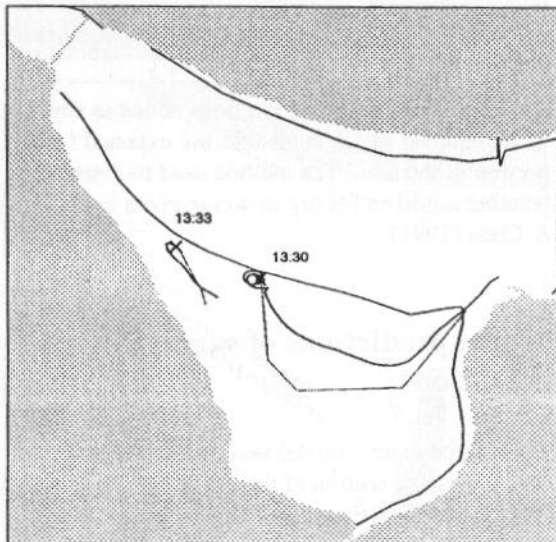
Observed and predicted drogue tracks for June 1994 are shown on Figure 4b. In general the predicted drogue movements followed the same patterns as the observations and the predicted distance of movement was similar to the observations. The predictions for 07:13, 07:15 and 07:19 on 27th June suggested low currents at the top of the Skinflats and the first two of these predicted movement in a more westerly direction than the observed drogues.

(b) Observed and predicted drogue movements

(c) Observed and predicted flooding of the skinflats
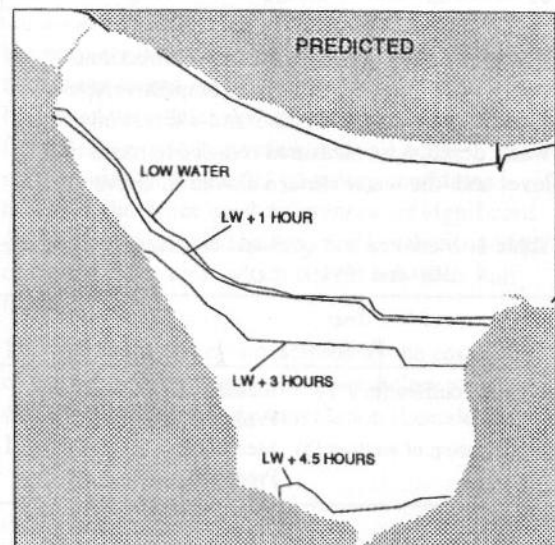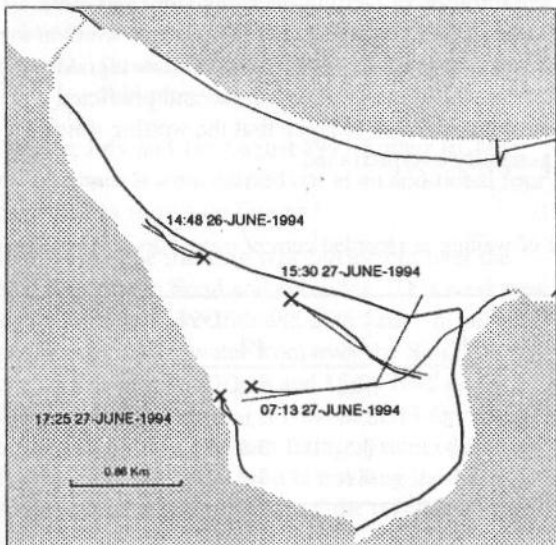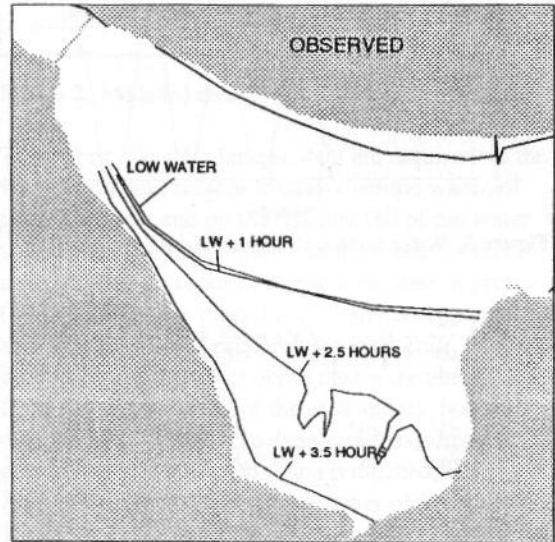
The predicted water front positions for 25th June 1994 are shown on Figure 4c. The front positions are similar to those observed, but the predicted flooding of the Skinflats occurs later than observed (0.5 hours later than the 13:40-13:53 data and 1 hour later than the 14:47-14:59 data). The data for 2.5 hours after low water show the presence of channels leading up the mudflats; however these are not defined in the model. The discrepancies between the observations and model predictions is due to poor definition of the bed levels for the mudflats.

The influence of wind on the tidal flows over the Skinflats

The hydrodynamic model has been used to investigate the effects of different wind direction on the flow pattern over the Skinflats. A moderate wind speed of 5 m s^{-1} has been used in eight different model simulations with the wind directions starting from north and then incrementing by 45° intervals around the compass. In addition a model simulation for calm conditions was carried out.

Different flow patterns over the Skinflats were obtained from all nine runs, however these could be grouped into two main categories. Referring to these two groups as 'EAST' and 'WEST' the flow circulation is anti-clockwise and clockwise respectively. The 1994 drogue tracking data shows this clockwise circulation under westerly wind conditions. Figure 5 shows the main features of the flow patterns for the flooding tide, when effluent could be carried over the Skinflats. The meteorological conditions for the two groups consisted of:

EAST calm conditions, winds with an easterly component, southerly winds

WEST winds with a westerly component, northerly winds

Meteorological data from Edinburgh Airport for the ten-year period 1975 to 1984 shows that on annual average the 'EAST' group may be expected for 47% of the year, including all the low wind speed (<2.5 m s^{-1}) and calm conditions and the 'WEST' group for 53% of the year.

Description of the water quality model

Movement and dispersion of the Zeneca effluent in the estuary has been simulated using a particle tracking model developed at the Brixham
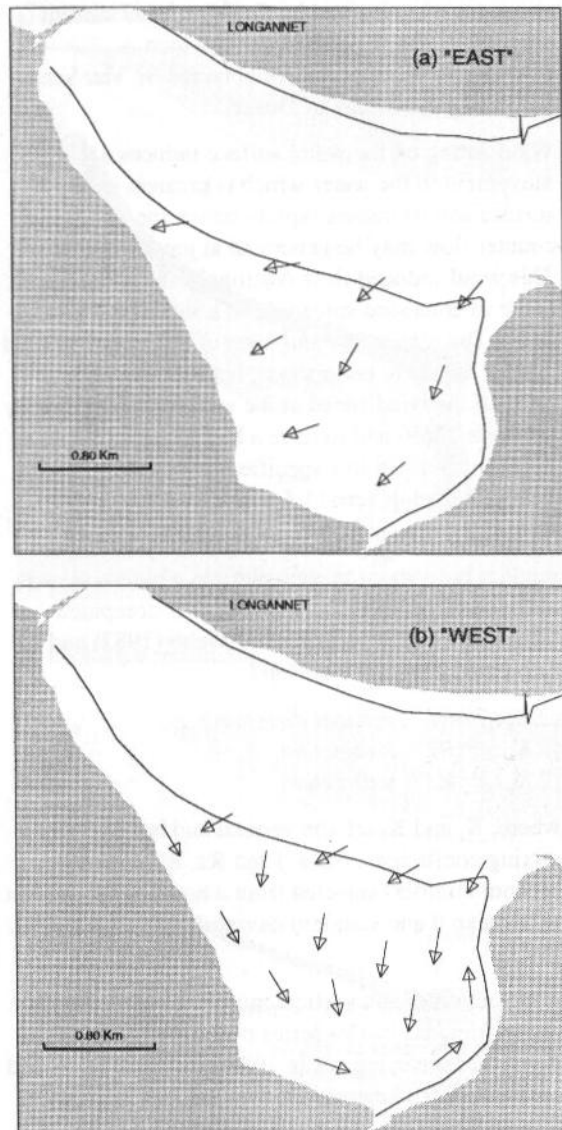
Figure 5. Flood tide flows over Skinflats on easterly and westerly winds.

Environmental Laboratory. The discharge is through a diffuser system on the bed of the estuary, and buoyancy brings the effluent to the estuary surface, entraining water during its rise. The initial dilution gained during this process is modelled using the work of Abraham (1963) for dilution in stagnant water together with a correction for flowing water due to Agg & Wakeford (1972). Particles are spread evenly over the initial field volume of the effluent on each time-step of the model.

The model then uses tidal data, generated by the hydrodynamic model described above, to compute the advective movement of the effluent using a time-step small enough to ensure each particle does not move more than half a grid square. The particle model is three-dimensional and so needs the vertical variation in the current to be specified. This is represented by a power law with mean flow equal to the predicted hydrodynamic current; the power law

exponent was obtained by fitting to local current profiles, giving a value of 0.192 which is comparable with the values obtained by Van Veen (1938) for the Straits of Dover.

Wind acting on the water surface induces a movement in the water which is greatest at the surface and decreases rapidly below the surface; a counter flow may be generated at greater depth. This wind-induced flow is strongly sheared and can result in enhanced spreading of a surface effluent field. The magnitude and form of this wind-induced current is poorly understood, but may be taken as 1.4% of the wind speed at the water surface (Dooley & Steele 1969) and to have a logarithmic profile in the vertical down to a specified depth where the current becomes zero (1.5 m in this study).

The spread of the patch is computed by adding a random movement to each particle which is related to the local mixing; this movement is computed using the method described by Webb (1982) and is calculated for each timestep t_s:

$(2.K_z.t_s)^{0.5}.R1$ *vertical direction*
$(2.K_y.t_s)^{0.5}.R2$ *x-direction*
$(2.K_y.t_s)^{0.5}.R3$ *y-direction*

where, K_z and K_y are the vertical and horizontal mixing coefficients ($m^2 s^{-1}$) and R1, R2, R3 are random numbers selected from a normal distribution with mean 0 and standard deviation 1 (Bjerken *et al.* 1993).

The horizontal and vertical mixing coefficients have been estimated from a series of dye tracking experiments carried out in 1986, 1987 and 1988, and are assumed to be constant over the whole model area and constant in time. Calculated values of K_y ranged from 0.05 to 0.85 $m^2 s^{-1}$ and of K_z from 0.0008 to 0.00473 $m^2 s^{-1}$ (Riddle 1991). A K_y of 0.1 $m^2 s^{-1}$ and a K_z of 0.0008 $m^2 s^{-1}$ have been selected for model predictions to simulate the poor mixing conditions.

The concentration of the effluent in the modelled area is determined using a counting grid; the number of particles in a grid square and over the depth interval from the surface down to a specified depth, d_c, are counted and converted to a concentration by:

$$C = \frac{N_p.P_{mass}}{dx^2.d_c}$$

where, C is the concentration, N_p the number of particles counted, P_{mass} the mass of effluent that each particle represents and dx is the horizontal grid size of the counting grid.

The model has been used to predict the movement and dispersion of the Zeneca effluent in the Forth Estuary for the two main flow patterns over the Skinflats.

Effluent movement

The effluent discharges continuously and has been given a nominal concentration of 100 so that concentrations in the estuary can be plotted as a percentage of the undiluted effluent concentration. Model simulations of the effluent discharge for the EAST and WEST flow patterns show there is a different distribution of effluent over the Skinflats area. Figure 6 shows all the areas where the effluent is predicted to reach over a whole tidal cycle and the maximum concentrations that are expected (NB Figure 6 does not show an instantaneous position of the effluent plume).

(a) "East" flow conditions

0.86 Km

(b) "West" flow conditions

BASE EFFLUENT (%)		
ABOVE	0.10	
0.05 -	0.10	
0.01 -	0.05	
BELOW	0.01	
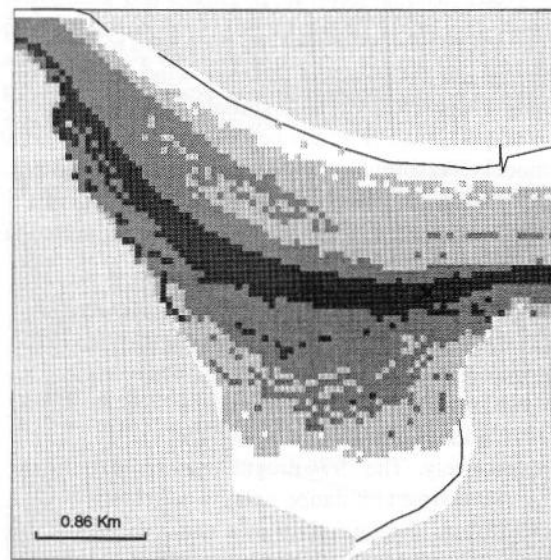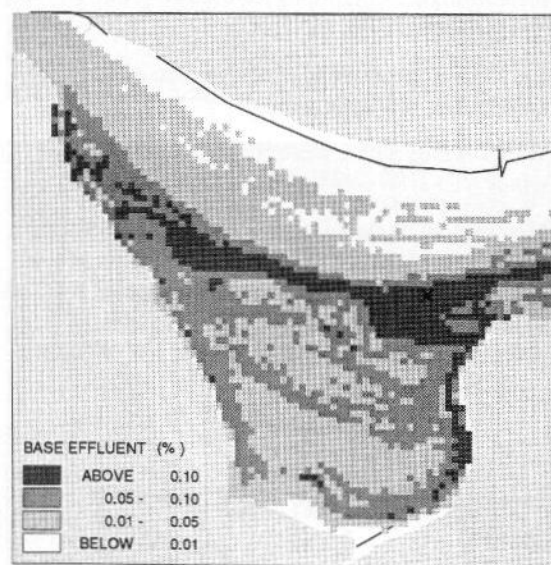
Figure 6. Areas affected by effluent during a whole tidal cycle for (a) easterly wind and calm conditions and (b) westerly wind conditions.

EAST   Diluted effluent moves up over the Skinflats area and extends over approximately 70% of the mudflat area. Concentrations are generally below 0.1%.

WEST   Effluent is carried over the whole of the Skinflats. Concentrations are generally below 0.1%, except along the eastern side of the area where this concentration is exceeded. Concentrations between 0.05 and 0.1% are moved up to the top of the mudflat area.

Where effluent is carried up over the Skinflats it is fully mixed over the water depth.

Impacted areas on the Skinflats

The model predicts the highest effluent concentrations (>0.1%) will occur along the edge of the Skinflats adjacent to the main channel of the estuary and that this area will be subject to these concentrations on each flood tide. The concentration predictions for the two flow patterns have been combined with the annual average wind speed, direction and frequency of occurrence data to estimate which areas of the Skinflats are subjected to the greatest effluent doses (integrated effect of concentration times exposure time); these are shown qualitatively on Figure 7a.

Results from ecological monitoring on the Skinflats (Ashman & Shillabeer 1993) show that the benthic community has been impacted along the edge of the mudflats adjacent to the main channel of the estuary with the community being sparse. On the eastern third of the Skinflats area the monitoring between 1975 and 1992 has shown a variable picture, with intermediate and diverse communities. At the western end of the Skinflats the distribution of fauna has been consistent with time and generally defined as an intermediate community, however, at the channel edge the community was sparse. Figure 7b shows a summary of the ecological monitoring.

Comparison of Figures 7a and 7b shows a good correlation between the predicted dose and the findings of the ecological monitoring. The model therefore forms a useful tool for the evaluation of effects of different modifications to the discharge, such as the planned biological treatment plant or modifications to the diffuser system.

Summary and conclusions

The liquid effluent outfall from Zeneca Fine Chemicals Manufacturing Organisation,

(a) Effluent dose
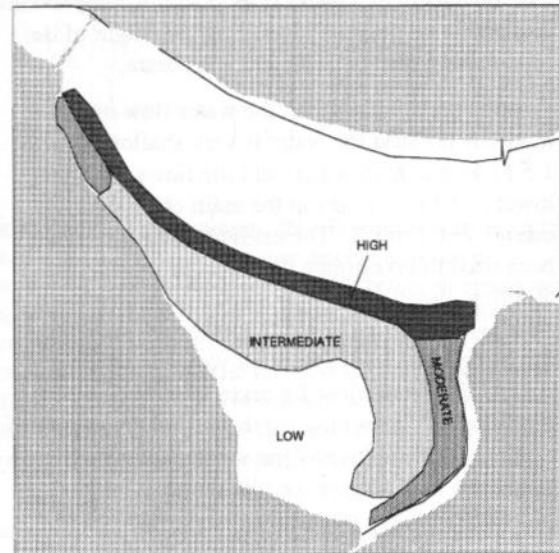
(b) Ecological monitoring
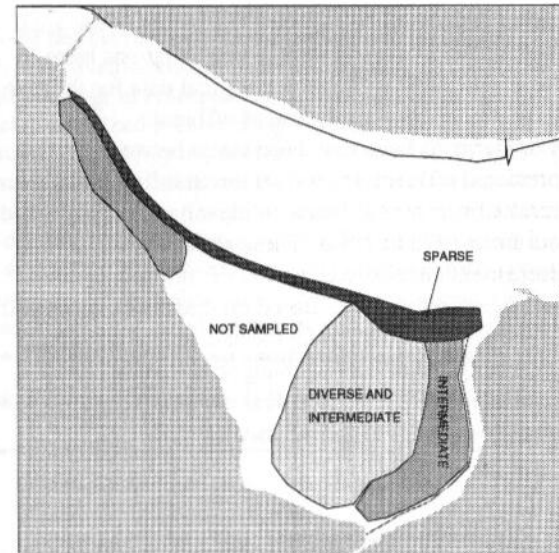
Figure 7. Effluent dose and ecological impact.

Grangemouth, is situated adjacent to the Skinflats intertidal mudflats in the Forth Estuary (Figure 1). The mudflats are of considerable ecological significance and are designated a Site of Special Scientific Interest.

Data from surveys in 1989, 1991 and 1994 have been used to assess the validity of a hydrodynamic model for predicting the water flows over the Skinflats under different tidal and wind conditions. The comparisons show that the model reproduces the observed flow patterns for different meteorological conditions, although in some cases the current speed was under-predicted, particularly near the landward margins of the mudflats. Comparisons between measured and predicted

currents and drogue movements were good, but the dye movement and water front position comparisons indicated that the data specifying the height of the mudbanks were not sufficiently accurate.

Winds significantly affect the water flow over the mudflats because the water is very shallow (0.5-1.5 m deep at high water) and the flows are much lower (~0.3 m s^{-1}) than in the main channel of the estuary (~1.4 m s^{-1}). The mathematical model has been used to investigate the effect of winds from different directions. From these results two main flow patterns over the Skinflats were determined, revealing a clockwise flow for westerly winds and an anti-clockwise flow for easterly winds or calm conditions. Meteorological data of the frequency of occurrence of different wind speeds and directions have been used to give the likelihood of each circulation pattern occurring.

Modelling predicts that during calm and easterly winds diluted effluent is carried over approximately 70% of the Skinflats area, and that during westerly winds effluent is carried over the whole of the area. These predicted concentration distributions have been combined with meteorological data for the area to produce a predicted dose of effluent.
Comparisons have then been made between the predicted effluent doses over the Skinflats and the results from annual fauna monitoring surveys carried out from 1975 to 1992. These show a good correspondence between areas of 'impacted' fauna and the effluent dose. Based on these comparisons it is believed that the model forms a useful tool for predicting the effects of changes to the discharge, such as the planned biological effluent treatment plant or changes to the diffuser system.

Acknowledgements

References

Abraham, G. 1963. *Jet diffusion in a stagnant ambient fluid.* Delft Hydraulics Laboratory, Publication No. 29.

Agg, A.R., & Wakeford, A.C. 1972. Field studies of jet dilution of sewage at sea outfalls. *Journal of the Institute of Public Health Engineers, V 71:* 26-153.

Ashman, C.M., & Shillabeer, N. 1993. *A review of the Grangemouth site ecological monitoring data 1971-1992.* Brixham, Brixham Environmental Laboratory. (Report BL5034/B, December 1993).

Bjerken, S., Mathisen, J-P., Mork, G., Slagstad, D., & Thendrup, A. 1993. *M&M System for Modelling and Monitoring of offshore discharge water.* Oceanographic Company of Norway AS. (Report No. OCN R-93036, June 1993).

Clarke, S. 1993. *A review of the distribution of sediments in the Estuary and the Firth of Forth.* Unit of Coastal and Estuarine Studies, University College of North Wales, Marine Science Laboratories, Menai Bridge, Gwynedd. (Report U93-7).

Dooley, H.D., & Steele, J.H. 1969. Wind driven currents near a coast. *Deutsche Hydrographische Zeitschrift,* 22 (5): 213-223.

Falconer, R.A. 1986. *A two-dimensional mathematical model study of the nitrate levels in an inland natural basin.* International conference on Water Quality Modelling in the Inland Natural Environment, Bournmouth, England, June 1986.

Falconer, R.A., & Chen, Y. 1991. An improved representation of flooding and drying and wind stress effects in a two-dimensional tidal numerical model. *Proceedings of the Institution of Civil Engineers, 91:* 659-678.

Hydrographer of the Navy. 1992. *Admiralty Tide Tables, Volume 1: European Waters.* Hydrographer of the Navy.

Leendertse, J.J. 1967. *Aspects of a computational model for long-period water-wave propagation.* Santa Monica, California, United States Air Force Project. Memorandum RN-5294-PR (May 1969).

Riddle, A.M. 1991. Spill model for the protection of the Forth Estuary. *In: Computer modelling in the environmental sciences,* ed. by D.G. Farmer & M.J. Rycroft. Clarendon Press.

Van Veen, J. 1938. Water Movements in the Straits of Dover. *Journal Conseil Permanent International pour l'Exploration de la Mer, 13:* 7-38.

Webb, A.J. 1982. *A Random Walk Model of the dispersion of caesium-137 in the Irish Sea.* MSc Thesis, University of Wales.

Webb, A.J., & Metcalf, A.P. 1987. Physical aspects, water movements and modelling studies of the Forth Estuary. *In: The natural environment of the Estuary and Firth of Forth: Proceedings of the Royal Society of Edinburgh,* 93B: 259-272.

Problems of charting the upper Forth Estuary (summary)

J. McManus & R.W. Duck

Water is perhaps the most important facet of any estuarine system. Its composition determines the areas within which organisms thrive or struggle to exist; its behaviour determines whether sediment is eroded from or deposited within the inlet; its depth determines whether an estuary can be used for navigation thus encouraging development of human settlements. The Forth Estuary is tidal and is navigable to small leisure and fishing boats from Stirling seawards. With a view to possible redevelopment of a trading port at Alloa, a bathymetric survey of the reach seawards to the Kincardine Bridge has been carried out. Although the use of charts of water depth is widespread among estuarine researchers, if only as maps of tidal flats and sandbanks, few have an awareness of the field data acquisition and factors taken into account in order to construct these documents.

Fundamental to chart making is a knowledge of the changing height of the water surface throughout the tide. As a tide penetrates an estuary it has the form of a wave which may take over an hour to pass from the seaward limit to the head. As it does so the water level reached at both high and low tide rises landward, the latter more rapidly than the former. Thus, it is vital that water level gauging is continuous during surveys, with boards or recorders surveyed to an appropriate datum. This will allow for the peculiarities such as the 'Lackie' tide (with double high and low water) of the upper Forth to be noted as routine. Whereas formerly the depth data used were derived from lead-lining, today a range of echosounding devices are available, with recorded traces providing continuous plots of the bed position along traverses. The detail and reliability of the resultant chart are partly determined by the spacing of the traverses. In open waters 100 m may suffice, but in the narrow waters of the upper Forth a 25 m interval was adopted for the 7 km reach under examination. Position fixing, formerly achieved by dead reckoning or sextant, was by distance-distance radio techniques, which are more precise than satellite navigation methods currently available. Over 300 traverses were run, principally across the estuary, but some interlinking controls were plotted along the channel. Ships with up to 5 m draft could use the port of Alloa for trading purposes, provided that they could pass beneath the Kincardine Bridge, which no longer swings open to encourage upstream passage of vessels.

J. McManus & R.W. Duck, Department of Geology, University of St Andrews, St Andrews, UK.

An overview of the quality status of the Forth Estuary

A.H. Griffiths

The Forth Estuary and its catchment, located on the east coast of Scotland, has been a focus for industrial and commercial activity for many decades. With 28% of the population resident in 5.7% of the total land area for Scotland, the pressure for development whether it be for business, leisure, housing or whatever is present and is a strong challenge to regulatory agencies to have in place effective management controls to ensure sustainable development and the proper protection of the environment, including nature conservation interests.

This presentation seeks to give, from a regulator's perspective, an overview of the quality of the Forth Estuary in terms described in the Department of the Environment's Estuarine Classification scheme. This scheme incorporates chemical, biological and aesthetic criteria which are then combined in order to allow an overall quality classification for a particular area.

In particular the major factors influencing overall quality in the Forth Estuary are described together with details of recent and past improvements to water quality, faunal and sedimentary environments.

A.H. Griffiths, Forth River Purification Board, Clearwater House, Avenue North, Riccarton, Edinburgh EH14 4AP, UK.

Introduction

Previous assessments of the overall quality status of the Forth Estuary have emphasised the importance of it as a resource for leisure and recreation, fishing, shipping, nature conservation and the disposal of municipal and industrial effluents (see Collett (1972); Leatherland (1987)). They have also highlighted that it requires protection as well as improvement, in order that the legitimate uses can continue.

Since the most recent of these overall assessments in 1985 a number of significant improvements and changes, especially in the disposal of municipal and industrial effluents, have taken place and resulted in improvements in the overall quality of the estuary. This paper describes recent improvements that have taken place around the Forth Estuary, quantifies the environmental changes and provides an overview of the overall quality status of the system.

Quality assessment - classification system

The quantitative overall assessment of estuarine quality has been carried out using the Department of the Environment's (DoE) Estuarine Classification Scheme adopted by Scottish Office Environment Department (SOEnD), the Association of Directors and River Inspectors (ADRIS) and hence the River Purification Authorities.

The water quality classification of estuaries is based on the recommendations of the final report of the Classification of Estuaries Working Party which reported to the DoE/National Water Council's Standing Technical Advisory Committee on Water Quality. A zone of estuary is classified according to the number of points that are allocated based on aesthetic, chemical and biological criteria. The scheme provides an overall quality classification as one of four possible classes: class A (good), class B (fair), class C (poor) or class D (bad). Full details of the scheme are shown in Appendix A.

In the Forth catchment estuarine areas are defined as those tidal waters upstream of grid reference NT 314000 plus the estuary of the River Tyne. Waters to the east of grid reference NT 314000 are classified as coastal.

The annual classification results for the Forth Estuary between 1989 and 1994 are shown in Table 1. The results show that over the period there has been a progressive improvement in overall quality. The reasons for improvements are discussed in detail in the following sections.

Inputs from direct discharge

The Forth Estuary and its tributary estuaries receive significant inputs from municipal and industrial discharges. The traditional measure used to assess the pollution potential of discharges has been the

Table 1. Quality status for the Forth Estuary and its tributary estuaries.

	1989	1990	1991	1992	1993	1994
			% of total estuarine area			
Class A	31.6	32.9	32.2	32.9	43.3	44.4
Class B	45.1	44.3	45.1	47.0	36.2	40.2
Class C	23.0	22.5	22.4	19.8	20.2	15.1
Class D	0.3	0.3	0.3	0.3	0.3	0.3

Total estuarine area in the Forth catchment is 87.0 km². Total area of the Forth Estuary is 85.4km².

biochemical oxygen demand (BOD). Expressed in terms of the total mean annual BOD loads, the loads for the period 1983 to 1993 which are shown in Figure 1 demonstrate there has been a significant overall reduction.

The commissioning of new treatment facilities at several sewage treatment works (STW), similar improvements in treatment facilities at industrial sites (see Table 2) and the implementation of waste minimisation schemes has brought about this overall reduction in organic loads, as well as similar reductions in other potentially polluting substances. The most significant of these reductions, in terms of potential oxygen demand (BOD), has been the improvements at Quest International's effluent discharge located at Alloa, which prior to treatment contributed over 70% of the oxygen demand load to the estuary.

Aesthetic assessment

Historically the presence of untreated sewage discharges around the shores of the estuary has
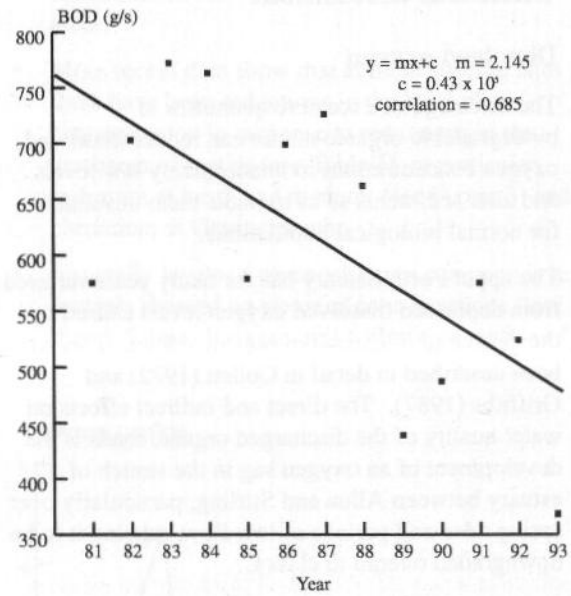
Figure 1. Total mean annual biochemical oxygen demand (BOD) load to the Forth Estuary, 1981-1993.

Table 2. Principal changes in municipal and industrial effluent treatment facilities between 1987 and 1995.

Site	Nature of improvement	Completion date
Stirling STW	Secondary treatment	1987
Bo'ness STW	Long sea outfall and primary treatment	1992
South Queensferry STW	Long sea outfall and preliminary treatment	1992
Alloa STW	Secondary treatment	1993
Ironmill Bay STW	Long sea outfall and secondary treatment	1993
Grangemouth West	Untreated discharge diverted to Falkirk STW for secondary treatment	1993
Cambus Distillery	Site closed	1993
Limekilns STW	Septic tanks and long sea outfall	1994
BP Refinery	Process water biological treatment	1994
BP Chemicals	In plant works. Wet oxidation and steam stripper units installed	
Weir Paper	Biological treatment	1995
	Sea outfall	1994
Torryburn	Reed-bed treatment of sewage	1995
Quest International	Biological treatment	1995
Zeneca	Source control of red-list substances (Hg, HCB, TCB)	
	Containment facilities	1994
	Biological treatment	Under construction

resulted in extensive fouling of the shoreline. The commissioning of municipal STW treatment facilities and long sea outfalls, in particular, at Ironmill Bay, Limekilns, South Queensferry and Bo'ness has significantly improved the shorelines adjacent to these schemes and has resulted in the upgrading of areas of the estuary off Bo'ness from class C to B or class B to A.

Chemical assessment

Dissolved oxygen

The discharge of excessive quantities of biodegradable organic matter can reduce dissolved oxygen concentrations to unacceptably low levels and alter sediments so as to make them unsuitable for normal biological populations.

The upper Forth Estuary has for many years suffered from depressed dissolved oxygen levels caused by the discharge of excessive organic matter. This has been described in detail in Collett (1972) and Griffiths (1987). The direct and indirect effects on water quality of the discharged organic loads is the development of an oxygen sag in the stretch of estuary between Alloa and Stirling, particularly over spring tides and periods of low flow, causing it to be downgraded overall to class C.

In response to the overall reduction in organic inputs the trend in dissolved oxygen levels in the estuary has been one of progressive improvement since 1957 when surveys commenced (see Figure 2). Recently the rate of improvement has slowed, the possible

reasons for this are discussed in more detail in Balls *et al.* (in press).

Nutrients

In a UK context the overall nutrient concentrations in the feeder rivers and in the Forth Estuary are low (Jones 1982).

Data on the concentration of nutrients in the feeder rivers and the Forth Estuary are given in FRPB (1993a). These data show that ammonia concentrations are well below levels which could cause a breach of the Environmental Quality Standard (EQS) for unionised ammonia. In addition nitrate concentrations are, for a UK estuary, comparatively low and in the winter months strongly correlated with salinity, reflecting the largely riverine source of this nutrient. Orthophosphate is lost from solution to the suspended particulate matter in the upper reaches of the estuary between Stirling and Alloa. Dobson (1995) discusses the behaviour of ammonia and the significance of the occurrence of nitrification in more detail.

No excessive algal growths or downgrading of areas of the estuary are caused by the current nutrient salt concentrations.

Persistent, toxic or tainting substances

The UK Government agreed at the second Intergovernmental Conference in 1987 to reduce the North Sea inputs of certain substances that are persistent, toxic or liable to bioaccumulate by 50%
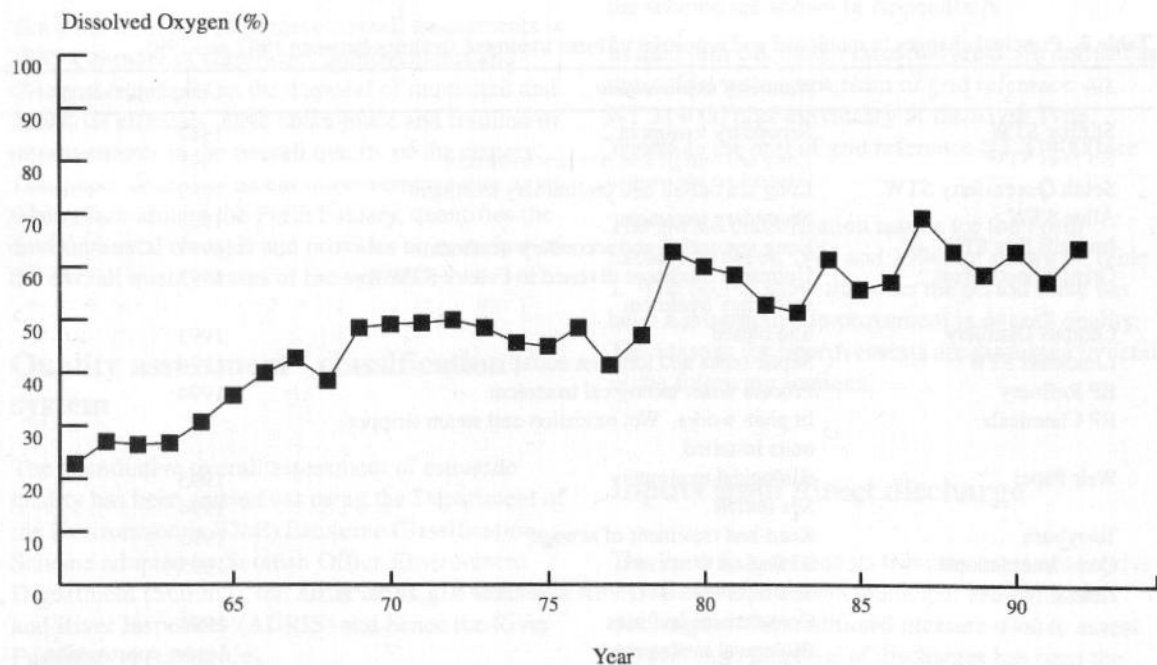
Figure 2. Average summer DO (% saturation) in the upper Forth Estuary.

between 1985 and 1995. Since 1985, after the reduction and minimisation of the point source discharges of these hazardous substances, substantial reductions have been recorded. The reductions in total inputs between 1985 and 1994 for selected substances are illustrated in Table 3.

The level of discharge of these substances is such that in the waters of the estuary all of the relevant Environmental Quality Standards for substances covered by the Dangerous Substances Directive 76/464/EEC are comfortably met. However, historically the concentrations have been high enough to leave a legacy of contamination of sediments that causes the downgrading of areas of estuary around Grangemouth and in Inverkeithing Bay.

Diffuse inputs in some areas also give rise to significant concentrations of these substances. For example γ-HCH concentrations in the Carron Estuary are elevated by the effluent discharge from Falkirk STW which is believed to be contaminated by run-off from wood yards in the area (FRPB 1995).

There have also been other indirect benefits from initiatives such as the reduction in use of leaded petrol. Total lead in river run-off to the estuary has reduced from 28 to 17 tonnes between 1985 and 1993. Campbell & Ridgway (1989) have described in detail the significant reductions in pollution arising from the elimination of pentachlorophenol (PCP) from discharges.

In the case of diffuse inputs of potentially hazardous substances, significant environmental benefits have also accrued, for example, from the Government action to ban the use of tributyltin (TBT) antifoulants on smaller boats and to ban the non-agricultural use of simazine and atrazine. Thus the extent of TBT-induced deformities in the dogwhelk *Nucella lapillus* has declined substantially since 1987 (FRPB 1994c).

Bioaccumulation in mussels

The value of the mussel *Mytilus edulis* as a sentinel organism for monitoring changes in the level of

contamination has long been recognised (Bryan *et al.* 1985). The results of such 'mussel-watch' surveys around the Forth Estuary, carried out between 1981 and the present, have been reported in detail elsewhere (FRPB 1994a) and are summarised here. The principal features are:

- As a direct consequence of the industrialised nature of the catchment there are specific sites around the Forth Estuary which show contamination as a result of discharges to these areas.

- More recent data show that at these specific sites there have been reductions in the level of contamination in response to reductions in the discharge of metals (see Table 3), in particular cadmium at Leith and mercury (see Figure 3) and chromium at Grangemouth.

- Generally levels of organochlorine compounds in mussels showed no elevated concentrations (less than 2.5 times background) with the exception of
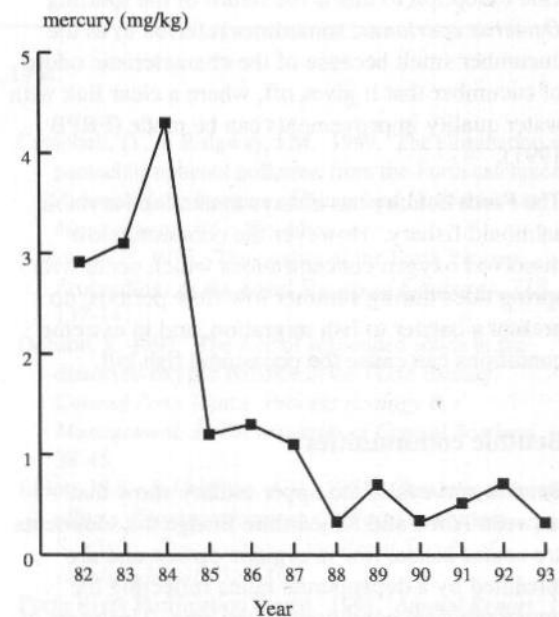
mercury (mg/kg)

Figure 3. Concentrations of mercury (mg kg⁻¹ dry weight) in mussels collected from Grangemouth, Forth Estuary.

Table 3. Persistent substances entering the Forth Estuary, kg year⁻¹ (includes rivers, industrial and sewage discharges)

Substance	1985 Baseline	1993 Actual	1994 Actual	1995 Target
Cd	3,700	500	240-390	660
Hg	1,730	67	48	100
Cr (t year⁻¹)	57	15	13	15
HCB	2,800	123	49-53	100
TCBs	60,000	1,040	226-278	750
PCP	3,200	280	60-132	190
γ-HCH	14	22	21-24	25
Dieldrin	8	5	1.3-5.1	8

γ-HCH, dieldrin and HCB close to known sources around Grangemouth.

Biological assessment

Fish population studies

In the Forth Estuary, estuarine monitoring of the fish community and associated environmental variables has been carried out for many years, commencing in 1981. Much of the data associated with these surveys has been reported elsewhere (Pomfret *et al.* 1991).

The most recently reported study (FRPB 1994b) assesses whether there have been significant changes in the fish community, concluding that the data tentatively show a small increase in species richness for the estuary around Longannet which may be linked to a greater incursion of marine adventitious species. It is not clear whether this is linked to improvements in water quality during the period. One exception to this is the return of the sparling *Osmerus eperlanus*, sometimes referred to as the cucumber smelt because of the characteristic odour of cucumber that it gives off, where a clear link with water quality improvements can be made (FRPB 1991).

The Forth Estuary has always maintained a viable salmonid fishery. However the occasional low dissolved oxygen concentrations which occur over spring tides during summer low flow periods, do present a barrier to fish migration, and in extreme conditions can cause the occasional fish kill.

Benthic communities

Benthic surveys of the upper estuary show that between Alloa and Kincardine Bridge the sediments are coarse sands, low in organic carbon and are inhabited by a depauperate fauna reflecting the severe physical conditions in the area. Upstream of Alloa the sediments become muddy with high organic carbon levels and moderate to high densities of oligochaetes.

The fauna of the lower estuary is dominated by a depauperate *Nepthys oligochaete* dominated community between Bo'ness and Grangemouth, which grades into a more diverse typically marine community towards the Forth bridges.

Investigations carried out across intertidal Kinneil mudflats by McLusky (1994) indicate that there remains a persistently impoverished area at the innermost corner of the mudflat related to historically contaminated sediments. There is some evidence that this area is improving. However, the sediments on the mudflat remain significantly contaminated with aliphatic and aromatic hydrocarbons at levels previously reported (see Elliott & Griffiths 1987).

The presence of significantly modified intertidal communities across the Kinneil mudflat, particularly at the innermost western corner causes the downgrading of the area to class C.

Overall assessment of the Forth Estuary

The overall result of applying the classification scheme described in Appendix A to the results of the various monitoring surveys is shown in Figure 4.

The class C areas are the stretches of estuary lying between upstream of the Black Devon and downstream of Stirling as a result of the organic pollution and consequent depression of dissolved oxygen; the Kinneil mudflats as a result of the modified intertidal communities and significant accumulations of persistent substances in sediments; the only class D area is within Inverkeithing Bay and has resulted from historic discharges of effluent from a paper mill.

Conclusions

In recent years there have been significant improvements in the overall quality of the Forth Estuary and its associated tributary estuaries, namely;

- Overall reduction in inputs of organic wastes discharged by municipal and industrial sites.

- Overall reduction in the discharge of quantities of sewage derived solids.

- Improved aesthetic quality of the shorelines around Limekilns, South Queensferry and Ironmill Bay.

- Overall reductions in the direct inputs of red-listed and other hazardous substances, in line with North Sea Action Plan requirements.

- Corresponding reductions in the level of some bioaccumulants in indicator species such as the mussel *M. edulis*.

- The return of the relatively pollution-sensitive cucumber smelt *O. eperlanus* to the Forth and the establishment of a breeding population.

The commissioning of the new treatment facilities has resolved the major pollution problems in the Forth Estuary. Despite these improvements some
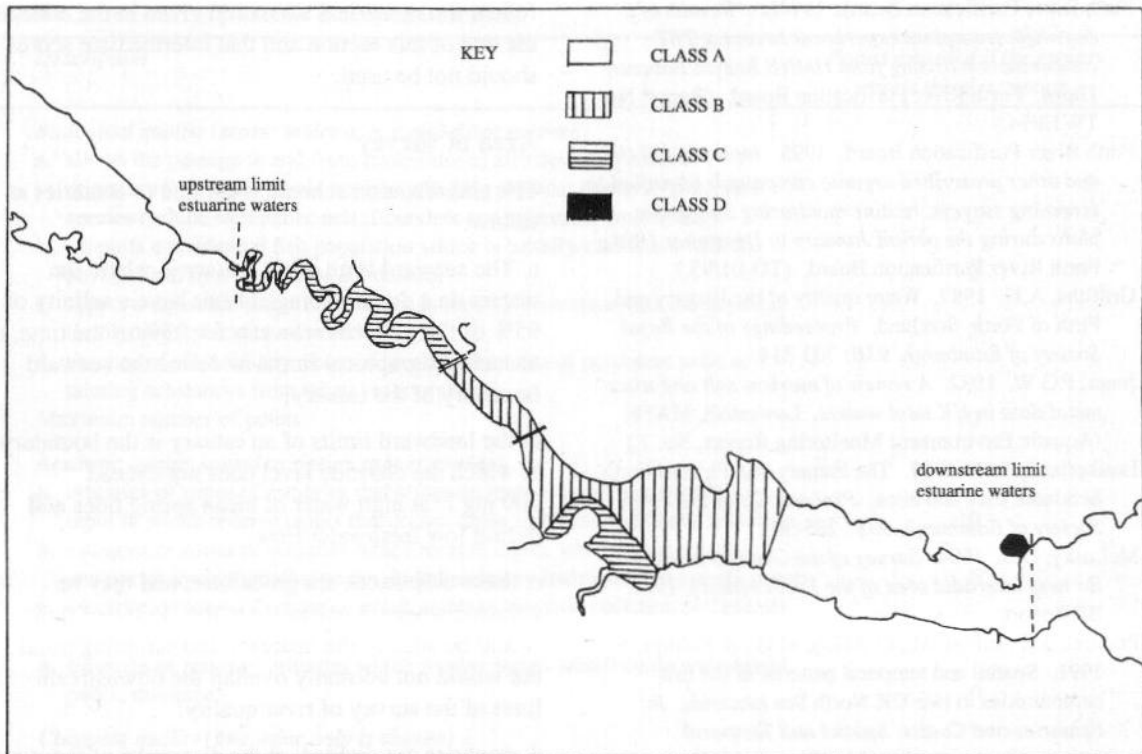
Figure 4. Overall quality classification for the Forth Estuary, 1994.

significant problems remain, with 15% of the estuarine area still of poor or seriously polluted quality. There also remains the potential for other threats to develop as a consequence of human activities around the estuary. The regulator, currently the Forth RPB and its successor organisation, the Scottish Environment Protection Agency (SEPA), will continue to work to achieve further water quality improvements wherever these can be justified on a cost/benefit basis, namely;

- Treatment for the remaining crude sewage discharges and improved treatment at some existing STWs.

- Further effluent treatment at some industrial sites.

Generally it appears realistic to be optimistic regarding the future health of the Forth ecosystem and the likely impacts of development activities.

References

Balls, W.P., Brockie, N., Dobson, J., & Johnston, W. In press. *Dissolved oxygen and nitrification in the upper Forth Estuary during summer (1982-1992): Patterns and trends.*

Bryan, G.W., Langston, W.J., Hummerstone, L.G., & Burt, G.R. 1985. A guide to the assessment of heavy metal contamination in estuaries using biological indicators. *Journal of the Marine Biological Association of the UK. Occasional Publication No. 4*: 1-92.

Campbell, D., & Ridgway, I.M. 1989. The elimination of pentachlorophenol pollution from the Forth catchment. *Journal of the Institute of Water and Environmental Management, 3(6):* 599-603.

Collett, W.F. 1972. The quality of the Forth Estuary. *Proceedings of the Royal Society of Edinburgh, 71B:* 137-141.

Dobson, J. 1995. The role of suspended solids in the dissolved oxygen balance in the Forth Estuary. *Coastal Zone Topics: Process Ecology & Management, 3: The estuaries of Central Scotland:* 38-45.

Elliott, M.E., & Griffiths. A.H. 1987. Contamination and effects of hydrocarbons on the Forth ecosystem, Scotland. *Proceedings of the Royal Society of Edinburgh, 93B:* 327-342.

Forth River Purification Board. 1991. *Annual Report 1990.* Forth River Purification Board.

Forth River Purification Board. 1993(a). *Annual summary of environmental data.* Forth River Purification Board.

Forth River Purification Board. 1993(b). *Annual monitoring of the fauna and sediments in the estuary and Firth of Forth 1991/92.* Forth River Purification Board. (Report No. TW04/93.)

Forth River Purification Board. 1994(a). *Bioaccumulation report 1991-1993.* Forth River Purification Board. (Report No. TW04/94.)

Forth River Purification Board. 1994(b). *A preliminary summary analysis of agassiz trawl fish data from the lower Forth Estuary 1981 to 1994.* Forth River Purification Board. (Report No. TW12/94.)

Forth River Purification Board. 1994(c). *Results of a dogwhelk transplant experiment to assess TBT contamination arising from HMNB Rosyth/Babcock Thorn.* Forth River Purification Board. (Report No. TW13/94.)

Forth River Purification Board. 1995. *Inputs of red-list and other proscribed organic compounds identified by screening surveys, routine monitoring and action plans during the period January to December 1994.* Forth River Purification Board. (TO-01/95.)

Griffiths, A.H. 1987. Water quality of the Estuary and Firth of Forth, Scotland. *Proceedings of the Royal Society of Edinburgh, 93B:* 303-314.

Jones, P.G.W. 1982. *A review of nutrient salt and trace metal data in UK tidal waters.* Lowestoft, MAFF. (Aquatic Environment Monitoring Report, No. 7.)

Leatherland, T.M. 1987. The Estuary and Firth of Forth, Scotland: uses and aims. *Proceedings of the Royal Society of Edinburgh, 93B:* 285-301.

McLusky, D.S. 1994. *Survey of the Grangemouth to Bo'ness intertidal area of the Forth estuary, 1994.* BP Report.

Pomfret, J.R., Elliott, M., O'Reilly, M.G., & Phillips, S. 1991. Spatial and temporal patterns in the fish communities in two UK North Sea estuaries. *In: Estuaries and Coasts: Spatial and Temporal Intercomparisons,* ed by M. Elliott & J.P. Ducrotoy, 277-284. (ECSA 19 Symposium.)

Appendix A

Classification of estuaries

The water quality classification of estuaries is based on the recommendations of the final report of the Classification of Estuaries Working Party which reported to the DoE/NWC Standing Technical Advisory Committee on Water Quality. In creating the classification system, the working party had regard to uses to which the estuary might be put (such as passage of migratory fish, fishing, shellfisheries and wildlife), amenities (such as sailing, bathing and appearance) and industry. The following notes provide the necessary information for classification of estuaries, but in order to maximise the benefit of the classification scheme it is recommended that the whole of the final report be read. Owing to the lack of relevant quantitative data for many estuaries the scheme is primarily subjective, but firm data should be used whenever possible. It should be noted that the scoring of the characteristics describing estuarial quality must

follow the numerical allocation given in the table at the end of this section and that intermediate scores should not be used.

Area of survey

The classification scheme is applied to estuaries as follow:

a. The seaward limit of an estuary is where the waters on a depth-averaged basis have a salinity of 95% of the adjacent seawater for 95% of the time, or at such geographical limits as define the seaward boundary of the estuary;

b. the landward limits of an estuary is the boundary at which the chloride level does not exceed 200 mg l^{-1} at high water of mean spring tides and during low freshwater flow;

c. these definitions are guidelines, and may be adjusted where necessary, e.g. the landward limit would be sited at the nearest fixed sampling point but would not normally overlap the downstream limit of the survey of river quality;

d. estuaries are divided, at the discretion of the river purification boards, into zones with reasonably uniform characteristics and classified separately. In large estuaries, with different qualities across their width, two or three zones may be identified laterally; and

e. a reduction in water quality caused by a single discharge is ignored, except where its effect is more than local.

Parameters to be measured

For each zone, points are allocated for biological quality, aesthetic quality and chemical quality as indicated in Table 4. Intermediate scores are not used. In the absence of data, scores are estimated on the basis of the biological quality expected from knowledge of polluting inputs, and hydrographic conditions.

Overall classification and description of each estuary or zone

The points awarded for each parameter (biological, aesthetic and chemical) are summed, and the estuary or zone is classified according to the scale shown in Table 5.

Table 4. Allocation of points for estuary classification.

Description	Points awarded if the estuary meets this description
Biological quality (scores under a, b, c and d are summed)	
a. allows the passage to and from freshwater of all relevant species of migratory fish, when this is not prevented by physical barriers. (Relevant species include salmonids, eels, flounders and cucumber smelts, etc.).	2
b. supports a residential fish population which is broadly consistent with the physical and hydrographical conditions.	2
c. supports a benthic community which is broadly consistent with the physical and hydrographical conditions.	2
d. absence of substantially elevated levels in the biota of persistent toxic or tainting substances from whatever source.	4
Maximum number of points	10
Aesthetic quality (one description only is chosen)	
a. estuaries or zones of estuaries that either do receive a significant polluting input or which receive inputs that do not cause significant aesthetic pollution.	10
b. estuaries or zones of estuaries which receive inputs which cause a certain amount of aesthetic pollution but do not seriously interfere with estuary usage.	6
c. estuaries or zones of estuaries which result in aesthetic pollution sufficiently serious to affect estuary usage.	3
d. estuaries or zones of estuaries which receive inputs which cause widespread public nuisance.	0
Chemical quality (one value only is chosen)	
Dissolved oxygen exceeds a saturation value of:	
60%	10
40%	6
30%	5
20%	4
10%	3
below 10%	0

Table 5. Estuary classification.

Classification	Number of points	Description
Class A	30-24	Good quality
Class B	23-16	Fair quality
Class C	15-9	Poor quality
Class D	8-0	Bad quality

Freshwater inputs and pollutant loads to the Tay Estuary

C. Anderson, J. Anderson & W. Proctor

The Firth of Tay is a major estuary on the east coast of Scotland. The main river flowing into the estuary is the River Tay which has the largest freshwater flow of any river in the United Kingdom.

This paper compares the freshwater inputs to the estuary with the data published in a paper presented to the Royal Society of Edinburgh in 1975 (Pontin & Reid 1975). The significance of, and possible reasons for, any change in the flow regime is discussed. The paper then goes on to identify the results of recent investigations into the relative significance of pollutant inputs from freshwater and point source sewage and trade discharges. The pollutants considered are nutrients and potentially toxic trace metals.

Finally the results of a loadings reduction programme are presented, showing the progress being achieved in reducing the potentially toxic trace metal loadings to the Tay Estuary. This programme has concentrated on a number of the major sewer outfalls from the City of Dundee, which represents a major population and industrial centre on the north shore of the estuary.

C. Anderson, Senior Pollution Control Officer; J. Anderson, Principal Hydrologist; W. Proctor, Principal Chemist, Tay River Purification Board, 1 South Street, Perth PH2 8NJ, UK.

Introduction

The Tay Estuary is a major estuary on the east coast of Scotland. The main rivers flowing into the estuary are the Tay and Earn which have a combined catchment area (Figure 1) of 6,000 km² (Tay River Purification Board Annual Report 1993) and the largest freshwater flow in the United Kingdom (Institute of Hydrology National Water Archive). The City of Dundee is the main population centre situated on the north shore of the estuary and there are navigable estuarine channels to service the commercial ports of Dundee and Perth. A small oil refinery in the dock area of Dundee uses this transport route to import crude oil and export some products from the area.

There are three Sites of Special Scientific Interest (SSSI) within the estuary, the largest of which, the Upper Tay Estuary, relates mainly to the use of the extensive tidal sand- and mudflats by overwintering and migrant populations of geese, ducks and waders. This area also contains one of the largest, continuous *Phragmites* reed beds in Britain. The estuarine waters around Broughty Ferry on the north shore

Figure 1. River Tay catchment.

and Newport and Tayport on the south shore are centres for water sports and there are popular beaches at Broughty Ferry, Monifieth and Tayport.

Circulatory patterns, sediment movements, salinity profiles and tidal exchange volumes were all extensively studied in a series of papers presented in the Proceedings of the Royal Society of Edinburgh in 1975. Suffice to say that the overall picture of the estuary from these papers is one of large freshwater input rates combined with a high tidal exchange volume within a relatively narrow estuary. These factors produce an estuary characterised by strong tidal currents, rigorous mixing and variable and temporary stratification.

In terms of water quality classification, the estuary is Class A (good), except for the middle section delineated by lines drawn between Kingoodie and Balmerino and between Broughty Ferry and Tayport. This section is downgraded to Class B (fair) mainly due to the untreated sewage discharges from Dundee which give rise to the presence of sewage solids. The section of downgraded waters is due to halve in area within the next two to three years with the commissioning of the full Invergowrie/Riverside Drainage Scheme (IRDS) serving the western part of Dundee. This consists of the interception of a number of sewers and the provision of fine screening and a long outfall. The remainder of the waters should attain Class A status by the end of the year 2000 when the central area of Dundee will receive similar improvement works. Indeed, under the provisions of the Urban Waste Water Treatment (Scotland) Regulations 1994, all sewage flows from the conurbation of Dundee will require full sewage treatment by 31st December 2000.

Finally, as far as analytical capability allows, it can be confirmed that all relevant environmental quality standards (EQSs) are complied with in the estuarine waters.

The aims of this paper are threefold. Firstly, the freshwater input flows will be compared with those reported in 1975. Then the nutrient and metal loads discharging to the estuary via riverine and direct point sources will be presented. Finally, the reduction in metal loadings which have been achieved from point sources will be shown.

Freshwater inputs

The freshwater input to the Tay Estuary was first examined by R.A. Pontin and J.A. Reid in a paper presented to the Royal Society of Edinburgh in 1975 (Pontin & Reid 1975). Inflows to the estuary were derived from the two principal gauging stations on the Rivers Tay and Earn at that time. These were

Ballathie on the River Tay 18 km upstream of Perth and Kinkell Bridge on the River Earn some 10 km downstream of Crieff. Mean monthly flow figures were presented for the periods 1958-72 at Ballathie and 1960-72 for Kinkell Bridge. Inflows to the estuary at the tidal limits of these two rivers were then estimated from these stations on the basis of the unit run-off per square kilometre.

This present exercise is intended to update the information available from the earlier paper and to look briefly at any trends that have become apparent through examining a longer period of record.

Since 1973 gauging station records have been available from Forteviot Bridge gauging station on the River Earn which is 14 km downstream of Kinkell Bridge. The catchment area at Forteviot is 782 km^2, compared with 591 km^2 at Kinkell Bridge and represents 89% of the River Earn catchment at the tidal limits, compared with only 67% for Kinkell Bridge.

Examination of the figures generated for the River Earn inflow in the earlier paper, compared with the flow records for Kinkell Bridge and Forteviot Bridge gauging stations in the period 1973-94, suggests that by using a unit run-off based on Kinkell Bridge the annual mean inflows to the estuary were overestimated by some 7%. In this paper it has been decided to use the flow figures recorded for Forteviot Bridge gauging station to represent the inflow to the Tay Estuary from the River Earn. The proportion of flow derived from the catchment downstream of Forteviot is insignificant in relation to the combined inflow of the Rivers Tay and Earn and can be discounted. For comparative purposes with the earlier paper mean monthly flows for the River Earn at Forteviot Bridge for the period 1960-72 have been generated by assuming the same proportional relationships between flows at Forteviot Bridge and Kinkell Bridge during the 1960-72 period as were actually observed in the period 1973-94.

Inflows from the River Tay in the earlier paper were also derived using a unit run-off ratio for Ballathie gauging station and applied to the catchment area at the tidal limit. Again this substantially overestimates flows from the ungauged catchment in the lower reaches, particularly in relation to the enhancement of summer run-off in the upper reaches due to storage for hydro-electric purposes and compensation flows. The inflows from the River Tay to the estuary at the tidal limits are considered to be virtually coincident with the flows recorded at Ballathie Gauging Station. This station covers 92% of the catchment area at the tidal limit and is probably much closer to 100% in terms of inflow.

Table 1. Mean flows at Ballathie and Forteviot Gauging Stations (cubic metres per second).

Period	Ballathie G.S. River Tay			Forteviot G.S. River Earn		
	1958-1972	1973-1994	1958-1994	1960-1972	1973-1994	1960-1994
January	214	295	262	37	53	47
February	200	233	219	34	40	38
March	190	261	232	31	41	38
April	152	172	164	23	25	24
May	135	114	122	22	15	18
June	95	73	82	12	10	11
July	74	63	68	10	8	9
August	92	83	87	14	11	12
September	113	130	123	22	21	21
October	187	197	193	33	32	33
November	186	235	215	34	41	38
December	210	254	236	35	44	41
Annual	154	176	167	26	29	27
October-March	198	248	227	34	43	39
April-September	110	106	107	17	15	16

Note: Forteviot Gauging Station figures for 1960-72 estimated from Kinkell Bridge Gauging Station.

Table 2. Mean inflow to Tay Estuary (cubic metres per second).

Period	1960-1972	1973-1994	1960-1994
January	257	348	314
February	241	273	261
March	229	302	275
April	177	197	190
May	163	129	142
June	110	83	93
July	85	71	76
August	103	94	98
September	137	151	146
October	222	229	227
November	222	276	256
December	234	298	274
Annual	182	205	196
October-March	235	291	268
April-September	129	121	124
Max. MDD	1,280	2,350	2,350
Min. MDD	37	27	27

Note: MDD = Mean Daily Discharge

Table 1 shows the mean monthly inflows for the River Tay at Ballathie, for the periods 1958-72, 1973-94 and 1958-94. (Note the year 1958 has been adopted in both papers as the year when the Tummel-Garry and Breadalbane hydro-electric schemes became fully effective, despite the Ballathie record extending back to 1953.) The table also gives the mean monthly flows for Forteviot Bridge on the River Earn for the period 1960-72 (derived using the method described above), 1973-94 and 1960-94. The mean inflows to the Tay Estuary have been calculated using mean figures for the River Tay at Ballathie based on the period 1960 onwards to obtain consistency with the period of

record available for the River Earn. The mean monthly inflows to the Tay Estuary for the periods 1960-72, 1973-94 and 1960-94 are provided in Table 2.

The selection of the periods 1960-72 and 1973-94 for examination does not have a particular objective basis but relates primarily to the historical timescale of the earlier investigation. However analysis of the trends in mean flows indicate that significant changes in the inflows to the Tay Estuary were nearly coincidental to these periods.

Figures 2 and 3 show the mean annual flows at Ballathie and Forteviot Bridge gauging stations for the periods 1958-94 and 1960-94 respectively. These demonstrate the marked upward trend in mean discharge on the Rivers Tay and Earn that began in the early 1970s. This increase in mean daily discharge is of the order of 13% in terms of the inflow to the estuary for the period 1973-94 over the earlier period of 1960-72.

Examination of the trends in terms of mean monthly figures indicates interesting divergences in discharge patterns between the two periods. The figures in Table 1 demonstrate a 21% increase in discharge for the months September to April in the second period whereas discharges for the months May to August have fallen by 18%. The most extreme months are January, where the increase in the flow over the two periods is of the order of 36%, and June, where a fall in mean discharge of 25% has been recorded.

Figures 4 and 5 show the trends in October to March and April to September flows for Ballathie Gauging Station for the period 1958-94. Whereas the October to March flows show a reasonably consistent upward trend from 1970 to the present
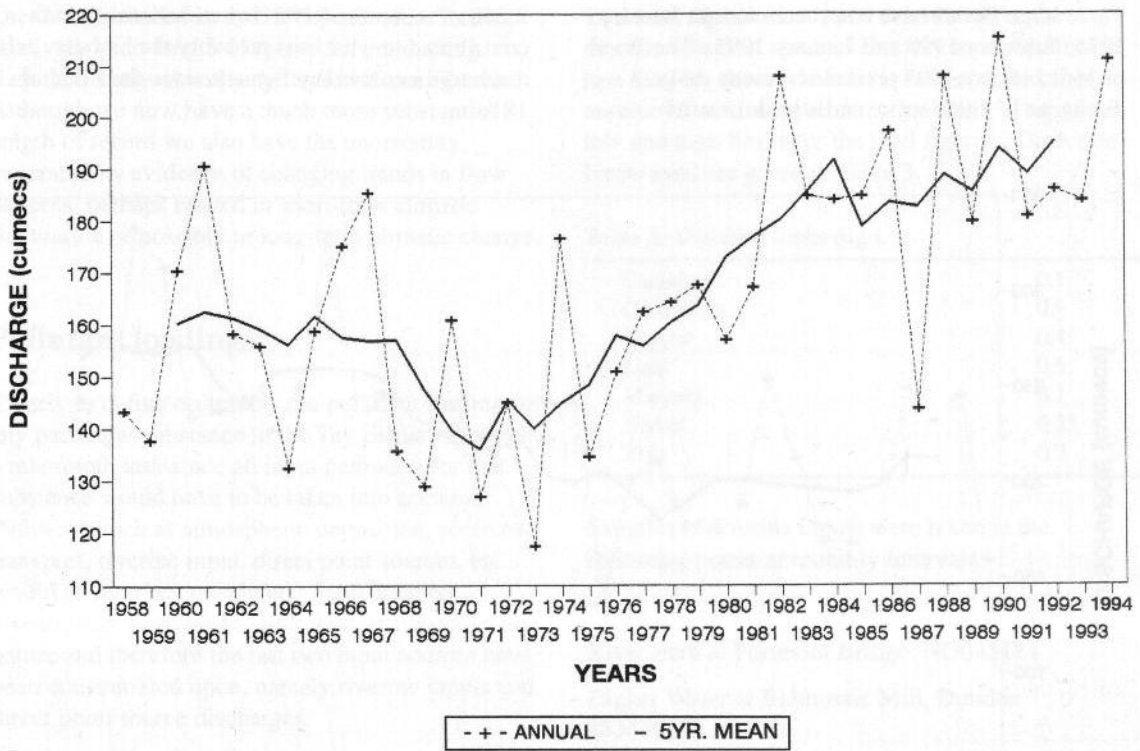
Figure 2. Annual mean daily flows at Ballathie, River Tay, 1958-1993.
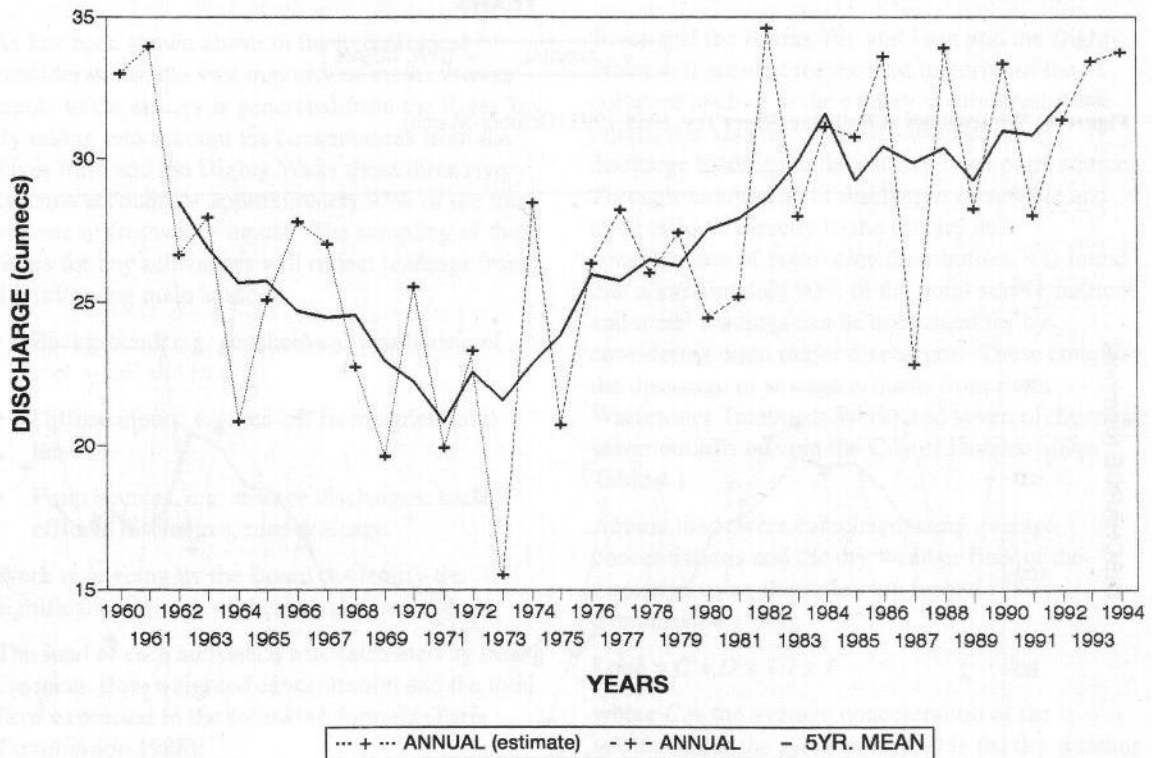
Figure 3. Annual flows at Forteviot Bridge, River Earn, 1960-1994.

day, the April to September discharge pattern is more complex with a consistent decline from the mid-1960s to a period of low inflows through the 1970s followed by an upward trend. Both winter

and summer inflows throughout the 1973-94 period have been marked by extremes. Notable droughts have been recorded in the summers of 1976 and 1984 and an exceptional wet summer in 1985.

Three large floods have been recorded: in January 1974, February 1990 and January 1993. The flood of 16th January 1993 produced a mean daily discharge of 1,965 m³ s⁻¹ and a peak flow of 2,268 m³ s⁻¹ on the River Tay at Ballathie which contributed to what was probably the highest discharge into the Tay Estuary since the flood of 1814.
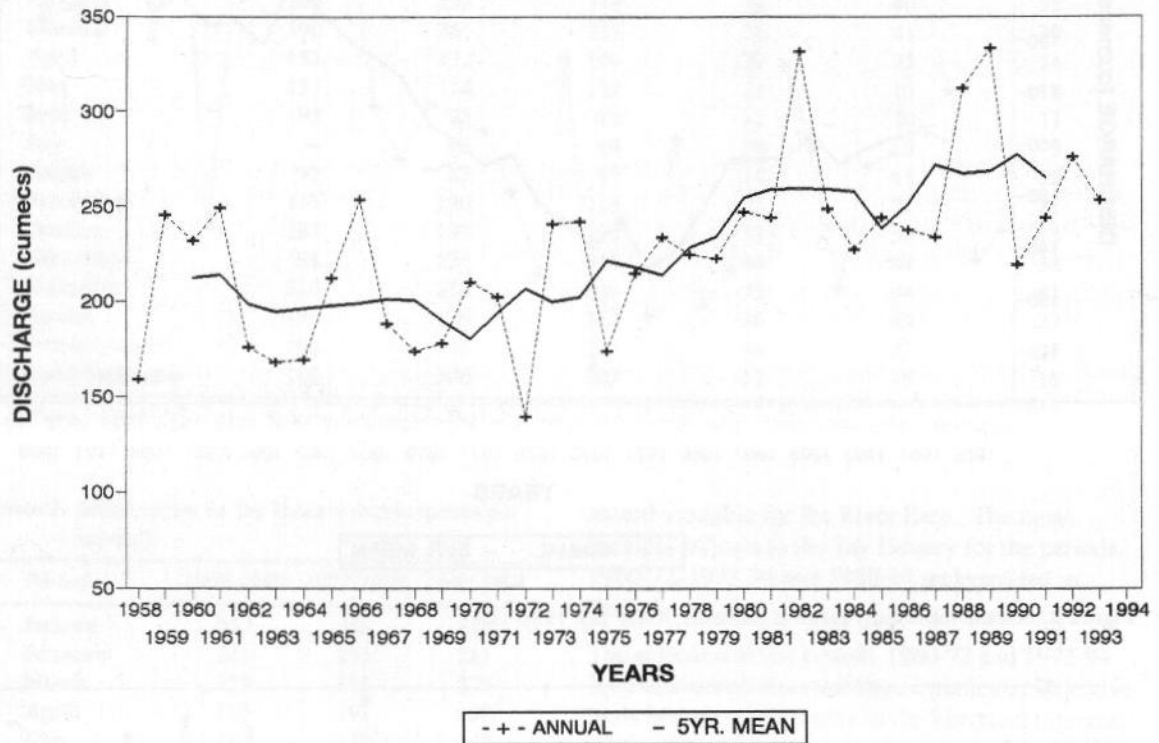
Figure 4. Winter flows at Ballathie, River Tay, 1958-1993 (October-March).
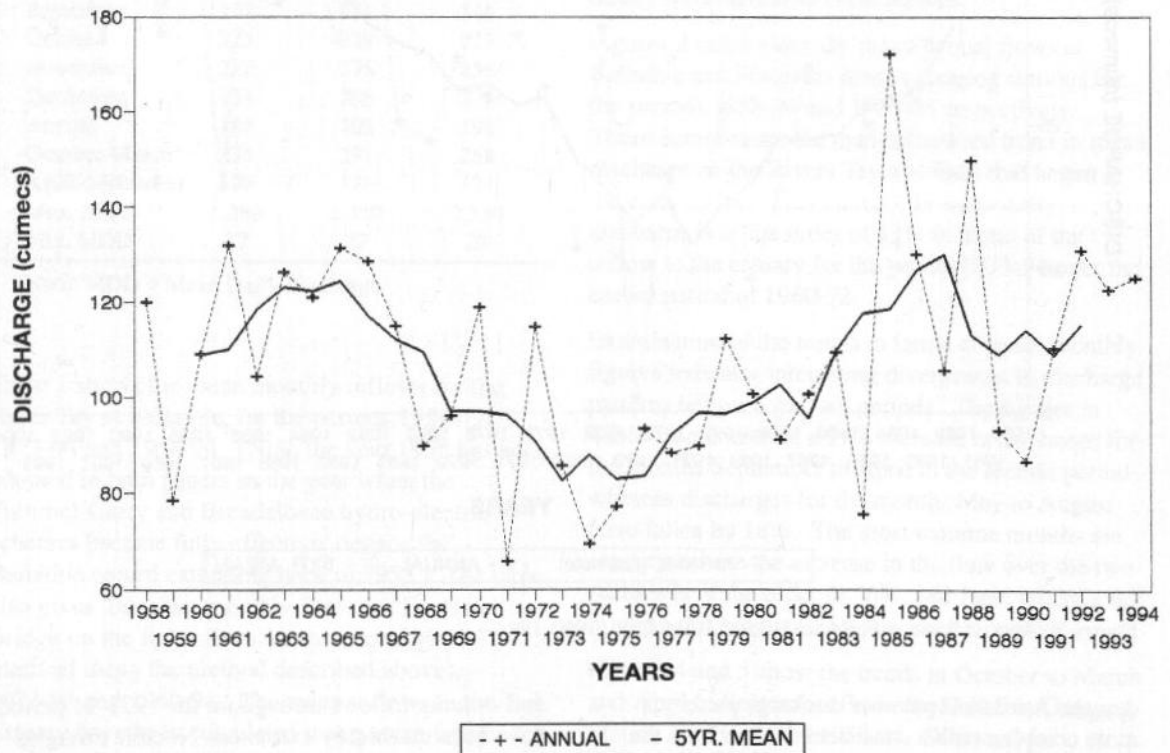
Figure 5. Summer flows at Ballathie, River Tay, 1958-1994 (April-September).

The data examined in the 1975 paper were from a relatively short length of record for conducting statistical analysis with any degree of confidence. Although we now have a much more substantial length of record we also have the uncertainty generated by evidence of changing trends in flow patterns, perhaps related to short-term climatic fluctuation or possibly to long-term climatic change.

Pollutant loadings

Clearly to define accurately the pollutant loadings of any particular substance to the Tay Estuary would be a mammoth task since all input pathways for that substance would have to be taken into account. Pathways such as atmospheric deposition, sediment transport, riverine input, direct point sources, etc. would have to be considered. Such detailed investigations cannot be dealt with in a paper of this nature and therefore the last two input sources have been concentrated upon, namely riverine inputs and direct point source discharges.

Riverine inputs

As has been shown above in the hydrological considerations, the vast majority of the freshwater inputs to the estuary is generated from the River Tay. By taking into account the contributions from the River Earn and the Dighty Water these three river systems account for approximately 95% of the total volume of freshwater inputs. The sampling of these rivers for any substances will reflect loadings from the following main sources:

- Background, e.g. geochemical weathering of rocks, soil and rainfall.

- Diffuse inputs, e.g. run-off from agricultural land.

- Point sources, e.g. sewage discharges, trade effluent discharges, road drainage.

Work is ongoing by the Board to identify the significance of each of these loading sources.

The load of each substance was calculated by taking the mean flow weighted concentration and the total flow expressed in the following formula (Paris Commission 1988):

$$\text{Load} = \frac{Qr \sum (CiQi)}{\sum Qi}$$

where Ci is the concentration measured in sample i; Qi is the corresponding flow for sample i; Qr is the mean annual flow rate.

Two load figures have been calculated for the metals. The first assumes that any analytical result less than the detection limit is zero and the other assumes that it is at the detection limit. This gives low and high limits for the load figures. Detection limits used are given in Table 3.

Table 3. Detection limits ($\mu g \, l^{-1}$)

Cadmium	0.1
Chromium	0.4
Copper	0.4
Lead	0.5
Mercury	0.1
Nickel	0.35
Zinc	0.7

Samples of riverine inputs were taken at the following points at monthly intervals:

River Tay at Queen's Bridge, Perth NO122234

River Earn at Forteviot Bridge NO045184

Dighty Water at Balmossie Mill, Dundee NO476325

Point source inputs

Given that the Rivers Tay and Earn and the Dighty Water will account for the vast majority of the pollutant loading to the estuary via the freshwater inputs, it is also necessary to consider direct discharge loadings to the estuary from point sources. Through monitoring of discharges of sewage and trade effluent directly to the estuary and consideration of population distribution, it is found that approximately 90% of the point source nutrient and metal loadings can be accounted for by considering eight major discharges. These comprise the discharge of sewage effluent from Perth Wastewater Treatment Works and seven of the major sewer outfalls serving the City of Dundee. (See Table 4.)

Annual loads were calculated using average concentrations and the dry weather flow of the discharge using the following formula (Paris Commission 1988):

Load = C x D x 1.7 x F

where C is the average concentration of the substance for the given period; D is the dry weather flow of the discharge; and F is a conversion factor. Sampling was carried out at monthly intervals.

The pollutant loading inputs from riverine and point source discharges are now dealt with by firstly considering nutrients and then potentially toxic trace metals.

Table 4. Sewage effluent discharges to the Tay Estuary.

Name	Type	Population discharge equivalent	Discharge point
Dighty Valley Sewer, Dundee	Screened	67,700	NO499298
Eastern Wharf Sewer, Dundee	Untreated	36,800	NO420306
Fish Dock Sewer, Dundee	Untreated	28,200	NO426308
Invergowrie Sewer, Dundee	Untreated	63,300	NO356288
King George V Sewer, Dundee	Untreated	65,300	NO417305
Ninewells Sewer, Dundee	Untreated	9,600	NO363292
Stannergate Sewer, Dundee	Untreated	41,700	NO438309
Perth Wastewater Treatment Works	Secondary	44,000	NO146220

Monitoring of the riverine and point source inputs to the Tay Estuary has been carried out since the mid-1960s. Since 1990 returns have been made to the Paris Commission (PARCOM) on all riverborne and direct inputs of selected parameters to the North Sea. The monitoring programme has been organised to ensure that 90% of the input of each pollutant is measured.

Nutrients

Table 5 shows the nutrient inputs to the Tay Estuary for 1993. These data show that over 90% of the input of nitrogen to the estuary comes from riverine inputs and of this 75% came from the River Tay. The majority of nitrogen entering the rivers and ultimately the estuary comes from agricultural usage and other diffuse sources. The River Tay receives sewage effluent from approximately 70,000 people and the River Earn from 21,000 people. Work is presently being carried out to quantify the various inputs to the rivers.

During the period 1990-93 nitrate nitrogen loads entering the estuary varied between 4,294 tonnes per year in 1992 and 7,451 tonnes per year in 1990, being influenced more by river flows than by changes in concentration. (See Figure 6.)

In contrast to the nitrogen nearly 60% of the phosphorus inputs to the estuary originated from point sources. Four of the point sources, Dighty, Fishdock and Stannergate Sewers and Perth Waste Water Treatment Plant contributed 225 tonnes of phosphorus, 90% of the point source input.

The proportion of phosphorus coming from point sources remained fairly constant over the period 1990-93 varying between 53% in 1992 and 59% in

1993. Total loads varied between 529 tonnes per year in 1992 and 376 tonnes per year in 1991.

As well as looking at the various sources of nutrients entering the estuary an examination was also made of changes in nutrient inputs from riverine source in recent years. Figures 6 and 7 show the mean annual nitrate nitrogen levels in the Rivers Tay and Earn and the Dighty Water for the period 1980-94. It is clear from Figure 6 that there has been no increase in nitrate nitrogen concentrations in the Rivers Earn and Tay in recent years. Levels during the period 1990-94 are comparable to those in the mid-1980s. This does not hold true however for the Dighty Water where levels have increased steadily since 1980 (Figure 7). It is thought that this is due to increased use of fertiliser in the catchment and further work is being undertaken to confirm this.

Metals

Table 6 shows the metal inputs to the Tay Estuary for 1993. It is quite clear from these data that, even taking the lower limit for metals' loadings (calculated assuming results less than the detection limit to be zero) for all metals except mercury the inputs from riverine sources predominate. These range from 82% in the case of chromium to 96% in the case of nickel.

The Dundee Sewers receive trade effluent from discharges from a wide range of industrial companies. These include engineering, food processing, natural and man-made fibre manufacturing and processing. As will be discussed later much work has been done to reduce metal inputs from these sources.

The differences between the lower and higher limits

Table 5. Nutrient inputs to the Tay Estuary 1993 (tonnes per year).

	Dundee Sewers	Perth WWTP	Rivers	Total
Total nitrogen	960	387	12,800	14,147
Nitrate nitrogen	19	6	6,650	6,675
Ammoniacal nitrogen	555	225	346	1,126
Total phosphorus	197	51	174	422
Soluble reactive phosphorus	106	40	101	247
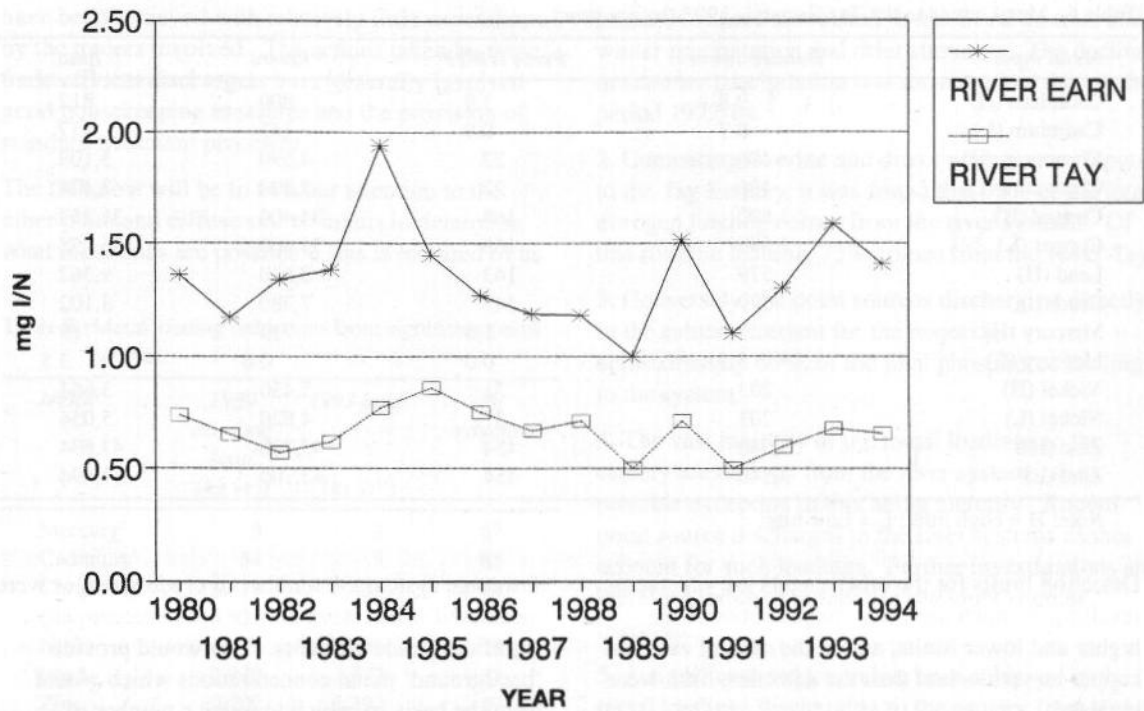
Figure 6. Rivers Tay and Earn - mean nitrate nitrogen levels 1980-1994.
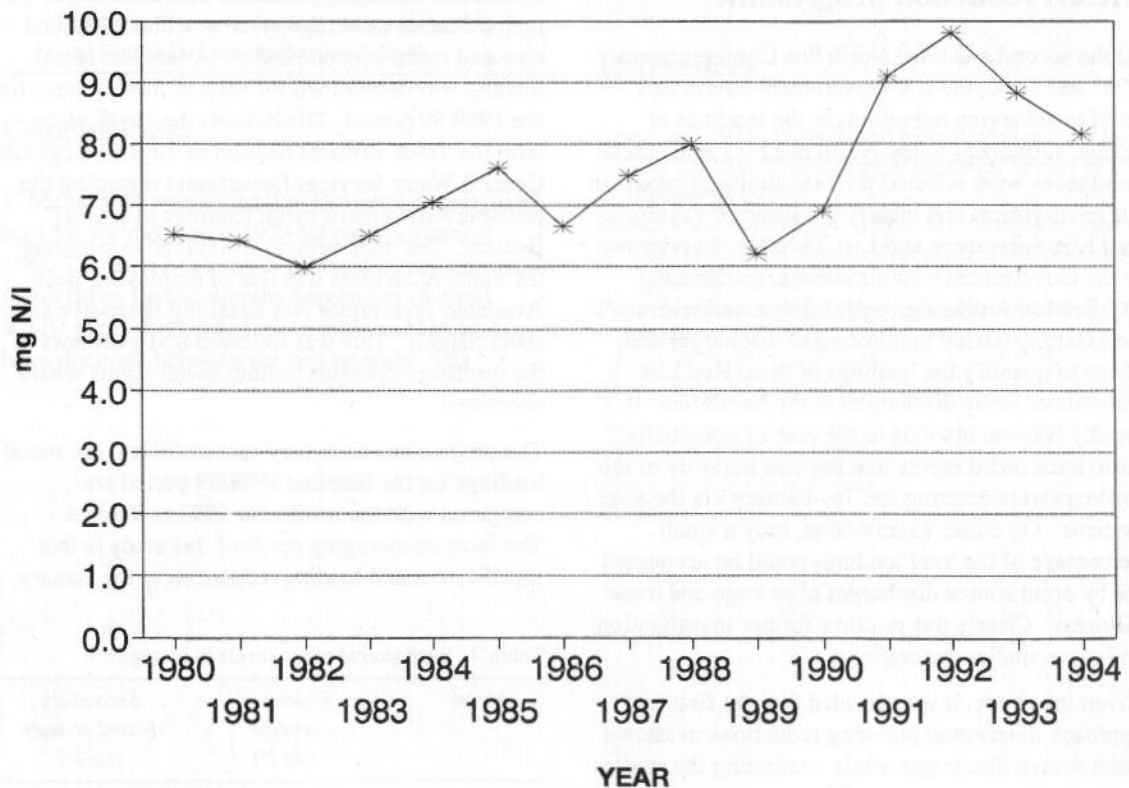
Figure 7. Dighty Water - mean nitrate nitrogen levels 1980-1994.

for metals are most noticeable in the cases of cadmium and mercury. The detection limits for both these metals is 0.1 μg l^{-1}. Because of the large flows involved in the rivers, when this detection limit is used to calculate the high limit, high loadings are produced. In the case of cadmium it produces an apparent load of 800 kg per year and for mercury an apparent load of 713 kg per year. Work is presently being undertaken to reduce detection limits and give truer load figures for both cadmium and mercury.

Table 6. Metal inputs to the Tay Estuary - 1993 (kg per year)

Metal input	Dundee sewers	Perth WWTP	Rivers	Total
Cadmium (H)	9.8	1.9	800	812
Cadmium (L)	8.7	0.9	147	157
Chromium (H)	496	22	4,590	5,108
Chromium (L)	496	22	2,890	3,408
Copper (H)	1,690	168	34,400	36,258
Copper (L)	1,690	168	34,400	36,258
Lead (H)	579	143	8,640	9,362
Lead (L)	579	143	7,380	8,102
Mercury (H)	5.1	1.3	713	719
Mercury (L)	3.5	0.0	0.0	3.5
Nickel (H)	203	31	5,430	5,664
Nickel (L)	203	31	4,820	5,054
Zinc (H)	3,540	454	43,700	47,694
Zinc (L)	3,540	454	43,700	47,694

Note: H = High limit; L = Low limit

Detection limits for the other metals are satisfactory resulting in much narrower ranges between the higher and lower limits, and in the case of zinc and copper no results less than the detection limit were obtained.

Metals reduction programme

At the second and third North Sea Conferences in 1987 and 1990, the UK Government committed itself to achieving reductions in the loadings of certain substances to the North Sea by 1995. These substances were selected on their ability to persist in the environment and mainly consisted of Priority Red List Substances and List 2 Metals. In response to the Government's commitments, the River Purification Authorities collated data and where necessary extended monitoring of discharges and rivers to quantify the loadings of these Red List Substances being discharged to the North Sea. It rapidly became obvious in the case of potentially toxic trace metal inputs that the vast majority of the loadings were entering the Tay Estuary via the river systems. On closer examination, only a small percentage of the total loadings could be accounted for by point source discharges of sewage and trade effluents. Clearly this requires further investigation and these studies are ongoing.

Given the above, it was decided that the first approach must entail pursuing reductions in known point source discharges while continuing the studies into other inputs of a more diffuse nature. When considering point sources, it became obvious that the metal inputs were being generated from a relatively small number of major sewerage systems within Dundee. The first task was to separate the metal loadings which represented purely domestic sewage as opposed to those elevated loadings indicative of metal-bearing trade effluent discharges to the

sewerage system. A number of crude sewages were monitored which were known not to receive any significant trade effluents. This would provide 'background' metal concentrations which would form the basis on which to judge a number of sewage discharges. The results of this study are presented in Table 7. This allowed us very rapidly to home in on initially two and then later five of the major Dundee sewerage systems which exhibited elevated metal concentrations. A baseline metal loading was determined for each of these sewers for the 1988/89 period. Discussions then took place with the Trade Effluent Section of Tayside Regional Council Water Services Department regarding the possible reduction of metal loadings to the Tay Estuary. The main principle involved in pursuing the metal reductions was that of employing Best Available Techniques Not Entailing Excessive Costs (BATNEEC). This was followed up by reviews of the discharge consents to limit metal inputs where necessary.

The process has been very successful and the metal loadings for the baseline 1988/89 period are compared with the results for 1993 in Table 8. The most encouraging result of this study is that significant metal loading reductions to the estuary

Table 7. Background metal levels in sewage

Metal	Untreated sewage[1] ($\mu g\ l^{-1}$)	Secondary treated sewage[1] ($\mu g\ l^{-1}$)
Mercury	0.1	0.1
Cadmium	0.4	0.2
Chromium	5	2
Copper	70	20
Nickel	5	2
Lead	20	5
Zinc	120	50

[1]expressed as average concentration from 36 samples.

have been achieved with relatively little expenditure by the traders involved. The actions taken by those trade effluent dischargers have generally involved good housekeeping measures and the provision of standard treatment processes.

The task now will be to turn our attention to the other point and diffuse source inputs to determine what reductions are possible if this is required of us.

Table 8. Metal loading reductions from significant point sources.

Metal	1989 baseline load[1] (kg yr^{-1})	1993 load[2] (kg yr^{-1})	% reduction
Mercury[1]	9	3	67
Cadmium[1]	54	8	85
Chromium	3,518	481	86
Copper	5,932	1,624	73
Nickel	749	195	74
Lead	2,939	572	81
Zinc	10,202	3,392	67

[1]Where the concentration was at or below limit of detection then this was taken as being at the limit of detection for load calculation purposes.
[2]Loads from five sewer outfalls serving Dundee. Load figures include 'background' loads.

Conclusions

1. Mean discharge to the Tay Estuary has increased by 13% for the period 1973-94 over the period 1960-72. This has been dominated by an increase in mean flows for the months September to April whilst mean discharge for the months May to August have declined between the two periods. The

principal causes are related to increased autumn and winter precipitation and drier summers. The decline in summer precipitation was most marked during the period 1972-84.

2. Comparing riverine and direct point source inputs to the Tay Estuary, it was found that 90% of the total nitrogen loading comes from the river systems. Of this riverine loading, 75% comes from the River Tay.

3. Conversely, the point sources discharging directly to the estuary account for the majority, approximately 60%, of the total phosphorus loading to the system.

4. The vast majority of the metal loadings to the estuary are derived from the river systems, the possible exception to this being mercury. Known point source discharges to the river systems cannot account for such loadings. Further investigations are therefore required to identify the input sources involved.

5. A significant reduction has been achieved in the metal loadings discharging to the estuary from direct point sources between 1988 and 1993. These reductions range from 67% to 86%.

References

Anon., *ed.* 1975. Physical and biological aspects of the Tay Estuary. *Proceedings of the Royal Society of Edinburgh (B),* 75.

Pontin, R.A., & Reid, J.A. 1975. The freshwater input to the Tay Estuary. *Proceedings of the Royal Society of Edinburgh (B),* 75: 1-9.

Paris Commission, Tenth Meeting Lisbon 15-17 June 1988.

The role of suspended solids in the dissolved oxygen budget of the Forth Estuary

J.E. Dobson

The removal of dissolved oxygen from the waters of the upper Forth Estuary during low river flows in summer was investigated on the 18th and 19th August 1993. Salinity, dissolved oxygen, suspended solids and the BOD in filtered and unfiltered samples were measured at 30 minute intervals over a tidal cycle at each of four locations in the upper Forth Estuary.

Suspended solids concentration was found to be significantly correlated with the BOD in unfiltered samples. Dissolved oxygen concentration was associated with salinity rather than suspended solids concentration. There was an exponential decrease in dissolved oxygen with increasing salinity up to a salinity of approximately 5. At salinities greater than 5 there was a linear increase in dissolved oxygen with salinity.

The BOD exerted by the suspended solids was calculated to consume approximately 40% of the total oxygen deficit in the upper Forth Estuary at the time of the survey. The relationship between dissolved oxygen and salinity is attributed to the consumption of permanently trapped suspended particles within the turbidity maximum which slowly degrade and consume available oxygen. It is estimated that the process of nitrification, which is associated with the suspended solids, consumes 33% of the total oxygen deficit in the upper estuary during the summer months.

J.E. Dobson, Forth River Purification Board, Clearwater House, Avenue North, Heriot-Watt Research Park, Riccarton, Edinburgh, EH14 4AP, UK.

Introduction

For many years it has been acknowledged that the most serious water quality problem in the Forth Estuary is the dissolved oxygen deficit which develops in the upper estuary during low river flows (Collett 1961; Covill, Davies & Chandler 1968). When low river flows coincide with spring tides dissolved oxygen concentrations can fall below 4 mg l^{-1}, presenting a barrier to the passage of migratory fish, and occasionally resulting in fish kills. The problem has been thoroughly studied by the Forth River Purification Board (Griffiths 1987; Webb & Metcalfe 1987) and management action has been taken to eliminate the root causes as rapidly as available resources would permit.

In order to identify the cause of the dissolved oxygen deficit consideration must be given to the inputs and the removal mechanisms, summarised below:

Inputs

Oxygen is supplied by the incoming, well oxygenated river and sea water, by transfer of oxygen across the air/water interface and by photosynthesis of fixed or floating vegetation.

Removal mechanisms

Oxygen is consumed by bacteria during the degradation of organic matter. The organic matter may be derived from allochthonous material or from discharges to the estuary. Oxygen is also consumed by purely chemical reactions such as the chemically catalysed oxidation of sulphides, certain chemo-autotrophic processes such as nitrification and respiration of vegetation and animals.

In practical terms oxygen consumption in a water sample is determined as the biochemical oxygen demand (BOD). This is an empirical test which measures oxygen consumption over five days in a sample and encompasses all the mechanisms above.

There is also a sediment oxygen demand (SOD) which results from the degradation of organic matter in the sediments and is determined by a variety of techniques described elsewhere (Nixon 1990).

In turbid estuaries suspended solids within the water column can be a major factor influencing the oxygen balance (Morris *et al.* 1982). The Forth Estuary is a typical well-mixed to partially-mixed estuary in that it exhibits a zone of high turbidity within the upper estuary where suspended solids concentrations can reach several orders of magnitude greater than those carried by the freshwater and saltwater end members. This zone is called the turbidity maximum and the theory behind its formation is discussed by Dyer (1986). The intensity and location of the turbidity maximum varies in response to river flow and tidal range (Uncles & Stephens 1993; Uncles, Barton & Stephens 1994). Essentially

the intensity of the turbidity maximum decreases with increasing freshwater flow and decreasing tidal range. During the summer months the turbidity maximum in the Forth Estuary is typically located 3-13 km downstream of Stirling at salinities <1 (Watson 1992).

The development and position of the dissolved oxygen minimum is closely coupled to the development and position of the turbidity maximum. However the two are not necessarily coincident, the dissolved oxygen minimum being frequently found downstream of the turbidity maximum. It has been calculated that 50-90% of the total biochemical oxygen demand (BOD) in the upper estuary is exerted by the suspended solids (Webb & Metcalfe 1987).

If numerical values can be assigned to the inputs and removal mechanisms the oxygen balance for the estuary can be modelled to give a clearer picture of the processes and their importance in the overall balance. The Forth River Purification Board (FRPB) developed in 1978 a 1-D tidally-averaged mathematical model to predict the distribution of dissolved oxygen in the upper estuary for given patterns of polluting loads and environmental variables. The model was modified in 1986 to include nitrification/denitrification processes and an oxygen demand from resuspended material. These modifications greatly increased the correlation between observed and predicted dissolved oxygen in the estuary (FRPB 1989).

Recent studies have shown that the organic carbon content of the sublittoral sediments in the upper Forth Estuary have decreased (McLusky, Hull & Elliott 1993). This has been achieved through reductions in discharges of domestic and industrial wastes to the upper estuary from 404 g s^{-1} BOD in 1984 to 185 g s^{-1} BOD in 1993 (FRPB 1990 and unpublished data).

Reductions in these organic inputs have been accompanied by a continuous improvement in the dissolved oxygen status of the upper estuary. This is evidenced by continuous monitoring carried out by the FRPB (Figure 1) and has, for example, resulted in the return of the sparling (*Osmerus eperlanus*) in 1989, an oxygen-sensitive species which has been resident in the Forth in the past (FRPB 1990a).

The original 1-D tidally-averaged model developed by FRPB has now been superseded by MIKE-11, a 1-D time varying model. Most of the parameters in the model can be assigned values from the literature, however typical values for the BOD resulting from resuspension are difficult to specify. The rate has to be determined by calibrating the model to measured values. The contribution of suspended solids to the dissolved oxygen budget was last evaluated in 1983 (FRPB 1984). That study assessed the BOD
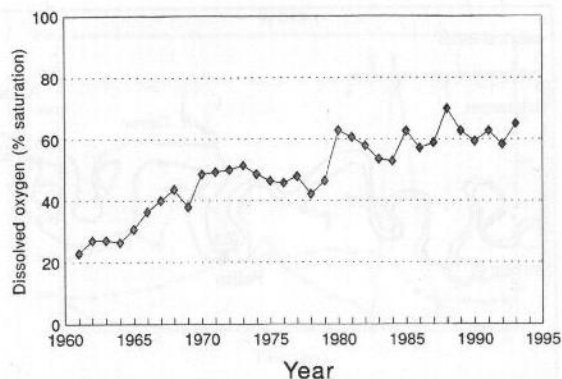
Figure 1. Long-term dissolved oxygen trend in the upper Forth Estuary 6 km downstream of Stirling at E6.

associated with the suspended solids at various sites in the upper estuary. The work described in this paper presents the results of a reassessment of the role of suspended sediments in the oxygen budget for the Forth Estuary; this was undertaken in 1993.

Given the continuing improvement in the dissolved oxygen status of the estuary, and the decrease in organic carbon content of the sediments, the relative importance of suspended solids in the overall oxygen balance of the estuary could have increased. The survey was designed to coincide with a period of low dissolved oxygen concentrations, i.e. on a spring tide with associated high suspended solids concentrations during the summer.

Methods

Samples were collected at half hourly intervals over a complete tidal cycle at four anchor stations in the upper Forth Estuary (Figure 2). Each of these sites were also sampled in the 1983 study. Salinity and temperature were determined at 1 m intervals through the water column using a YSI model 33 conductivity meter or an MC5 salinity bridge. At salinities less than 1 conductivity was determined and converted to salinity using a calibrated conductivity meter (Beckmann). Dissolved oxygen was determined at the same depths using a dissolved oxygen meter (YSI model 58). Samples for suspended solids and BOD determination were collected in 250 ml glass reagent bottles from a depth of 1 m using air displacement samplers.

One discrete sample was immediately filtered through a pre-weighed and labelled glass fibre filter (Whatman GF/C). The filters were washed with deionised water, oven-dried and weighed to give the mass of suspended solids in the sample.

The filtrate was carefully decanted back into a 250 ml reagent bottle and stored under water,

Figure 2. Location of Sampling Stations in the upper Forth Estuary.

together with the unfiltered samples, until required for the analysis of BOD in the laboratory.
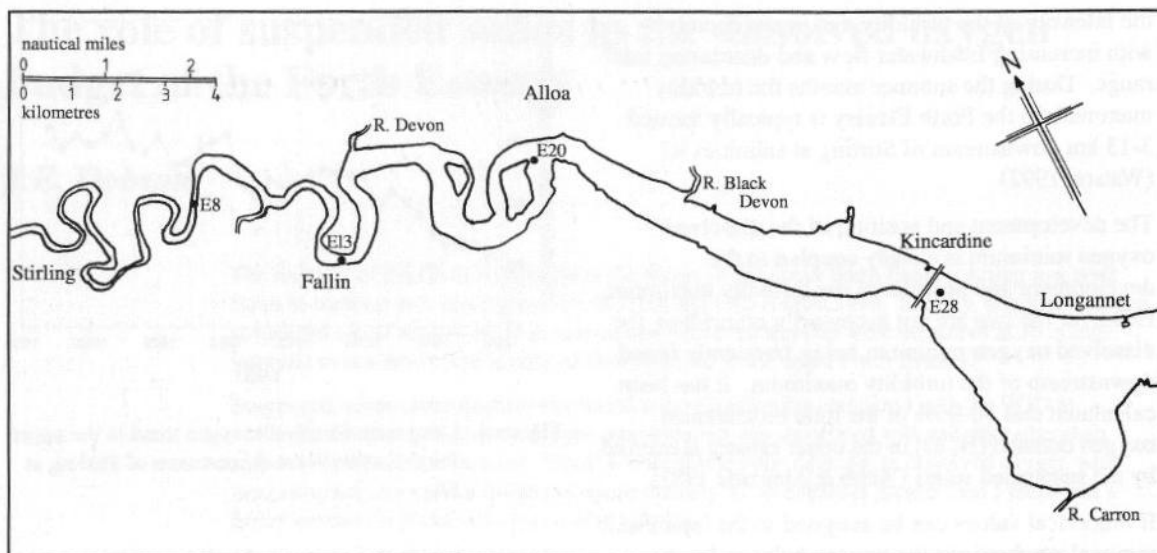
BOD was determined on both filtered and unfiltered samples following the procedure detailed in HMSO (1988). Samples containing less than 5 mg l^{-1} dissolved oxygen were diluted prior to incubation with distilled water which contained essential micronutrients required for bacterial growth. Despite this precaution some samples were lost due to total depletion of oxygen in the sample during the incubation period.

Surveys were carried out on the 18th and 19th August 1993 on spring tides (5.7 and 6.0 m tidal range respectively). E13 and E20 were sampled on the 18th, E8 and E28 on the 19th.

Results

The mean daily river flows into the upper estuary on the 18th & 19th August were 18.64 and 17.7 $m^3 s^{-1}$ respectively. This equates to approximately 67 percentile flows, i.e. 67% of flows are greater than this. Therefore although river flows were low they were not the exceptionally low flows, (i.e. 95 percentile) associated with extremely low dissolved oxygen concentrations. The residence time of water in the region of the estuary associated with the dissolved oxygen sag was estimated from the flushing time, i.e. the time required to replace the existing freshwater in an estuary at a rate equal to the river discharge (Officer 1976). The freshwater fraction was calculated at a salinity of 5 as this is where the lowest dissolved oxygen concentrations were found. The volume of the estuary at which this salinity occurred was taken from calculations carried out by the FRPB using a planimeter (FRPB 1978).

The residence time of water with a salinity of 5 was found to be six days at these flows.

Suspended solids, salinity and dissolved oxygen

The variations in depth-averaged salinity, dissolved oxygen and suspended solids concentrations at a depth of 1 m over the tidal cycle at each of the 4 stations are shown in Figure 3.

All stations show advection of suspended solids from upstream on the ebb tide and a decrease in suspended solids over low water as the particles settle out. Suspended solids concentrations on the ebb tide were greatest at E8 and E13, this is consistent with the location of the turbidity maximum 2-5 km upstream of E8 at high water. There is local resuspension at the start of the flood tide at all sites except E28. The highest suspended solids concentrations on the flood tide occurred at E13 (7,400 mg l^{-1}). Averaged over the tidal cycle suspended solids concentrations decreased in the following order E13 (2,082 mg l^{-1}), E8 (1,460 mg l^{-1}), E20 (445 mg l^{-1}), and E28 (157 mg l^{-1}).

Depth-averaged dissolved oxygen varied with depth-averaged salinity at all sites. At E8 and E13 dissolved oxygen increased at low water as oxygenated river waters arrived at the site. At E20 and E28 dissolved oxygen was low at low water and increased as salinity increased. A combined plot of dissolved oxygen concentrations against salinity for all the stations (Figure 4) indicates a rapid decrease in concentration with increasing salinity up to a salinity of 5. At salinities greater than 5 an approximately linear increase in dissolved oxygen concentrations with salinity is apparent. These observations indicate a zone of oxygen depleted
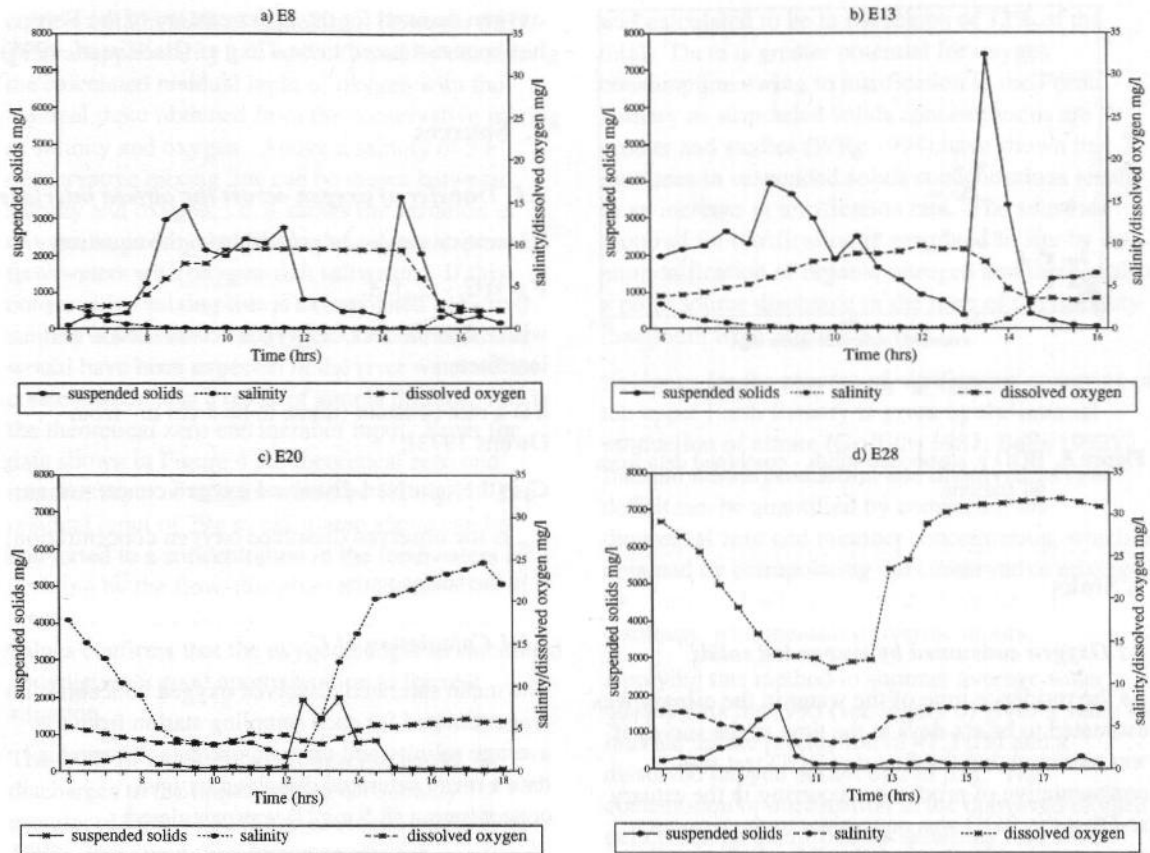
Figure 3. Suspended solids, salinity and dissolved oxygen over a tidal cycle at (a) E8, (b) E13, (c) E20 and (d) E28.

water centred at a salinity of about 5 which migrates up and down the upper estuary in association with the semi diurnal tide. From the data it appears that the minimum dissolved oxygen concentration was lower on the 19th than on the 18th.

Biochemical oxygen demand

Biochemical oxygen demand (BOD) increased with suspended solids concentrations at all sites. BOD associated with suspended solids ranged from 18 mg l^{-1} to 0.1 mg l^{-1} whilst dissolved BOD ranged from 1.8 to 0.1 mg l^{-1}. The BOD associated with the suspended solids accounted for 50 to 90% of the total depending on the suspended solids load. A combined plot of suspended solids against BOD from the four sites (Figure 5) shows a strong correlation between the two parameters, the equation for which is given below.

BOD mg l^{-1} = 0.71 + 2.5.10^{-3} x SS mg l^{-1} r^2 = 0.929

The mean BOD over the tidal cycle followed the same trend as the suspended solids concentrations, i.e. the BOD decreased in the order E13 (6.6 mg l^{-1}) >E8 (3.3 mg l^{-1}) >E20 (1.8 mg l^{-1}) >E28 (1.1 mg l^{-1}).
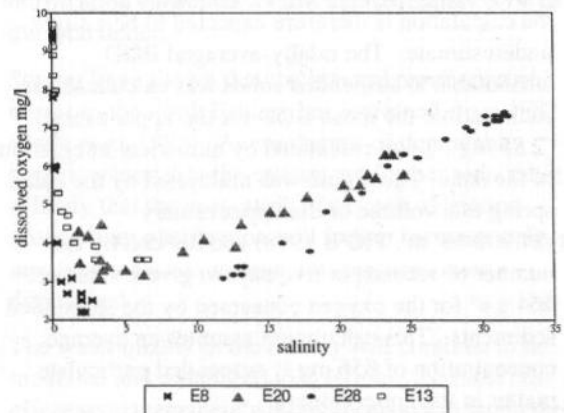
Figure 4. Dissolved oxygen v. salinity - combined data from all stations.

Discussion

BOD as determined in this study includes the processes of degradation of organic matter, chemical oxidation of reduced inorganic species, nitrification and respiration of vegetation. The contribution of these processes to the dissolved oxygen budget in the upper estuary were calculated using the data gathered in this study as follows:

Figure 5. BOD v. suspended solids - combined data from all stations.

1. Sinks

1.1 Oxygen consumed by suspended solids

As the residence time of the water in the estuary was estimated to be six days at the time of the survey it was assumed that the five-day BOD test was representative of processes occurring in the estuary and that the BOD was equivalent to the oxygen consumed by the suspended solids. Other studies (Department of Science and Industrial Research 1964) have shown that the five-day BOD test slightl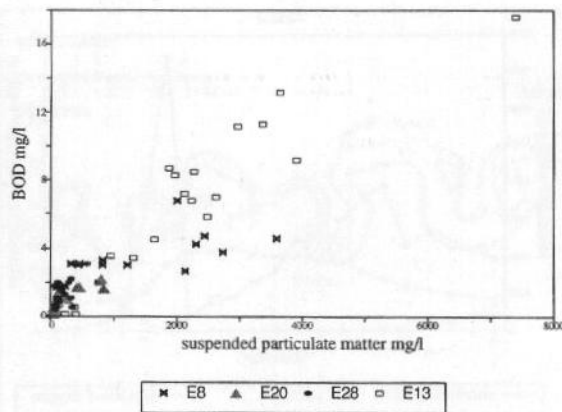y underestimates the ultimate oxygen demand, the calculation is therefore expected to be a slight underestimate. The tidally-averaged BOD attributable to suspended solids was calculated for each station, the mean BOD for the upper estuary (2.85 mg l^{-1}) was calculated by numerical integration of the data. This figure was multiplied by the mean spring tide volume of the upper estuary (24,900 10[3] m[3], FRPB 1978) and divided by the number of seconds in five days to give a value of 164 g s^{-1} for the oxygen consumed by the suspended sediments. This calculation assumes an average concentration of 856 mg l^{-1} suspended particulate matter in the upper estuary.

1.2 Oxygen consumed by dissolved BOD

A mean concentration of 1 mg l^{-1} was taken for the dissolved BOD in the upper estuary. This was multiplied by the mean spring tide volume of the upper estuary to give a value for oxygen consumption of 57 g s^{-1}.

1.3 Sediment oxygen demand

There is also a loss to the sediments which was not measured during this study but which can be estimated from published data. The sediment

oxygen demand for the upper estuary of the Forth has been estimated to be 176 g s^{-1} (Balls *et al.* 1995).

2. Sources

2.1. Transfer of oxygen across the air/sea interface

Reaeration can be calculated from the equation:

$$F = k(C_s - C_{ob}).A.$$

where F is the flux of oxygen across the air/sea interface;

k is a rate constant (taken to be 5 cm hr^{-1} from Owens 1973);

C_s is the saturated dissolved oxygen concentration;

C_{ob} is the observed dissolved oxygen concentration;

A is the surface area.

2.1.1 Calculation of C_s

The mean saturated dissolved oxygen concentration was estimated for each sampling station from the average salinity and temperature data. From this data a mean saturated dissolved oxygen concentration (8.5 mg l^{-1}) was calculated.

2.1.2 Calculation of C_{ob}

Tidally averaged dissolved oxygen concentration was calculated for each sampling station. The mean observed oxygen concentration (6.0 mg l^{-1}) was estimated by numerical integration of the tidally averaged data for the upper estuary.

2.1.3 Surface area A

The surface area was taken as the average of the mean low water springs (MLWS) and mean high water springs (MHWS) surface areas (7,317 10[3] m[2], FRPB 1978).

Substitution of these values into the equation gives a value of 254 g s^{-1} for the flux of oxygen across the air/sea interface.

2.2. Freshwater input

The average river flow over the two days of the survey was 18.17 m[3], this flow, when multiplied by the measured freshwater dissolved oxygen concentration of 9.5 mg l^{-1}, gives a freshwater input of 172 g s^{-1}.

These calculations produce a total dissolved oxygen loss from the upper estuary of 397 g s^{-1}, and an input of 426 g s^{-1} leaving a residual input of 29 g s^{-1}. These calculations are only approximations to the real situation as a more accurate description requires

complex mathematical modelling. However their general applicability can be confirmed by comparing the calculated residual input of oxygen with the residual input obtained from the conservative mixing of salinity and oxygen. Above a salinity of 5 a conservative mixing line can be drawn between salinity and oxygen, i.e. it shows the variation in oxygen caused by the dilution of oxygen depleted freshwaters with oxygen-rich saltwaters. If this conservative mixing line is extrapolated back to 0 salinity it will show the oxygen concentration that would have been expected in the river waters if the concentration was a result of simple dilution; this is the theoretical zero end member input. From the data shown in Figure 4 the theoretical zero end member input of oxygen would be 1.3 mg l^{-1}. The residual input of 29g s^{-1} calculated above can be converted to a concentration in the freshwaters by dividing by the flow, this gives a concentration of 1.6 mg l^{-1}. The close agreement between these two values confirms that the oxygen budget as calculated above gives a good approximation to the real situation.

The BOD of industrial and domestic waste discharges to the upper estuary is routinely monitored by the FRPB and averaged 185 g s^{-1} in 1993. This input therefore accounts for approximately 50% of the total oxygen deficit calculated above. These discharges are absorbed into the system and partition between particulate and dissolved phases. It is not possible to separate their effect from naturally occurring processes using the results of this study. However the dominance of particulate matter in the consumption of oxygen suggests that the effects of reducing these discharges will be long-term rather than short-term.

From the data it is apparent that dissolved oxygen is related to salinity rather than suspended solids concentration. A similar correlation between dissolved oxygen and salinity in the Tamar led Morris *et al.* (1982) to conclude that particulate organic detritus becomes trapped within the high turbidity zone, increasing the concentration and residence time of degradable organic material in the low salinity region of the estuary and that it was these permanently suspended trapped particles that are the predominant oxygen consumers. The data from the Forth agree with this hypothesis.

Further investigations into the processes behind the development of the dissolved oxygen sag in the Tamar by Owens (1986) found that nitrifying bacteria were attached to particles in the turbidity maximum. He likened the turbidity maximum to a fluidised bed reactor: a mobile and reactive bed which is periodically injected into the overlying waters. The contribution of nitrification to the observed sags in oxygen concentration in the Tamar

was calculated to be in the region of 12% of the total. There is greater potential for oxygen consumption owing to nitrification in the Forth Estuary as suspended solids concentrations are greater and studies (WRc 1994) have shown that increases in suspended solids concentrations result in an increase in nitrification rate. The substrate required for nitrification is generated *in situ* by the ammonification of organic nitrogen and there is also a point source discharge in the zone of the turbidity maximum from Stirling STW.

Evidence for the process of nitrification occurring in the upper Forth Estuary is given by the internal production of nitrate (Griffiths 1987; Balls 1992). Internal nitrate production and dissolved oxygen deficit can be quantified by comparing the theoretical zero end member concentration, which is obtained by extrapolating the conservative mixing line for dissolved oxygen and nitrate back to 0 salinity, with measured riverine inputs.

Applying this method to summer average water quality data for 1993 (see Figure 6) gives a value for internal nitrate production of 41.3 μM and a dissolved oxygen deficit of 178 μM. The contribution of nitrification to the dissolved oxygen deficit can be quantified by assuming that 1.43 moles of oxygen are required to produce 1 mole of nitrate from 1 mole of ammonia (Nixon 1990). Applying this stoichiometry to the 1993 data, nitrification consumes 59 μM approximately 33% of the total deficit.

Studies have shown that the internal production of nitrate in the Forth Estuary has increased since 1982 (Balls *et al.* 1995). As discharges of degradable organic material to the estuary are further reduced, it is likely that the proportion of oxygen utilisation arising from nitrification will further increase, unless inputs of reduced nitrogen are commensurately diminished.

The water quality in the estuary will continue to be modelled and monitored to determine the most cost effective management actions necessary to attain the EQS objective of a 95 percentile dissolved oxygen concentration of 4.5 mg l^{-1}.

Conclusions

Up to 90% of the BOD of the water column in the upper estuary is associated with the suspended solids.

A reasonable approximation to the BOD of the suspended solids can be obtained by multiplying the suspended solids concentration by a factor 0.0025. This figure can be used to calibrate 1-D model of the Forth Estuary MIKE-11.
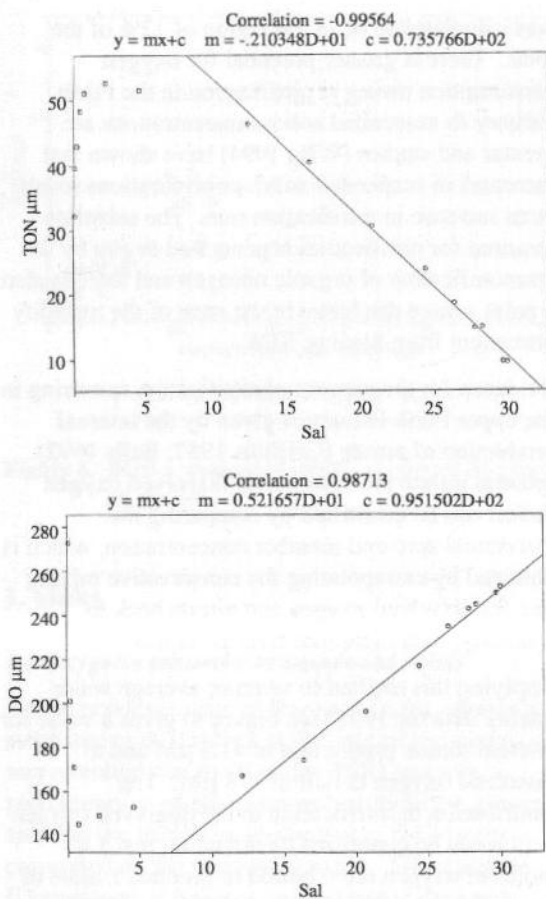
Correlation = -0.99564
y = mx+c   m = -.210348D+01   c = 0.735766D+02

Correlation = 0.98713
y = mx+c   m = 0.521657D+01   c = 0.951502D+02

Figure 6. Summer average (June-August) water quality
data in the Forth Estuary 1993.

Dissolved oxygen concentrations are correlated to
salinity rather than to suspended solids
concentrations. This suggests that permanently
trapped organic material in the low salinity region is
the predominant consumer of dissolved oxygen.

At the time of the survey suspended solids
consumed approximately 40% of the total oxygen
lost from the upper estuary.

The process of nitrification is enhanced by the high
concentrations of suspended particles in the turbidity
maximum. Calculations suggest that nitrification
consumes 33% of the total dissolved oxygen deficit
in the upper Forth Estuary.

References

Balls, P.W. 1992. Nutrient behaviour in two contrasting
Scottish estuaries, the Forth and Tay. *Oceanologica
Acta, 15*: 261-277.

Balls, P.W., Brockie, N., Dobson, J., & Johnston, W.
1996. Dissolved oxygen and nitrification in the upper
Forth Estuary during summer (1982-1992): patterns
and trends. *Estuarine and Coastal Shelf Science,
42(1)*: 117-134.

Collett, W.F. 1961. *A preliminary investigation of the
pollution of the upper Forth Estuary.* The Institute of
Sewage Purification. Glasgow 8th Feb.

Covill, R.A., Davies, A.W., & Chandler, J.R. 1968.
Parameters of marine pollution in the Forth Estuary.
The Public Works and Municipal Services Congress.

Department of Science and Industrial Research. 1964.
*Oxidation processes and the ultimate oxygen demand
in effects of polluting discharges on the Thames
Estuary.* HMSO.

Dyer, K.R. 1986. *Coastal and estuarine sediment
dynamics.* Chichester, John Wiley.

FRPB. 1978. *The physical dimensions of the Firth of
Forth and the Forth Estuary.* ES4/78. Edinburgh,
FRPB.

FRPB. 1984. *Suspended solids survey of the Upper Forth
Estuary.* ES2/84. Edinburgh, FRPB.

FRPB. 1989. *The 1-D tidally averaged Water Quality
Model for the Forth Estuary - an update.* TW06/89.
Edinburgh, FRPB.

FRPB. 1990a. *An assessment of the major loadings to the
Forth Estuary 1981-1988.* TW8/90. Edinburgh,
FRPB.

FRPB. 1990b. *Forth River Purification Board Annual
Report 1989.* Edinburgh, FRPB.

Griffiths, A.H. 1987. Water quality of the estuary and
Firth of Forth, Scotland. *Proceedings of the Royal
Society of Edinburgh, 93B*: 303-314.

HMSO. 1988. *5 Day Biochemical Oxygen Demand
(BOD_5). Methods for the examination of waters and
associated materials.* HMSO.

McLusky, D.S., Hull, S.C., & Elliott, M. 1993. Variations
in the intertidal and subtidal macrofauna and
sediments along a salinity gradient in the Upper Forth
Estuary. *Netherlands Journal of Aquatic Ecology,
27(2-4)*: 101-109.

Morris, A.W., Loring, D.H., Bale, A.J., Howland, R.J.M.,
Mantoura, R.F.C., & Woodward, E.M.S. 1982.
Particle dynamics, particulate carbon and the oxygen
minimum in an estuary. *Oceanologica Acta, 51*:
349-353.

Nixon, S.C. 1990. *Oxygen balance in Estuaries.* WRC
PRS 2462-M.

Officer, C.B. 1976. *Physical oceanography of estuaries
(and associated coastal waters).* New York, John
Wiley & Sons.

Owens, N.J.P. 1986. Estuarine nitrification: a naturally
occurring fluidized bed reaction? *Estuarine and
Coastal Shelf Science, 22*: 31-44.

Owens, M. 1973. Sources of oxygen in estuaries. *In:
Mathematical and hydraulic modelling of estuarine
pollution,* 26-37. London, HMSO. (Water Pollution
Research Technical Paper No. 13.)

Uncles, R.J., & Stephens, J.A. 1993. Nature of the
turbidity maximum in the Tamar Estuary, UK.
Estuarine and Coastal Shelf Science, 36: 413-431.

Uncles, R.J., Barton, M.L., & Stephens, J.A. 1994.
Seasonal variability of fine sediment concentrations in
the turbidity maximum region of the Tamar Estuary.
Estuarine and Coastal Shelf Science, 38: 19-39.

Watson, F.R. 1992. *Investigation into key chemical fluctuations and relationships in the Forth Estuary with particular reference to suspended solids, particulate organic carbon, BOD and dissolved oxygen.* MSc Thesis, Napier University, Edinburgh.

Webb. A.J., & Metcalfe, A.P. 1987. Physical aspects, water movements and modelling studies of the Forth Estuary, Scotland. *Proceedings of the Royal Society of Edinburgh, 93B*: 259-272.

WRc. 1994. *Nitrification Rates in Rivers and Estuaries.* R&D 305/14/NW.

Dissolved trace metals in the Clyde, Forth and Tay Estuaries - a synopsis and comparison with other UK estuaries

P.W. Balls, R.E. Owens & F.L.L. Muller

The results from recent surveys of dissolved trace metals (Cd, Cu, Pb, Mn, Ni, Zn) in the Clyde, Forth and Tay Estuaries are summarised. For Pb, Ni and Zn concentrations are greatest in the Clyde, lowest in the Tay and intermediate in the Forth. Relative to the Tay, the Clyde and Forth Estuaries contain high concentrations of dissolved Mn, this is linked to the under-saturation with dissolved oxygen which is a feature of the last two estuaries. Individual point sources are demonstrated to affect the distributions of some metals, e.g. Cu in the Forth. As a direct consequence of the high turbidity in the Forth Estuary, particle/water interactions are demonstrated to be more important there than in the Tay and Clyde.

Input data for Pb, Cu, Cd and Zn from riverine, sewage and industrial sources are used to explain some of the features observed. Despite the Tay having the greatest input of fresh water, metal inputs from rivers are generally less than those to the Forth and Clyde. This is attributed to relatively low metal concentrations in the River Tay, which is supported by survey data from the low salinity part of the estuary. Relative to the Forth and Tay Pb inputs to the Clyde are high, this is the likely explanation for the greater concentrations observed throughout the estuary.

A survey of recent literature has been made to extend the comparison of trace metal concentrations (Cu, Cd, Zn, Ni, Pb) to other UK estuaries (Tyne, Tees, Wear, Humber, Thames, Severn and Mersey). Individual estuaries may have relatively high concentrations of one or two metals (e.g. Pb and Cd in the Severn) but none appear to be enriched in all metals. This is likely to be related to particular activities associated with individual estuaries.

P.W. Balls, Scottish Office Agriculture and Fisheries Department, Marine Laboratory, PO Box 101, Victoria Road, Aberdeen, AB9 8DB, UK.

R.E. Owens, MAFF Fisheries Laboratory, Remembrance Avenue, Burnham on Crouch, Essex, CMO 8HA, UK.

F.L.L. Muller, Department of Oceanography, The University, Southampton, SO9 5NH, UK.

Introduction

The toxic effects of trace metals to biota are well known. Experiments which employ stringent anticontamination procedures have demonstrated that trace metals can inhibit primary productivity (Fitzwater, Knauer & Martin 1982) even at very low concentrations, e.g. 0.19 µg l⁻¹ Cu (Knauer & Martin 1983). Exposure to trace metals is rarely lethal to biota but it may result in the contamination of fish and shellfish (e.g. Clark & Topping 1989) or slower growth rates and reduced rates of recruitment (Bryan 1984). Concentrations at which deleterious effects have been noted range from 1.1-3.4 µg l⁻¹ for Cd (Vernberg *et al.* 1977; Thurberg *et al.* 1977), 0.95 µg l⁻¹ for Cu (Moraitu-Apostolopoulou & Verriopoulos 1979), 49 µg l⁻¹ and for Pb 24.8 µg l⁻¹ for Zn (Benijts-Claus & Benijts 1975). When combined with other environmental stresses, effects are likely at lower concentrations (Bryan 1984).

On a global scale, riverine transport is the dominant source of trace metals to the ocean. In coastal waters and estuaries, rivers are even more important, and may be augmented by waste water and industrial discharges. With few exceptions, therefore, trace metal concentrations in estuaries are greater than in oceanic waters and influence those in coastal waters. It has been demonstrated that fresh waters and estuaries are the areas in which the results of efforts to reduce trace metal inputs will be most readily detected (Yeats, Bewers & Walton 1978; Balls 1989). Differences in trace metal concentrations between estuaries can provide an indication of their relative state of contamination, caution must be exercised however to take into account the geochemical behaviour of individual metals.

The Clyde, Forth and Tay are the three most important estuaries in Scotland. The population of the Clyde catchment is approximately 2.5 million, of which 1.75 million reside in the Clydeside conurbation centred on Glasgow (Farmer 1983). The effluent of approximately half of Scotland's

population and industry drains into the Clyde
Estuary and Firth of Clyde (Haig 1986).
Approximately a further quarter of Scotland's
population (1.3 million) enters the Forth Estuary and
Firth of Forth (Leatherland 1987). By contrast the
catchment of the Tay is characterised by low
population densities and the estuary has been
described as "one of the least contaminated in
Europe" (Sholkovitz 1979).

The quantity of reliable information on dissolved
trace metal concentrations in these three estuaries
has until recently been rather limited (e.g. MacKay
& Leatherland 1976; Davies 1987). New projects to
examine trace metal distributions in the Clyde, Forth
and Tay Estuaries have however recently been
completed. The detailed interpretation of the data
appears in recent and planned publications (Muller,
Tranter & Balls 1994; Laslett 1993; Laslett & Balls
1995). The present paper summarises the dissolved
trace metal data and contrasts their distributions and
behaviour between the three estuaries.

Description of the study areas

Detailed descriptions of the three estuaries will not
be given here since they are available elsewhere
(Clyde: Muller, Tranter & Balls 1994; Forth and
Tay: Balls 1992) and Figure 1 gives details of the
sampling locations used during the studies presented
here. Annual average freshwater inputs to the
Clyde, Forth and Tay Estuaries are respectively 80
(Poodle 1986), 63 and 198 m^3 s^{-1} (Balls 1992).
Estimates of the residence time of water in the three
estuaries are also available, Clyde 3-7 days
(Muller,Tranter & Balls 1994), Tay and Forth 2-14
and 7-50 days respectively (Balls 1992).

Methods

Survey dates for each estuary are summarised in
Table 1. All surveys were completed around high
water, in the Forth and Tay this was always during
spring tides. Sampling and analytical details are
given elsewhere (Muller, Tranter & Balls 1994;
Laslett 1993; Laslett & Balls 1995), only a brief
summary will be given here.

Samples for trace metal analysis were obtained using
either the sampler described by Balls and Laslett
(1991) or the pump system described by Muller,
Tranter & Balls (1994). All samples were filtered
through 0.4 μm polycarbonate membranes
(Nuclepore) and preserved by the addition of high
purity acid. Analysis was based on the extraction
procedure of Danielsson *et al.* (1982) as modified by
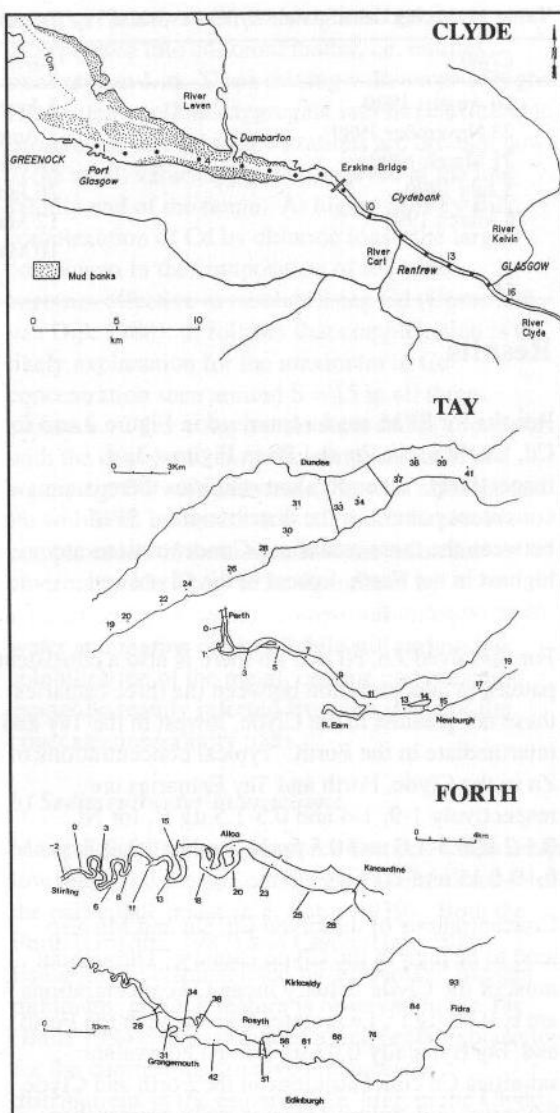
Figure 1. Location map of the Clyde, Forth and Tay
Estuaries. The larger scale maps indicate
sampling positions. In the Forth numbers relate
to km below Stirling, in the Tay to km below
Perth.

Statham (1985). Quality control was achieved by
the inclusion of a certified reference material
(CASS-2, National Research Council of Canada).
At all stages of sampling and analysis precautions
were taken to minimise the possibility of
contamination. These included the acid washing of
sample bottles and laboratory ware and the use of
laminar flow cabinets to reduce the possibility of
atmospheric contamination.

Suspended particulate matter (SPM) concentrations
were determined gravimetrically by filtering known
volumes of water through pre-weighed membranes.
These were subsequently rinsed with distilled water
to remove salt and dried prior to reweighing.

Table 1. Survey dates in the Clyde, Forth and Tay Estuaries.

Clyde	Forth	Tay
20 August 1989	5 June 1989	4 July 1989
23 November 1989	3 August 1989	1 August 1989
22 March 1990	14 November 1989	28 September 1989
5 July 1990	26 January 1990	28 November 1989
4 March 1991	12 March 1990	28 February 1990
	10 May 1990	26 April 1990
		22 June 1990

Results

Results for SPM are summarised in Figure 2 and for Cd, Cu, Mn, Ni, Zn and Pb in Figures 3a-f respectively. At equivalent salinities there is a consistent pattern in the distribution of SPM between the three estuaries. Concentrations are highest in the Forth, lowest in the Clyde and intermediate in the Tay.

For dissolved Zn, Ni and Pb there is also a consistent pattern in concentration between the three estuaries, these are greatest in the Clyde, lowest in the Tay and intermediate in the Forth. Typical concentrations of Zn in the Clyde, Forth and Tay Estuaries are respectively 1-9, 1-4 and 0.5-1.5 μg l^{-1}, for Ni, 0.5-2.0, 0.5-1.0 and 0.5 μg l^{-1}, for Pb, 0.3-0.7, 0.10-0.15 and <0.1 μg l^{-1}.

Concentrations of dissolved Cd, Cu and Mn also tend to be high in the Clyde Estuary. Throughout most of the Clyde Estuary mean Cd concentrations are *c.* 0.05 μg l^{-1}, i.e. greater than those in the Forth and Tay (typically 0.03 μg l^{-1}). At equivalent salinities Cu concentrations in the Forth and Clyde Estuaries (1-1.5 μg l^{-1}) are generally greater than those in the Tay (<1 μg l^{-1}). For salinities <20, Cu concentrations in the Clyde tend to be higher than those in the Forth, but this situation is reversed at salinities >20. Dissolved Mn concentrations in the Clyde (*c.* 20-120 μg l^{-1}) and Forth (*c.* 15-70 μg l^{-1}) are much higher than those in the Tay (<10 μg l^{-1}). In the Clyde the maximum concentrations tend to occur at low salinity (<10) while in the Forth they do so at mid-salinity (10-25).

Discussion

SPM distributions

The elevated SPM loadings in the Forth (Figure 2) are due to the presence of a distinct turbidity maximum in the upper estuary. The location and magnitude of this feature have been demonstrated to be a function of river flow (Balls 1992). Low river flow conditions allow the turbidity maximum to penetrate farther upstream, resuspension of sediments then occurs in a low volume part of the estuary, SPM concentrations are consequently high. The turbidity maximum is moved downstream and is of lower intensity under high river flow conditions.

A less dramatic turbidity maximum is observed in the Tay Estuary, there however it is controlled by wind-induced resuspension rather than by river flow and channel topography (Weir & McManus 1987). By comparison with the estuaries of the Forth and Tay the turbidity of the Clyde is very low. The maintenance of a navigable channel to the city of Glasgow necessitates the removal of sediment from the estuary (480,000 tonnes in 1992 - SOAFD unpublished data). The dredging and canalisation of the estuary are considered to be important factors in determining the low turbidity of the estuary. The small mean spring and neap tidal ranges of the Clyde Estuary (3.1 and 1.8 m at Greenock) relative to those in the Tay (4.7 and 2.4 m at Dundee) and Forth (5.0 and 2.5 m at Rosyth) are also likely to contribute to the contrasting turbidities.

Processes influencing dissolved trace metal distributions

If trace metal distributions in the Clyde, Forth and Tay Estuaries were controlled by simple mixing between river water and sea water then the concentration/salinity plots could be represented by a straight line. From Figure 3, however, it is apparent that such a simple explanation cannot satisfactorily explain any of the distributions observed. While clear gradients related to salinity exist for Cu, Mn, Ni, Pb and Zn in the Clyde, the variability indicates that other processes are also involved. Rather than discuss each metal individually, it is the intention to identify some of these processes and select specific examples to demonstrate their importance.

a) Complexation

Relative to Cd concentrations at mid-salinity, those at low salinity are small (Forth, Tay <0.01 μg l^{-1}, Clyde *c.* 0.03 μg l^{-1}. This effect has been observed in other estuaries (Elbaz-Poulichet *et al.* 1987) and has been attributed to the changes in the physico-chemical conditions which occur in the transition from fresh water to sea water. In the fresh
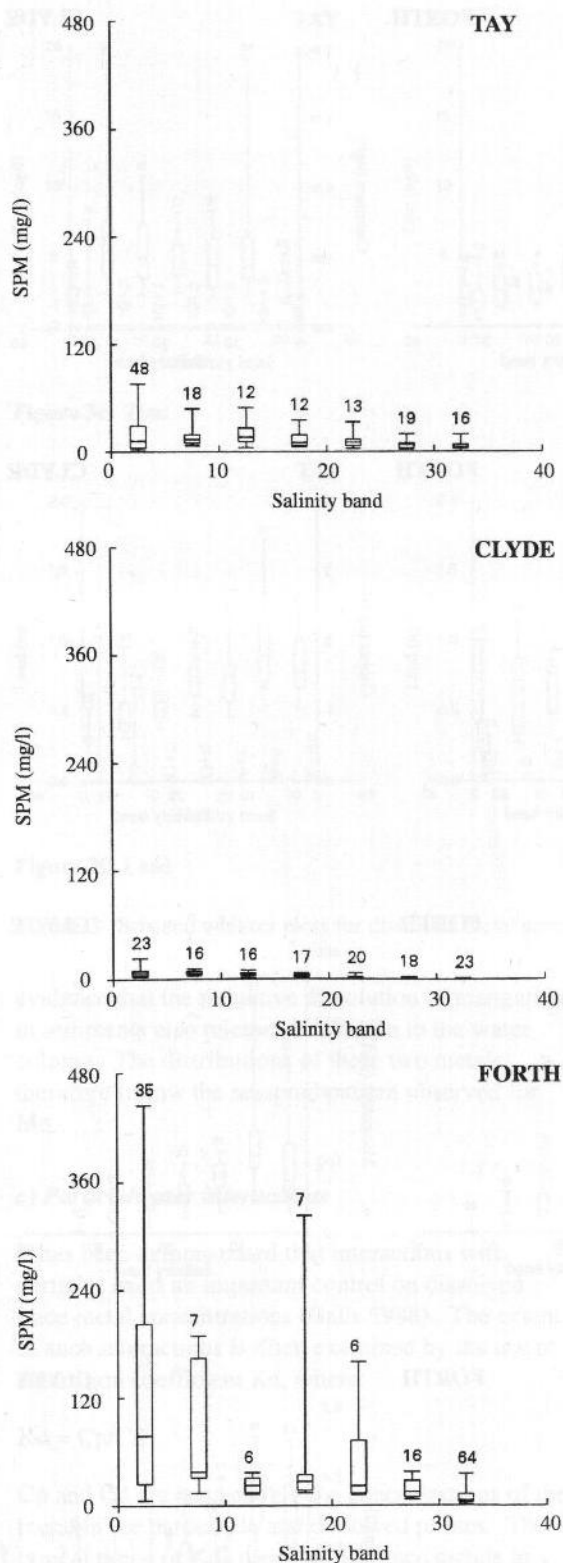
Figure 2. Box and whisker plots of SPM distribution in the Tay, Forth and Clyde Estuaries for salinity bands 0-5, 5-10, 10-15, 15-20, 20-25, 25-30 and >30. The middle of the box gives the median concentration, the edges of the box include half the values between this and the range (indicated by the whiskers). The number of data points included in each band is given at the top of each box and whisker plot.

water environment Cd is thought to be largely incorporated into colloidal matter, i.e. entities smaller than 1 m. Upon mixing with water of higher salt content, colloids aggregate into larger, filterable particles so that Cd concentrations are brought down to the small values typically observed at the low salinity end of the range. At higher salinity still, complexation of Cd by chloride ions - the largest component in the composition of sea water - becomes effective in resolubilising Cd (Comans & van Dijk 1988). It follows that complexation is the likely explanation for the maximum in Cd concentration seen around S = 15 in all three estuaries. Other trace metals form stable complexes with the dissolved inorganic components of sea water, e.g. Cu with carbonate, Zn with chloride and Pb with both carbonate and chloride. However, complexation of these metals in the estuarine environment is likely to be dominated by interactions with organic compounds of both fresh water and marine origin. While still promoting solubilisation of the metal, organic complexation cannot be readily inferred from the shape of the concentration/salinity plots.

b) Sediment/water interactions

Manganese is a redox-sensitive element which under low dissolved oxygen conditions is solubilised from the particulate phase (e.g. Eaton 1979). Both the Forth (Griffiths 1987) and Clyde (Haig 1986) Estuaries are characterised by a dissolved oxygen minimum; no such feature is observed in the Tay (Balls 1994). This provides a first order explanation for the contrasting dissolved manganese distributions in the estuaries, i.e. high in the Clyde and Forth, low in the Tay (Figure 3c).

Maximum Mn concentrations in the Clyde and Forth occur in mid-estuary rather than at low salinity. Similar features in other estuaries have been attributed to inputs from sediments (e.g. Tamar, Knox *et al.* 1981). In the Forth, the magnitude of the mid-estuary maximum has been demonstrated to be related to the residence time of water in the estuary and the intensity of dissolved oxygen minimum (Laslett & Balls 1995). Maximum Mn concentrations are therefore associated with summer conditions when river flow and dissolved oxygen exhibit their annual minima. Maximum Mn concentrations in the Clyde are also associated with low flow summer conditions in the estuary (Muller, Tranter & Balls 1994). In the case of the Forth inputs of dissolved Mn have also been shown to occur during periods of sediment resuspension (Laslett & Balls 1995).

In the Forth, the distributions of dissolved nickel and zinc exhibit broad mid-estuarine maxima (Figures 3d and 3e respectively). This can be taken as

TAY   FORTH   CLYDE

Figure 3a. Cadmium
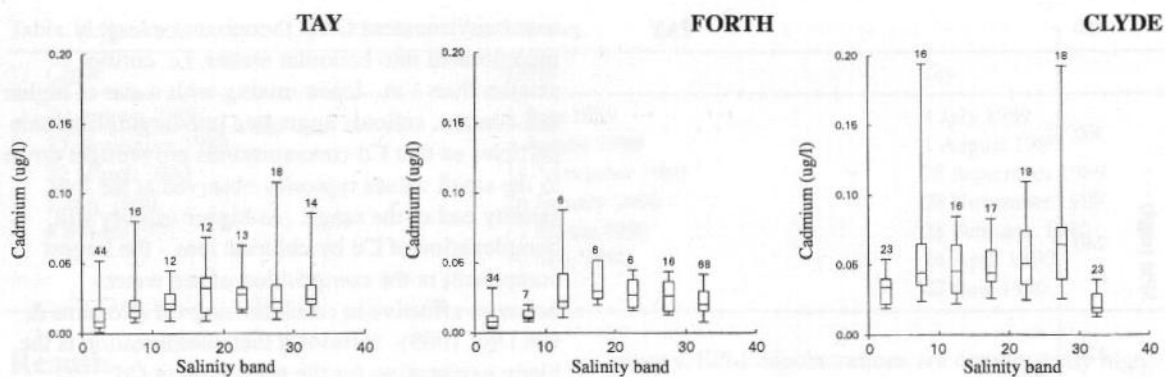
TAY   FORTH   CLYDE
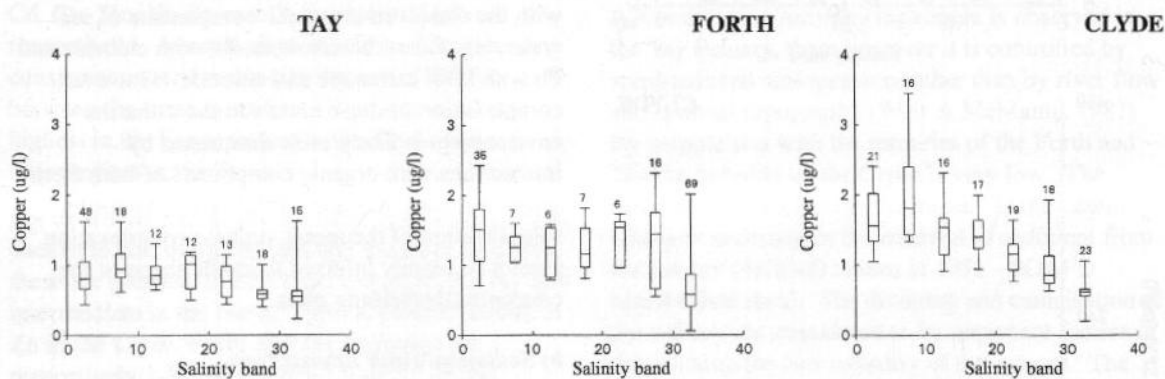
Figure 3b. Copper
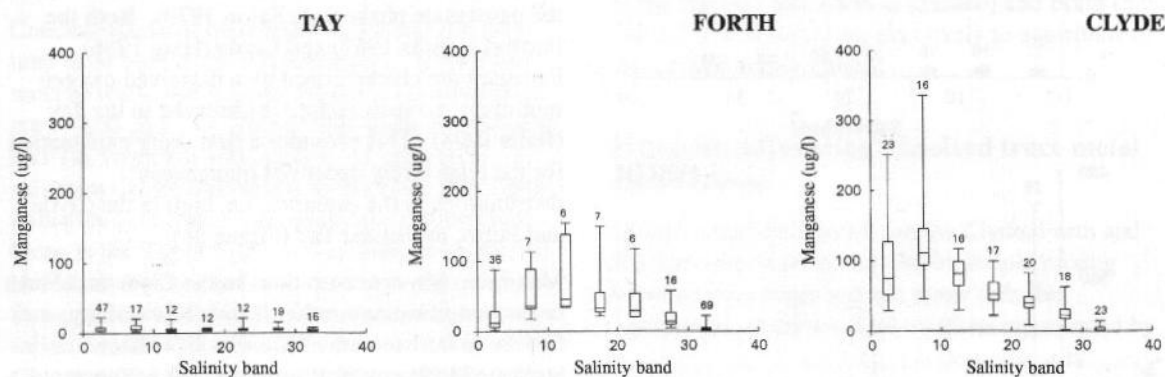
TAY   FORTH   CLYDE

Figure 3c. Manganese
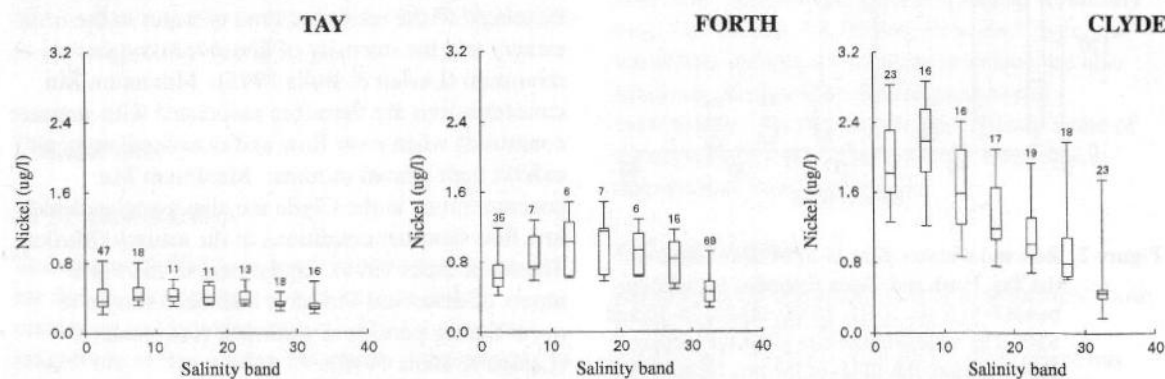
TAY   FORTH   CLYDE

Figure 3d. Nickel

Figure 3e. Zinc
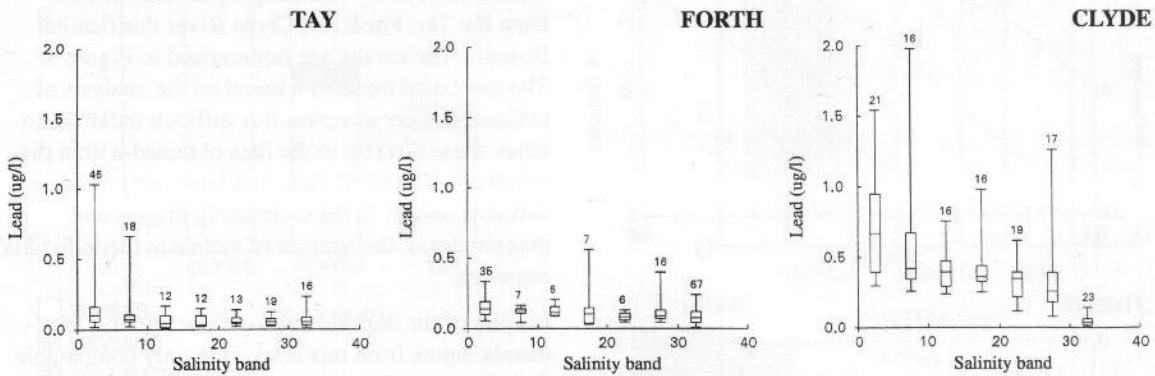
Figure 3f. Lead

Figure 3. Box and whisker plots for dissolved metal concentrations in the Tay, Forth and Clyde Estuaries.

evidence that the reductive dissolution of manganese in sediments also releases Ni and Zn to the water column. The distributions of these two metals therefore follow the seasonal pattern observed for Mn.

c) Particle/water interactions

It has been demonstrated that interactions with particles exert an important control on dissolved trace metal concentrations (Balls 1988). The extent of such interactions is often examined by the use of a partition coefficient Kd, where:

Kd = Cp/Cd

Cp and Cd are respectively the concentrations of the metal in the particulate and dissolved phases. The typical range of Kds observed for trace metals in natural waters is 10^5-10^7. Typical values of the metals studied here are Cd 10^4, Cu, Zn and Ni 10^5 and Pb, Mn 10^7. The effects of the contrasting SPM concentrations in the Clyde, Forth and Tay Estuaries can be examined using Figure 4. From this diagram it is clear that a higher proportion of the total metal concentration will be associated with the dissolved phase in the Clyde, i.e. interactions with particulates are more important in the Forth and Tay.

This may explain why only in the Clyde is there any clear relationship between dissolved Pb and salinity. In the Forth and Tay sorption onto SPM within the estuary is likely to be the dominant controlling process. There is evidence that this is also the case for other metals, e.g. Cu. In the Clyde Estuary concentrations show a decrease with increasing salinity whereas in the Forth they remain relatively constant over large stretches of the estuary.

d) Point sources and discharges

The distribution of trace metals in the vicinity of point sources has been shown to result in patchy distributions which are difficult to explain on the basis of me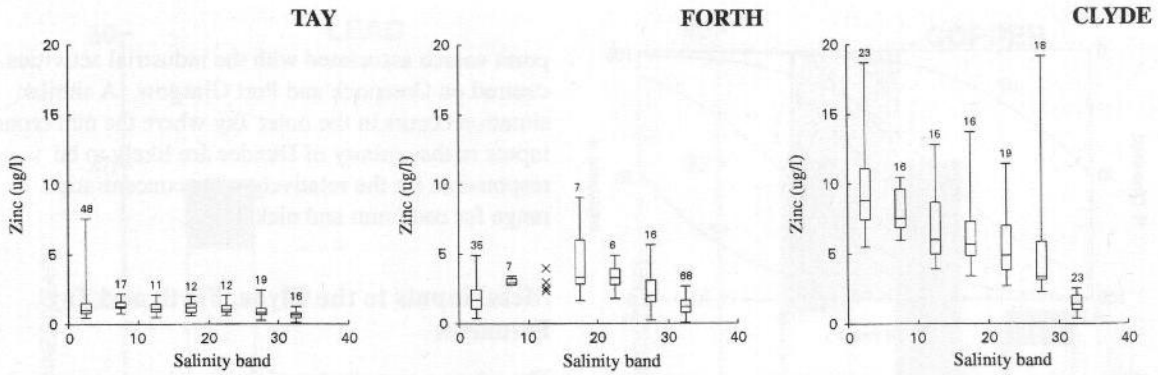tal/salinity plots (Paulson, Curl & Feely 1989). This heterogeneity is attributable to sampling in locations where point sources have had insufficient time to lose their individual identity in the main water mass. In the present study, some of the variability in the averaged data has been attributed to seasonal factors associated with geochemistry, e.g. Mn, Ni and Zn in the Forth. While it is difficult to link particular features with specific discharges, some examples are apparent.

In the Forth, a wide range is evident in copper concentrations in the two high salinity bands.

CLYDE

TAY

FORTH

Figure 4. The effect on the % of the total concentration in the dissolved and particulate phases of varying SPM loading and Kd value. Typical SPM loadings for the three estuaries are indicated.
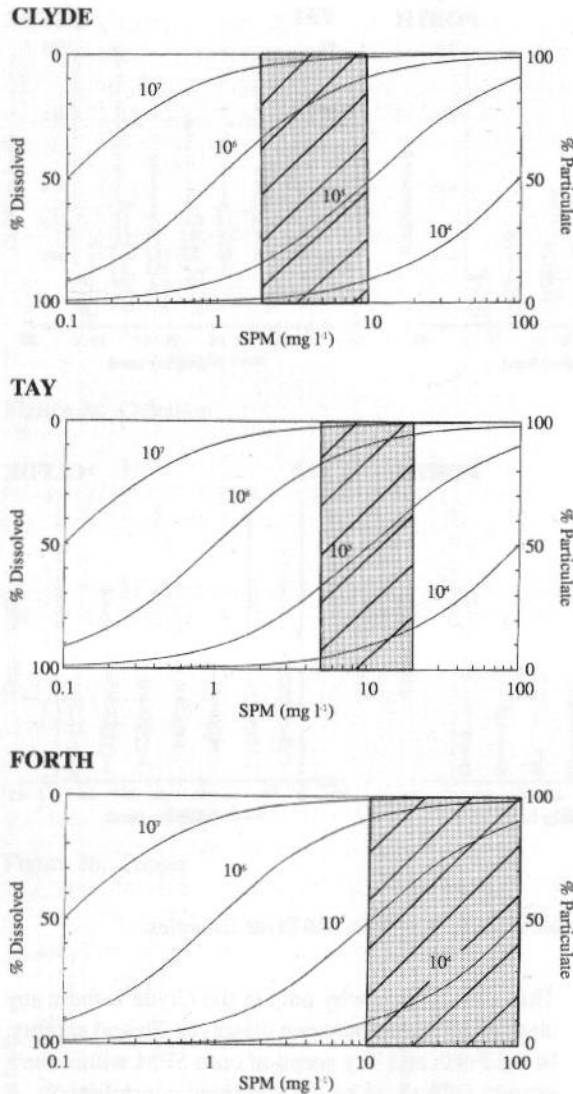
The presence of a known industrial input at Grangemouth was evident in all surveys (Laslett 1993). This always occurred at the same geographical position in the estuary, even though the salinity varied due to differences in river flow. In the presentation used here, the effect of the input is apparent in both the 25-30 and >30 salinity bands.

Other examples are difficult to identify positively but some general comments can be made. The distribution of dissolved Cd in the lower Clyde Estuary is occasionally influenced by local sources of contamination from unidentified inputs. Yet, the concentration/salinity relationship in this part of the estuary is always linear. This militates against desorption from SPM - whose Cd content is, in any event, far too low to support the observed increase in Cd concentration - and supports the hypothesis of a

point source associated with the industrial activities centred on Greenock and Port Glasgow. A similar situation occurs in the outer Tay where the numerous inputs in the vicinity of Dundee are likely to be responsible for the relatively wide concentration range for cadmium and nickel.

Metal inputs to the Clyde, Forth and Tay Estuaries

The relative magnitudes of the riverine, sewage and industrial sources of four metals (Pb, Cu, Cd and Zn) were examined by obtaining input data for 1989 from the Tay, Forth and Clyde River Purification Boards. The results are summarised in Figure 5. The estimated inputs are based on the analysis of unfiltered water samples, it is difficult therefore to relate these directly to the data obtained within the estuaries. The input data does however provide a valuable insight to the contrasting origins and magnitudes of the sources of metals to the individual estuaries.

In spite of the high freshwater flow into the Tay, metals inputs from this source are only comparable to or less than those into the Forth and Clyde. This observation is consistent however with the relatively low metal concentrations in the low salinity part of the estuary (Figure 2).

There are other features of the survey data which are consistent with the input estimates. Inputs of Pb to the Clyde are 2-4 times higher than those to the Forth and Tay. The relatively high dissolved Pb concentrations in the Clyde (Figure 2f) appear to be a direct consequence of this. The relative importance of the industrial source of Cu to the Forth is also evident, the local elevation of Cu concentrations in the estuary has already been discussed. Sewage-related inputs of trace metals to the Tay are significant, these are clustered around Dundee and may explain the higher concentrations of some metals observed in this area, e.g. Cd (Figure 3a).

Comparison with other UK estuaries

Literature data can be used to extend the comparison of dissolved trace metal concentrations to other major UK estuaries. Those selected for this comparison were the Tyne, Wear, Tees, Humber, Thames, Severn and Mersey. All of these are included in the UK National Monitoring Plan. The results are summarised in Table 2 and in histogram form in Figure 6. The extended comparison is limited to concentration range, a more detailed statistical approach has not been attempted since the publications cited present summarised information
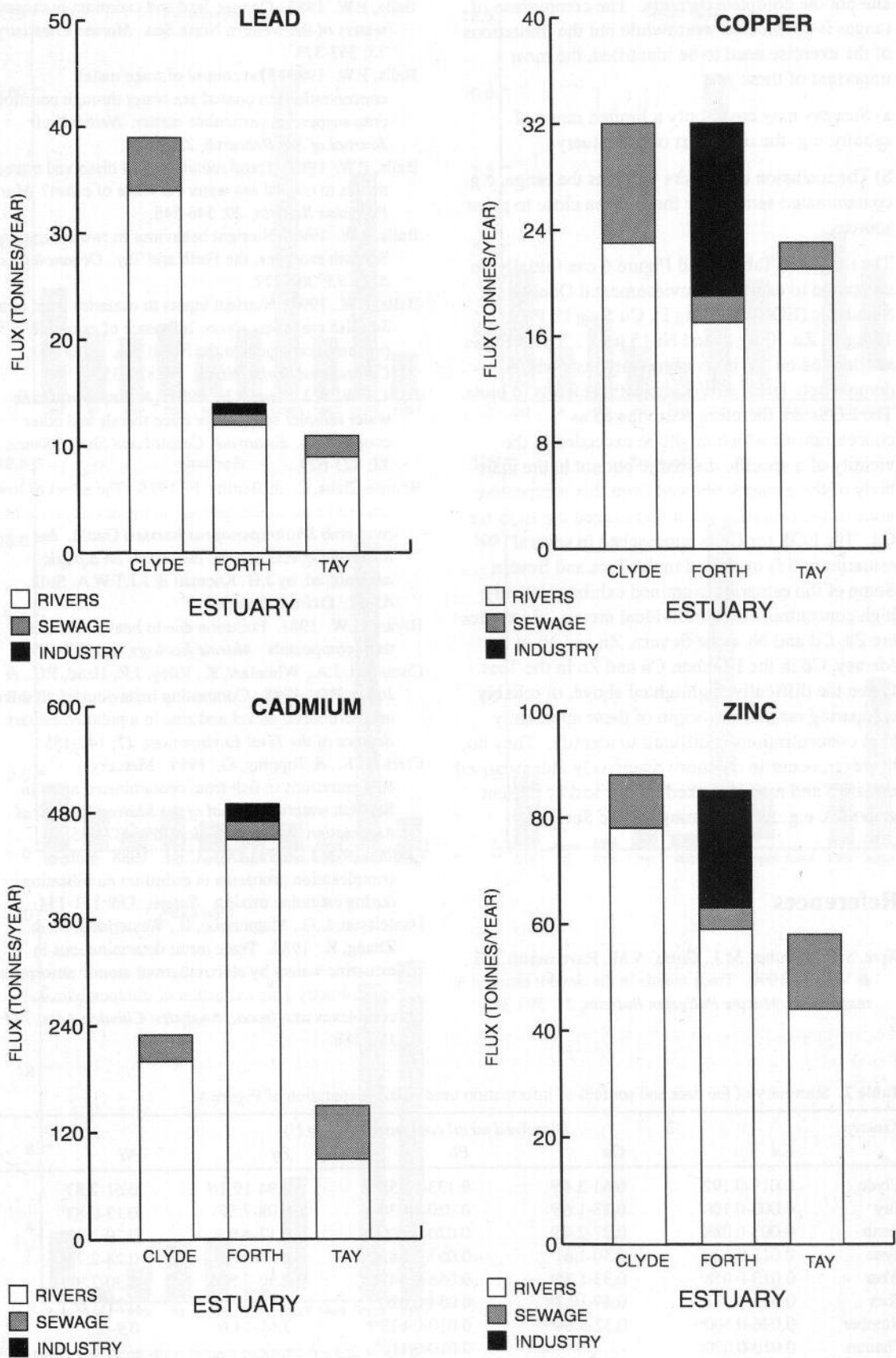
Figure 5. Estimates of the total inputs (dissolved + particulate) of Pb, Cu, Cd and Zn to the Clyde, Forth and Tay Estuaries. Each estimate is broken down into river, sewage and industrial sources. Data provided by the Clyde, Forth and Tay River Purification Boards.

and not the complete datasets. The comparison of ranges is considered worthwhile but the limitations of the exercise need to be identified, the most important of these are:

a) Surveys may cover only a limited range of salinity, e.g. the outer part of the estuary.

b) The inclusion of outliers will bias the range, e.g. contaminated samples or those taken close to point sources.

The ranges in Table 2 and Figure 6 can initially be compared to estuarine Environmental Quality Standards (EQS), Cd 5 µg l^{-1}, Cu 5 µg l^{-1}, Pb 10 µg l^{-1}, Zn 10 µg l^{-1} and Ni 15 µg l^{-1}. These EQSs are derived on the basis of toxicity tests which demonstrate lethal and/or sub-lethal effects to biota. The EQSs are therefore best viewed as concentrations which might be exceeded in the vicinity of a specific discharge but not in the main body of the estuary. Viewed from this perspective none of the estuaries examined exceed the EQS for Cd. The EQS for Cu is approached in several estuaries and is exceeded in the Tees and Severn. Some of the estuaries examined exhibit relatively high concentrations of individual metals. Examples are Pb, Cd and Ni in the Severn, Zn and Ni in the Mersey, Cd in the Humber, Cu and Zn in the Tees. Given the difficulty, highlighted above, of reliably comparing ranges, the origin of these apparently high concentrations is difficult to identify. They do, however, occur in the more intensively industrialised estuaries and may be linked to past and/or present activities, e.g. metal refining for the Severn.

References

Apte, S.C., Gardner, M.J., Gunn, A.M., Ravenscroft, J.E., & Vale, J. 1990. Trace metals in the Severn estuary: a reappraisal. *Marine Pollution Bulletin, 21*: 393-396.

Balls, P.W. 1985. Copper, lead and cadmium in coastal waters of the western North Sea. *Marine Chemistry, 15*: 363-378.

Balls, P.W. 1988. The control of trace metal concentrations in coastal sea water through partition onto suspended particulate matter. *Netherlands Journal of Sea Research, 23*: 7-14.

Balls, P.W. 1989. Trend monitoring of dissolved trace metals in coastal sea water - a waste of effort? *Marine Pollution Bulletin, 20*: 546-548.

Balls, P.W. 1992. Nutrient behaviour in two contrasting Scottish estuaries, the Forth and Tay. *Oceanologica Acta, 15*: 261-277.

Balls, P.W. 1994. Nutrient inputs to estuaries from nine Scottish east coast rivers: Influence of estuarine processes on inputs to the North Sea. *Estuarine, Coastal and Shelf Science, 39*: 329-352.

Balls, P.W., & Laslett, R.E. 1991. A simple estuarine water sampler suitable for trace metals and other constituents. *Estuarine, Coastal and Shelf Science, 33*: 623-629.

Benijts-Claus, C., & Benijts, F. 1975. The effect of low lead and zinc concentrations on the development of the mud crab *Rhithropanopeus harrissi* Gould. *In: Sublethal effects of toxic chemicals on aquatic animals*, ed. by J.H. Koeman & J.J.T.W.A. Strik, 43-52. Oxford, Elsevier.

Bryan, G.W. 1984. Pollution due to heavy metals and their compounds. *Marine Ecology, 5*: 1289-1431.

Campbell, J.A., Whitelaw, K., Riley, J.P., Head, P.C., & Jones, P.D. 1988. Contrasting behaviour of dissolved and particulate nickel and zinc in a polluted estuary. *Science of the Total Environment, 17*: 141-155.

Clark, G.K., & Topping, G. 1989. Mercury concentrations in fish from contaminated areas in Scottish waters. *Journal of the Marine Biological Association, United Kingdom, 69*: 437-445.

Comans, R.N.J., & van Dijk, C.P.J. 1988. Role of complexation processes in cadmium mobilisation during estuarine mixing. *Nature, 336*: 151-154.

Danielsson, L.G., Magnusson, B., Westerlund, S., & Zhang, K. 1982. Trace metal determinations in estuarine waters by electrothermal atomic absorption spectrometry after extraction of dithiocarbamate complexes into freon. *Analytica Chimica Acta, 144*: 183-188.

Table 2. Summary of the data and sources of information used in the preparation of Figure 4.

| Estuary | Dissolved metal concentration (µg l^{-1}) | | | | |
	Cd	Cu	Pb	Zn	Ni
Clyde	0.019-0.192[j]	0.63-3.45[j]	0.133-1.955[j]	2.94-19.16[j]	0.61-2.87[j]
Tay	0.003-0.108[b]	0.23-1.63[b]	0.020-1.030[b]	0.08-7.57[b]	0.13-0.83[b]
Forth	0.003-0.088[b]	0.27-2.43[b]	0.020-0.400[b]	0.12-4.92[b]	0.29-1.49[b]
Tyne	0.011-0.126[a]	0.30-1.61[a]	0.057-1.087[a]	0.55-25.2[a]	0.28-2.75[a]
Wear	0.013-0.058[a]	0.33-1.35[a]	0.058-0.547[a]	0.50-7.53[a]	0.30-2.93[a]
Tees	0.015-0.097[a]	0.49-10.3[a,c]	0.054-0.820[a]	0.70-117[a,c]	0.21-1.0[c]
Humber	0.026-0.600[a,g]	0.32-3.64[a,g]	0.010-0.618[a,g]	3.61-14.6[a]	0.9-6.3[a]
Thames	0.010-0.070[i]	-	0.010-0.110[i]	-	-
Severn	0.005-0.450[b,d]	0.50-5.0[d,e,h]	0.020-10.00[i]	1.61-23.0[e,d]	0.3-15.8[e,d]
Mersey	0.009-0.061[a]	1.28-3.30[a]	0.032-0.877[a]	1.5-55.6[a,f]	0.8-17.4[a,f]

[a] = Law *et al.* (1992); [b] = Laslett (1993); [c] = Taylor (1982); [d] = Apte *et al.* (1990); [e] = Morris (1984); [f] = Campbell *et al.* (1988); [g] = Balls (1985); [h] = Harper (1991); [i] = Harper (1988); [j] = Muller *et al.* (1994)
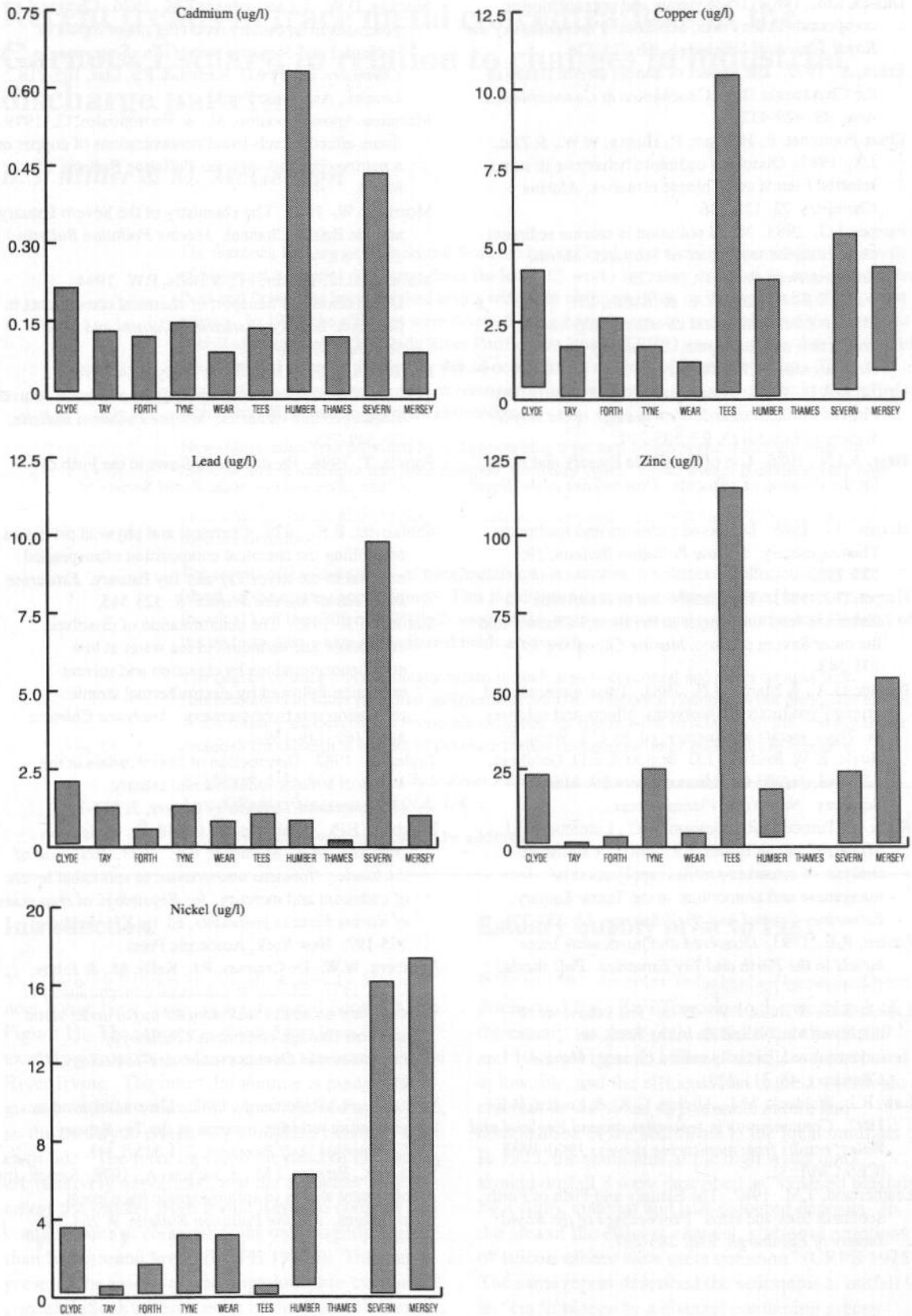
Figure 6. Concentration ranges reported for Cd, Cu, Pb, Zn and Ni for the Clyde, Tay, Forth, Tyne, Wear, Tees, Humber, Thames Severn and Mersey Estuaries. Sources of data are given in Table 2.

Davies, I.M. 1987. Trace metals and organochlorine compounds in the Forth, Scotland. *Proceedings of the Royal Society of Edinburgh, 93*: 315-326.

Eaton, A. 1979. The impact of anoxia on Mn fluxes in the Chesapeake Bay. *Geochimica et Cosmochimica Acta, 43*: 429-432.

Elbaz-Poulichet, F., Holliger, P., Huang, W.W., & Zhu, J.X. 1987. Dissolved cadmium behaviour in some selected French and Chinese estuaries. *Marine Chemistry, 22*: 125-136.

Farmer, J.G. 1983. Metal pollution in marine sediment cores from the west coast of Scotland. *Marine Environmental Research, 8*: 1-28.

Fitzwater, S.E., Knauer, G.A., & Martin, J.H. 1982. Metal contamination and its effects on primary production measurements. *Limnology and Oceanography, 27*: 544-551.

Griffiths, A.H. 1987. Water quality of the estuary and Firth of Forth, Scotland. *Proceedings of the Royal Society of Edinburgh, 93*: 303-314.

Haig, A.J.N. 1986. Use of the Clyde Estuary and Firth for the disposal of effluents. *Proceedings of the Royal Society of Edinburgh, 90B*: 393-405.

Harper, D.J. 1988. Dissolved cadmium and lead in the Thames estuary. *Marine Pollution Bulletin, 19*: 535-538.

Harper, D.J. 1991. The distribution of dissolved cadmium, lead and copper in the Bristol Channel and the outer Severn estuary. *Marine Chemistry, 33*: 131-143.

Knauer, G.A., & Martin, J.H. 1983. Trace elements and primary productivity: problems, effects and solution. *In: Trace metals in seawater*, ed. by C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton & E.D. Goldberg, 825-840. NATO Conference Series IV: Marine Sciences. New York, Plenum Press.

Knox, S., Turner, D.R., Dickson, A.G., Liddicoat, M.I., Whitfield, M., & Butler, E.I. 1981. A statistical analysis of estuarine profiles: application to manganese and ammonium in the Tamar Estuary. *Estuarine, Coastal and Shelf Science, 13*: 357-371.

Laslett, R.E. 1993. *Dissolved and particulate trace metals in the Forth and Tay Estuaries*. PhD thesis, University of Edinburgh.

Laslett, R.E., & Balls, P.W. 1995. The behaviour of dissolved Mn, Ni and Zn in the Forth, an industrialised, partially mixed estuary. *Marine Chemistry, 48*: 311-328.

Law, R.J., Waldock, M.J., Allchin, C.R., & Laslett, R.E. 1992. *Contaminants in sea water around England and Wales: results from monitoring surveys 1990-1992*. ICES CM/E:31.

Leatherland, T.M. 1987. The Estuary and Firth of Forth, Scotland: uses and aims. *Proceedings of the Royal Society of Edinburgh, 93B*: 285-297.

Mackay, D.W., & Leatherland, T.M. 1976. Chemical processes in an estuary receiving major inputs of industrial and domestic wastes. *In: Estuarine Chemistry*, ed. by J.D. Burton & P.S. Liss, 185-218. London, Academic Press.

Moraitou-Apostolopoulou, M., & Verriopoulos, G. 1979. Some effects of sub-lethal concentrations of copper on a marine copepod. *Marine Pollution Bulletin, 10*: 88-92.

Morris, A.W. 1984. The chemistry of the Severn Estuary and the Bristol Channel. *Marine Pollution Bulletin, 15*: 57-61.

Muller, F.L.L., Tranter, M., & Balls, P.W. 1994. Distribution and transport of chemical constituents in the Clyde Estuary. *Estuarine, Coastal and Shelf Science, 39*: 105-126.

Paulson, A.J., Curl, H.C. Jr., & Feely, R.A. 1989. Estimates of trace metal inputs from non-point sources discharged into estuaries. *Marine Pollution Bulletin, 20*: 549-555.

Poodle, T. 1986. Fresh water inflows to the Firth of Clyde. *Proceedings of the Royal Society of Edinburgh, 90B*: 55-66.

Sholkovitz, E.R. 1979. Chemical and physical processes controlling the chemical composition of suspended material in the River Tay and Tay Estuary. *Estuarine and Coastal Marine Science, 8*: 523-545.

Statham, P.J. 1985. The determination of dissolved manganese and cadmium in sea water at low nmol/lconcentrations by chelation and solvent extraction followed by electrothermal atomic absorption spectrophotometry. *Analytica Chimica Acta, 169*: 149-159.

Taylor, D. 1982. Distribution of heavy metals in the waters of a major industrialised estuary. *Environmental Technology Letters, 3*: 137-144.

Thurberg, F.P., Calabrese, A., Gould, E., Greig, R.A., Dawason, M.A., & Tucker, F.K. 1977. Response of the lobster, *Homarus americanus*, to sub-lethal levels of cadmium and mercury. *In: Physiological responses of marine biota to pollutants*, ed. by F.J. Vernberg, 185-197. New York, Academic Press.

Vernberg, W.W., De Coursey, P.J., Kelly, M., & Johns, D.M. 1977. Effects of sub-lethal concentrations of cadmium on adult *Palaemonetes pugio* under static and flow through conditions. *Bulletin of Environmental Contamination and Toxicology, 17*: 16-24.

Weir, D.J., & McManus, J. 1987. The role of wind in generating turbidity maxima in the Tay Estuary. *Continental Shelf Research, 7*: 1,315-1,318.

Yeats, P.A., Bewers, J.M., & Walton, A. 1978. Sensitivity of coastal waters to anthropogenic trace metal emissions. *Marine Pollution Bulletin, 9*: 264-268.

Recent trends in trace metal concentrations in the Garnock Estuary, in relation to changes in industrial discharge patterns

B.S. Miller & M. McGeough

The Garnock Estuary in west central Scotland has suffered trace metals contamination as a result of historical industrial discharges from the local ICI works for many decades. In consequence the flora and fauna was impoverished over a wide area of the mudflats on the west bank of the estuary. In 1981, the effluents were diverted away from the estuary and discharged via a long sea outfall to Irvine Bay. The Clyde River Purification Board (CRPB) was optimistic that recovery of the biological status of the estuary would occur, due to removal of the major inputs. This recovery was delayed by the need to remove inputs from another source of contamination, of which the CRPB had no previous knowledge.

New information was provided by ICI concerning a pit into which waste materials from the manufacture of silicones had been dumped, for many years. These wastes contained very high concentrations of copper in very acid solution. Discussions with the discharger prompted action to treat these wastes, and to change the method of disposal. The resultant improvements with time are described.

The results of a wider survey of trace metals concentrations in sediments collected along the length of the estuary are presented. This highlighted three areas where elevated levels were found: (1) off the 'Silicones Pit'; (2) south of this near to a historical tip site area; and (3) north of the pit in an area where red-coloured muds are found.

The degree of trace metals contamination in each area is described and set in context with contamination of other intertidal sediments in the UK. Temporal changes in the biological status of the estuary are described. Proposals are made for future work in relation to the 'red muds', to establish the biological impact of the trace metals contamination of sediments in this area.

B. Miller* & M. McGeough, Clyde River Purification Board, Rivers House, Murray Road, East Kilbride, Glasgow, G75 0LA, UK.

*To whom correspondence should be addressed.

Introduction

The Garnock Estuary is a small estuary in Ayrshire, near Irvine New Town, in west central Scotland (see Figure 1). The estuary is about 5 km long, extending from its confluence with the estuary of the River Irvine. The intertidal volume is many times greater than the volume of water retained at low tide, so the estuary is effectively completely flushed with each tide. The river inputs to the head of the estuary are relatively unpolluted, and the sea water which enters the estuary from Irvine Bay also contains contaminants at concentrations only slightly higher than background levels (CRPB 1985a). This paper presents the results of investigations into trace metal concentrations in three areas of the Garnock Estuary, the Silicones Pit, the Tip Site and the Red Muds area (see Figure 2).

Estuary quality prior to 1981

Prior to 1981, complex industrial effluents had been discharged from the ICI works to the west bank of the estuary via three main outfalls, numbered 8, 9 and 10 (see Figure 2). These outfalls were exposed at low tide, and the effluents had caused significant changes in the visual appearance, nature and composition of the sediments in the local mudflats. In 1975, the sediments at the high water mark around outfall 8 were described as "covered patchily by a slimy material and rust-coloured deposits. In the area of the effluent channel, glutinous eruptions of silicon rubber were quite common" (CRPB 1975). The same report described the sediments at outfall 9 as "cut in places by a channel containing greeny-white steaming fluid. Effluent winds its way to the river at low water between banks severely contaminated with nitroacetate fragments so dense as to prevent penetration of the core tube. No mud or sand is visible in the vicinity of the effluent.
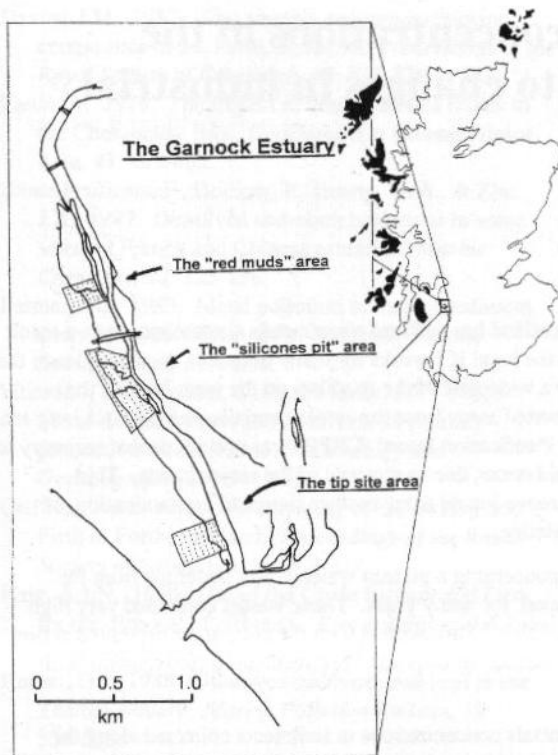
Figure 1. Location map for the Garnock Estuary in west central Scotland.
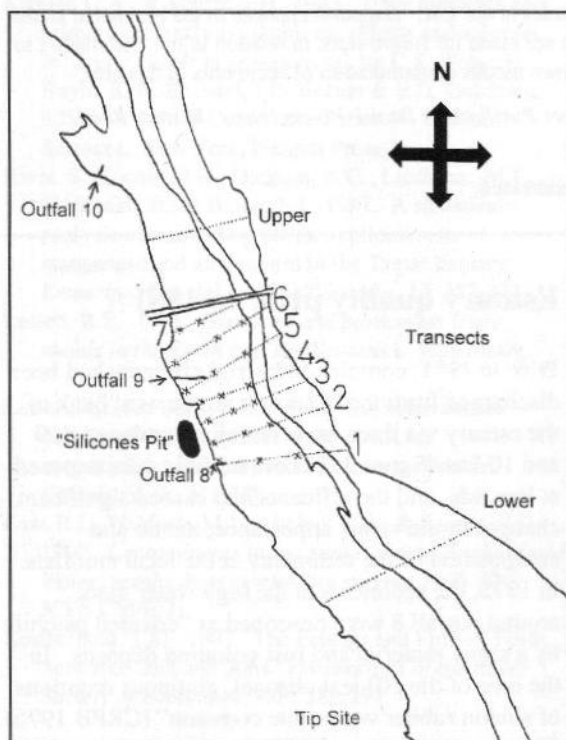

Figure 2. Position of outfalls 8, 9 and 10, 'Silicones Pit' and survey transects.

The 'pseudo-sediment' assumes a totally white fibrous consistency not like estuary sediments".

The effluents badly affected water and sediment

quality, particularly on the west shore of the estuary. Severe ecological impact resulted, such that the local flora and fauna were very impoverished, with macrofaunal species very limited in coverage.

A major change in discharge patterns

In 1981, at a cost of £10 million, ICI commissioned a long sea outfall to discharge the effluents to Irvine Bay, instead of to the Garnock Estuary. The Clyde RPB as regulatory authority was optimistic that recovery of the estuary would take place with time, with re-colonisation by estuarine species as the contaminant concentrations declined. However, the discharger provided new information on another source of contamination resulting from the manufacture of silicones. Waste materials from this process had been dumped for many years into a pit in the sand, close to the factory boundary with the west shore of the estuary. The waste materials discharged to the pit contained copper at very high concentrations, together with hydrochloric acid, so had very low pH, below 1.

The Silicones Pit

The existence of the Silicones Pit caused concern to the CRPB, since metals are particularly mobile in acid solutions (Forstner & Wittmann 1981). Copper has been shown to be released from contaminated sludges into water at pH values below 4.5 (Adams & Sanders 1984), and is highly toxic to marine and freshwater species (Mance 1987). It was feared that the high concentrations of copper in leachate from the pit could threaten local wildlife and prevent or limit re-colonisation of the estuary by macrobenthic infaunal species. The Silicones Pit was situated between outfalls 8 and 9 (Figure 2). Soon after being informed of its existence, the CRPB carried out a survey to assess the degree and extent of its impact. Samples of sediments and pore waters were collected at a grid of sites at high, mid- and low water on nine transects (Figure 2).

Pore waters were sampled since these would directly reflect contamination of the local sediments by the highly acidic, copper-containing leachate seeping into the mudflats area from the pit. At each sampling site a hole was dug to about 0.5 m depth and allowed to fill with pore (or interstitial) water. A 1l polyethylene bottle was filled with pore water for metals analysis, and pH was measured on site. On return to the laboratory, replicate 100 ml portions of the water samples were decanted off and diluted to 1l, for metals analysis. This was carried out using a complexation-extraction method with APDC in

citrate buffer and chloroform, with quantification by flame AAS. Sediment samples for metals analysis were also collected as surface scrapes and from 0.5 m depth in the hole, directly into small plastic pots. These sediments were transferred to plastic petri dishes on return to the laboratory, and the sediments were frozen then lyophilised. The dried sediments were sieved at 500 μm then digested with a mixture of nitric and perchloric acids prior to quantification by flame AAS. These methods for waters and sediments have produced excellent results in recent intercalibration exercises (NMAQC 1994).

Very high pore waters copper concentrations were found for the first survey in June 1982 (Figure 3a), together with low pH values. The samples collected from the high water mark at transects 1 to 4 close to the 'silicones pit' were most affected, with copper concentrations up to 42.3 mg l⁻¹ and pH levels as low as 1.0 in the pore waters. The survey was repeated the following month, and similar levels were found (Figure 3b). Pore waters from the high water site at transect 3 contained 59.5 mg l⁻¹ copper, with pH at 0.7.

Discussions with ICI produced prompt action to treat the wastes. The copper-containing wastes were segregated from the acid wastes, and discharged into separate pits. Lime was added to neutralise the acid wastes, and bunding was installed around the pits. Ground water was pumped out of boreholes close to the pits area and discharged via the long sea outfall. As a result of these measures, improvements were observed during late 1982 and into early 1983 in the copper concentrations and pH values measured in water samples collected from boreholes around the pit. The results for the survey carried out in January 1985 reflected these improvements, with copper levels much lower than before (Figure 3c). The highest pore water copper concentration was 10.4 mg l⁻¹ and the lowest pH value 3.2, for the sites at the high water mark (CRPB 1985b).

Despite the reductions in copper concentrations, the CRPB qualitative biological survey carried out in March 1985 reported that the area between outfalls 8 and 9 remained barren at the high tide and mid-tide positions (CRPB 1985c). However, some small polychaetes had re-established beside outfall 9, and a small area was re-colonised by *Corophium volutator* down-estuary from outfall 8. Re-colonisation further downstream was continuing at a more rapid pace and had reached the lower tidal levels near outfalls 8 and 9.

Improvements in water quality and biological quality were noted in CRPB survey reports over the next few years. In June 1987 pore water copper concentrations had fallen to only 540 μg l⁻¹ at the high tide position on transect 1 (CRPB 1987a). The
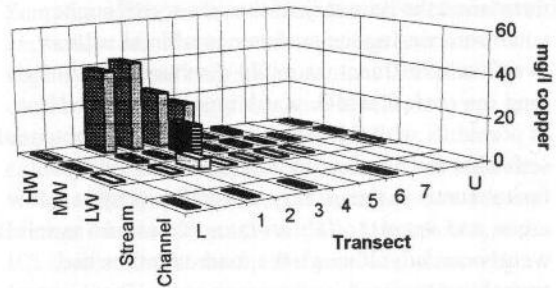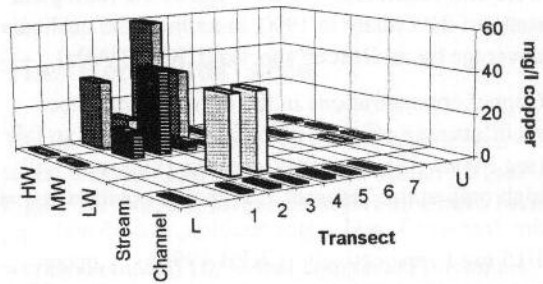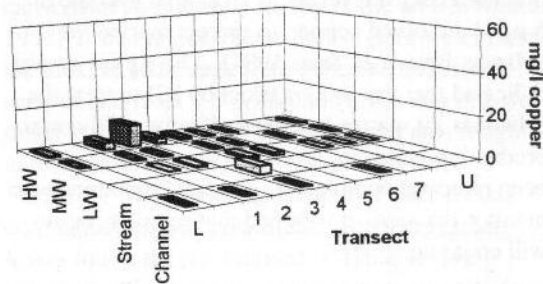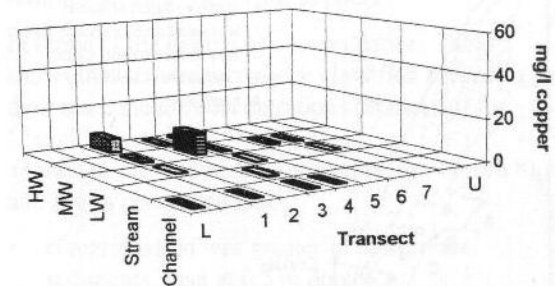
Figure 3. Spatial and temporal trends in pore water copper concentrations mg l⁻¹ in the mudflats area off the 'silicones pit'.

west shore showed some signs of recovery in the mudflats area off the Silicones Pit, but the sediments were reported as capable of supporting only a very impoverished benthos. Unexpected problems were also located, particularly downstream of outfall 8, where large faunal mortalities were found. Some species had extended their coverage, but others appeared to be less common than previously (CRPB 1987b).

During 1989 both natural and man-induced events threatened the recovery of the estuary: drought conditions during the summer combined with an overflow of effluent normally discharged from the long sea outfall, which was temporarily closed due to problems with the pumps. Despite these potential setbacks, re-colonisation continued. In 1990 the faunal status in the estuary was still patchy in a few areas, and some mortalities in mollusca and annelids were recorded, although the macrobenthos had probably recovered its former ranges. There were one or two localities where molluscs particularly were still restricted. Figure 4 shows the biological status of the estuary in 1990, in terms of the qualitative coverage by molluscan species (CRPB 1990a).

Copper concentrations in the pore waters in the mudflats area off the Silicones Pit continued to fall (see Figure 3d), such that levels in 1990 were still high only at the Transect 1, high tide position and at the Transect 3, mid-water position, at 6.46 and 10.5 mg l^{-1} respectively (CRPB 1990b). Copper concentrations in estuary waters were measured by the CRPB as below the Environmental Quality Standard (EQS) level set as an annual average of 5 µg l^{-1} dissolved copper, to protect marine life (Mance, Brown & Yates 1984). The survey results indicated that the actions taken by ICI to treat the Silicones Pit wastes had been effective. Silicones production halted in 1990, and the plant has now been removed completely. The CRPB continues to monitor the area. It is hoped that re-colonisation will continue.

□ Littorinidae (Winkles)
■ *Mytilus edulis* (Mussels)
× *Macoma balthica* (Baltic Tellin)
○ *Mya arenaria* (Soft Clam)
● Cardiaceae (Cockles)
◆ Mortalities
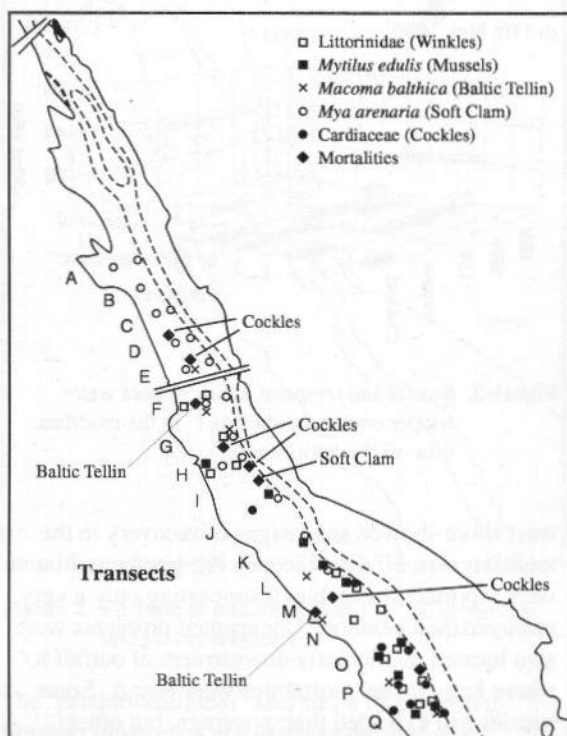
Figure 4. Distribution of molluscan species, 1990.

Developments in the estuary

In January of 1987 the area known as Bogside Flats was designated as a Site of Special Scientific Interest (SSSI) by the then Nature Conservancy Council (now Scottish Natural Heritage). This area extends all the way up the estuary and includes the mudflats on both east and west banks. The area was designated as the only extensive expanse of merse and mudflats between the Solway Firth and the Clyde. The saltmarsh is the best example of this habitat type in Ayrshire and displays a variety of plant and animal communities representative of different degrees of tidal inundation. The intertidal mudflats, saltmarsh and adjacent pasture land are important, since they are extensively used by migrant and wintering wildfowl and waders. There are large wintering flocks of golden plover and redshank, and other species regularly occurring in large numbers include lapwing, dunlin, oystercatcher, shelduck and wigeon (NCC 1987). The CRPB obtained the necessary consents to continue survey work in the estuary. This included permission to collect wild animals and to extract sediment samples as necessary, and to use small boats as sampling platforms.

Garnock Estuary sediment trace metals levels

In 1989 the CRPB carried out an extensive survey of sediment trace metals along the length of the estuary. This survey was planned before the CRPB knew about the discharge of effluents to the estuary via outfalls 8 and 9 caused by the temporary problem with the pumping mechanism for the long sea outfall. Sediment samples were collected at high, mid- and low tide positions on a series of transects (Figure 5). Copper concentrations in the range 13.8 to 326 mg kg^{-1} dry weight were found (Figure 6).

Uncontaminated sediments have been classed as those with copper concentrations below 100 mg kg^{-1} dry weight (Society of the Chemical Industry 1980), while 'safe' concentrations have been calculated as below 85 mg kg^{-1}, using the equilibrium partitioning approach to protect water quality (see Adams, Kimerle & Barnett 1992, and Webster & Ridgway 1994). Most sediments had copper concentrations below these thresholds, but elevated levels were recorded in three areas: (1) at the Silicones Pit; (2) in the lower part of the estuary off the southern part of the tip site; and (3) in the upper part of the estuary around outfall 10. It was not possible to determine to what extent the re-routing of effluent had affected sediments in the 'silicones pit' area, since these were already known to be contaminated. The other two
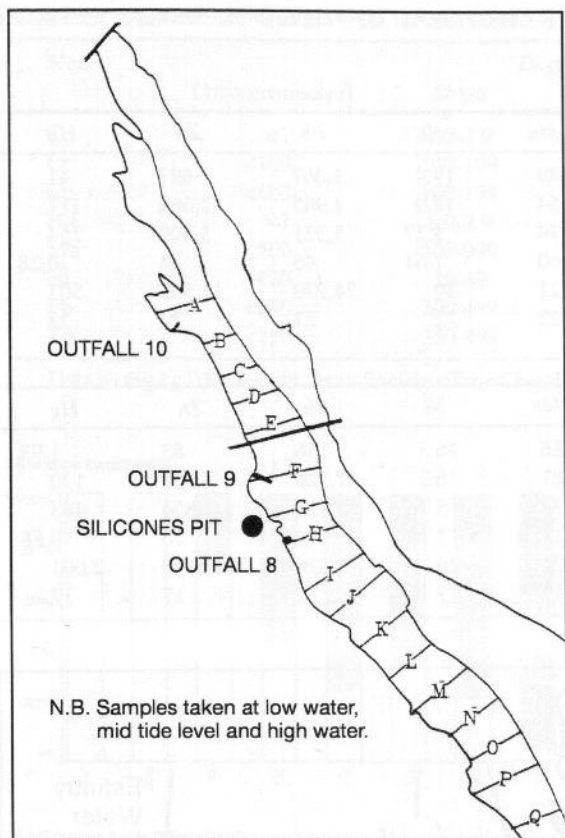
Figure 5. Transects for sediment sampling, 1989.
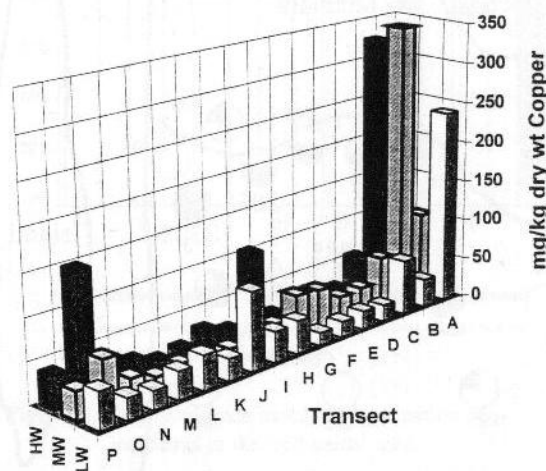
Figure 6. Sediment copper concentrations for transects in the Garnock Estuary, 1989.

areas were investigated further to delineate the affected areas.

The tip site area

The tip site area lies between the silicones pit area and the ICI wharf, on the west side of the estuary. A series of small streams crosses the mudflats at low tide, taking leachate from the tip site to the estuary. Samples of the surface waters run-off were collected and analysed. Trace metals concentrations were slightly elevated only in the sample from the southernmost stream, but these levels were not high enough to cause concern (CRPB 1992). It was calculated that the EQSs set to protect marine life were unlikely to be exceeded in estuary waters, so marine life should not be at risk. Discussions with ICI indicated that the tip site area would soon be 'capped', reducing further the volume of leachate affecting this part of the mudflats area.

The 'Red Muds' area

The third area highlighted as having high metals levels was the 'Red Muds' area off outfall 10 (see Figure 2). Surface sediments in this area have been altered in type by historical discharges from the ICI works via outfall 10, so that compacted fine muds crimson-red in colour now cover the local coarse sands, hence the name of the area. The CRPB carried out an intensive survey of the area in March 1993. It was impossible to collect pore water from the area, so sediments were collected as surface scrapes and from 0.5 m depth in holes dug into the muds at 22 sites on a grid covering an area roughly equivalent in size to 5 football pitches (see Figure 7). The degree and extent of trace metals contamination was quantified. The trace metals levels found are summarised in Table 1. The geographical spread of contamination was similar for lead, copper, zinc and mercury in the surface sediments (see Figure 7 for copper).

In terms of the degree of contamination, Table 2 shows that sediments may be classified according to their trace metals concentrations (Society of the Chemical Industry 1980). These classifications were applied to the 'red muds' sediments (see Figure 8), and it was concluded that:

- contamination was greater in the surface sediments, than at 0.5 m depth;

- the degree of contamination was different for each element;

- all sediments were uncontaminated by chromium and manganese, and about 75% were uncontaminated by nickel;

- more than 50% of the surface sediments were contaminated or more severely contaminated by lead, copper, zinc and mercury; and

- the sediments were most contaminated by mercury, with over 70% of the surface sediments either unusually heavily contaminated, or heavily contaminated.

Table 1. Summary of Garnock Estuary sediment trace metals levels (as mg kg⁻¹ dry weight) in the 'red muds' area for the survey of 31st March 1993.

a) Surface sediments

Statistic	Cd	Cr	Cu	Mn	Ni	Pb	Zn	Hg
Median	1.44	23	250	129	19.4	1,067	697	41
Mean	6.60	24	1,004	154	18.9	2,965	2,662	117
s.d.	9.79	8.48	1,468	74	5.27	5,321	3,809	154
Min	<0.10	6.89	6.06	60	7.64	46	34	0.28
Max	34	45	4,439	321	30	24,979	11,502	503
n	22	22	22	22	22	22	22	22

b) Sediments at 0.5 m depth

Statistic	Cd	Cr	Cu	Mn	Ni	Pb	Zn	Hg
Median	0.05	22	16.3	86	16.3	156	83	1.93
Mean	1.31	23	139	81	16.3	1,328	455	130
s.d.	3.38	8.06	354	32	5.73	3,113	824	483
Min	<0.10	12	3.21	17.8	7.75	14.2	20	0.68
Max	13.8	36	1,287	127	26	12,326	3,170	2,001
n	17	17	17	17	17	17	17	17
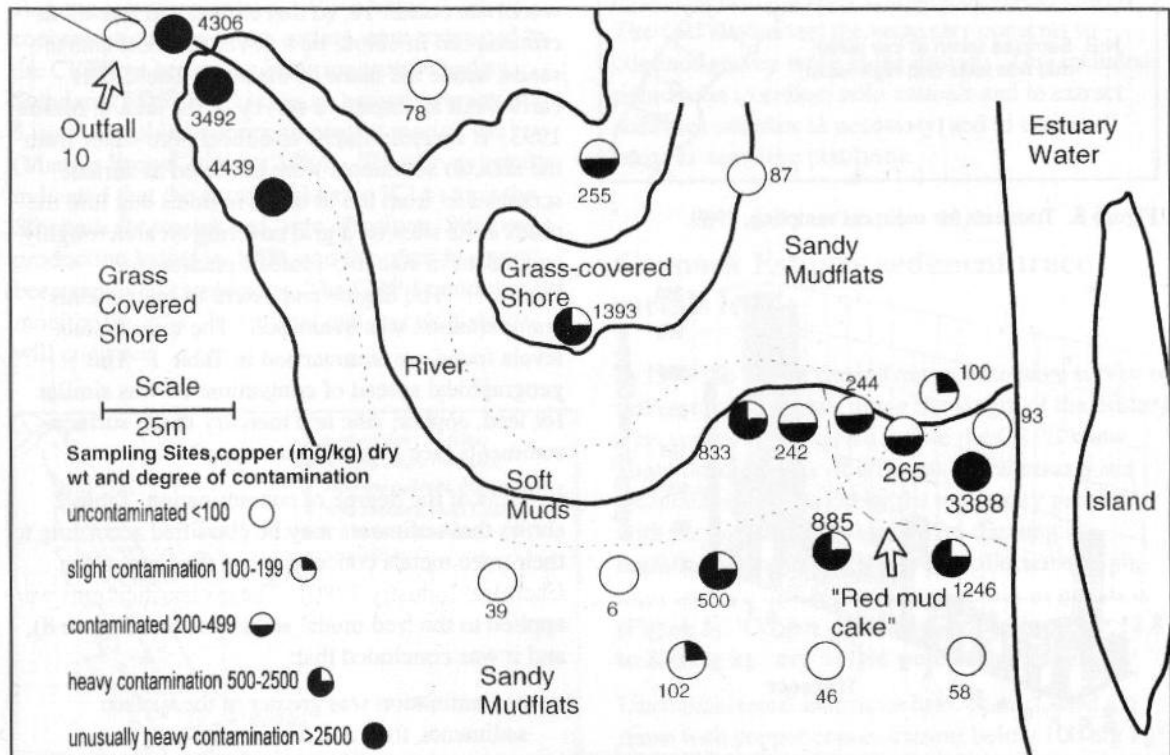
Figure 7. Geographical spread and degree of copper contamination, March 1993.

Two areas in particular were badly affected by contaminated sediments. One area was close to outfall 10 (see Figure 2), and the other was beside the estuary channel, in the area where the muds are visibly red-coloured. The total volume of contaminated sediment was estimated as about 675 m³.

The results were set in context by comparison with average trace metals levels for other saltmarsh and intertidal sediments from other UK estuaries (see

Figure 9). The Garnock Estuary 'Red Muds' were concluded to be highly contaminated compared to UK saltmarsh areas (O'Reilly Weise, Bubb & Lester 1995) and intertidal sediments, even in comparison to estuaries with historic trace metals pollution, such as the Gannel and Restronguet Creek in south-west England (Bryan & Langston 1992).

Direct evidence has yet to be obtained on whether the sediments are causing harm to local flora and fauna, although there are indications that this is

Table 2. Classification of soils for trace metals contamination.

Metal	Degree of Contamination				
	Uncontaminated	Slight	Contaminated	Heavy	Unusually heavy
Cd	<1	1.0-2.9	3.0-9.9	10.0-50	>50
Cr	<100	100-199	200-499	500-2,500	>2,500
Cu	<100	100-199	200-499	500-2,500	>2,500
Hg	<1	1.0-2.9	3.0-9.9	10.0-50	>50
Mn	<500	500-999	1,000-1,999	2,000-1%	>1%
Ni	<20	20-49	50-199	200-1000	>1,000
Pb	<200	200-499	500-999	1,000-2,500	>2,000
Zn	<250	250-499	500-999	1,000-5,000	>5,000

Data as mg kg^{-1} dry weight, from Society of the Chemical Industry (1980).

Surface sediments

Sediments from 0.5m depth

Uncontaminated
Contaminated
Unusually Heavily Contaminated
Slightly Contaminated
Heavily Contaminated
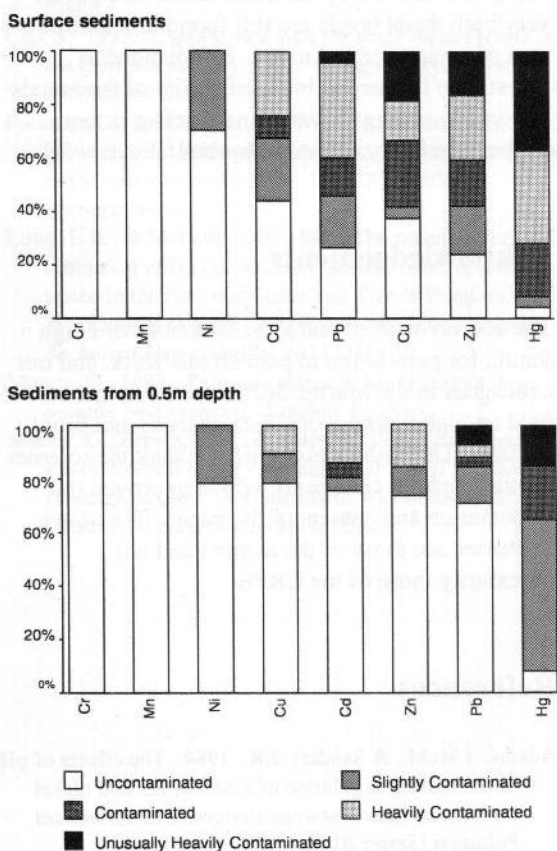
Figure 8. Degree of trace metals contamination of sediments in the 'red muds' area.

Mercury
Zinc
Lead
Copper

mg kg^{-1} dry weight

Figure 9. Comparison of Garnock Estuary 'red muds' trace metals concentrations with other UK intertidal sediments.

likely. Firstly, the area is not being re-colonised by macrofaunal species other than the one or two which are very pollution-tolerant; the shrimp *Corophium volutator* and the ragworm *Nereis diversicolor* were noted by the CRPB in February 1995. The modified sediment type may also be a factor in the limited number of species found. Secondly, the metals levels at many sites exceed sediment quality criteria set using different approaches (compare Table 1 with Table 3).

The 'safe' levels in Table 3 have been set using the equilibrium partitioning approach (Adams, Kimerle & Barnett 1992). This assumes that contaminants in

bulk sediments are in equilibrium with the surrounding waters. A partition coefficient is used to describe the equilibrium, and together with an appropriate water quality standard set to protect marine life, a 'safe' sediment concentration can be calculated for a variety of substances, including trace metals (Webster & Ridgway 1994).

Comparison is also made in Table 3 against ER-L and ER-M levels set using the apparent effects threshold approach. This approach was used by the US National Oceanic and Atmospheric Administration (Long & Morgan 1990) to review 200 datasets from various studies, including spiked sediment bioassays. The biological effects were ordered, and the lower 10 percentile and median identified. These two concentrations were designated Effects Range-Low (ER-L) and Effects Range-Median (ER-M). The median is therefore the concentration above which adverse effects were almost always observed. The median 'Red Muds' metals levels for surface sediments exceed this threshold for mercury, lead and zinc.

The final set of criteria in Table 3 is based on overt

Table 3. Sediment trace metals criteria.

Metal	'Safe' level (1)	ER-L (1)	ER-M (1)	No Effect level (2)	Lowest Effect level (2)	Limit of Tolerance level (2)
Cd	1.60	5.0	9.0	0.6	1.0	10.0
Cr				22	31	111
Cu	85	70		15.0	25	114
Hg	0.024	0.15	1.3	0.1	0.12	2.0
Ni				15.0	31	90
Pb	152	35	110	23	31	250
Zn	132	120	270	65	110	800

Data as mg kg^{-1} dry weight from (1) Webster & Ridgway 1994 and (2) Persaud, Jaagumagi & Hayton 1989. See text for description of terminology.

toxicity to benthic invertebrates, and these are used by the Ontario Ministry of the Environment as sediment management guidelines (Persaud, Jaagumagi & Hayton 1989). Comparison of Table 1 with Table 3 shows that the median metals concentrations for surface sediments in the Garnock Estuary 'Red Muds' area exceed the 'limit of tolerance' levels for copper, lead and mercury, with the zinc levels approaching this threshold, indicating that it is likely that these sediments will cause toxic effects in invertebrates.

Future work

The CRPB recognises the need for the assessment of sediment contamination by laboratory bioassay testing in addition to chemical analysis. A biological response has the advantage of reflecting the bio-available portion of the contaminants, which may be very different from the total amounts determined by chemical analysis (SETAC 1993). The CRPB intends to carry out sediment toxicity tests using the amphipod *Corophium volutator*, since this species is found in the estuary, and to measure metals uptake by other local flora and fauna, such as algae and fish. In this way, the bio-availability of trace metals in the 'red mud' sediments and the degree of harm being caused by the contaminated sediments will be assessed, and decisions made about whether the contaminated material should be left in place, or whether removal should be considered.

Conclusions

Environmental monitoring carried out by the Clyde RPB in the Garnock Estuary identified sediments contaminated by exceptionally high concentrations of trace metals. To meet Clyde RPB requirements, ICI has carried out work to eliminate the major discharges to the estuary. Metals concentrations have subsequently declined, and some areas are being re-colonised by flora and fauna. However, very high metal levels are still found in a limited area of compacted red muds. It is planned to investigate further the bio-availability of the metals by toxicity testing to determine whether or not further regulatory action is required.

Acknowledgements

References

Adams, T.McM., & Sanders, J.R. 1984. The effects of pH on the release to solution of zinc, copper and nickel from metal-loaded sewage sludges. *Environmental Pollution (Series B), 8:* 85-89.

Adams, W.J., Kimerle, R.A., & Barnett, J.W. 1992. Sediment toxicity and aquatic life assessment. *Environmental Science and Technology, 26 (10):* 1864-1875.

Bryan, G.W., & Langston, W.J. 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. *Environmental Pollution, 76:* 89-131.

CRPB. 1975. *Garnock Estuary survey: report on qualitative biological survey, 1975.* Internal Report, Glasgow, Clyde River Purification Board.

CRPB. 1985a. *Water quality: a baseline report.* Glasgow, Clyde River Purification Board.

CRPB. 1985b. *The Garnock Estuary: a report on the chemical status of the sediments on the west bank of the Garnock Estuary in the area adjacent to ICI's 'Silicones Pit'.* Internal Report. Glasgow, Clyde River Purification Board.

CRPB. 1985c. *Garnock Estuary survey: report on qualitative biological survey 1985.* Internal Report. Glasgow, Clyde River Purification Board.

CRPB. 1987a. *Garnock Estuary survey, 1987. Trace metals in waters.* Internal Report. Glasgow, Clyde River Purification Board.

CRPB. 1987b. *Garnock Estuary survey: report on qualitative biological survey, 1987.* Internal Report. Glasgow, Clyde River Purification Board.

CRPB. 1990a. *Garnock Estuary survey: report on qualitative biological survey, 1990.* Internal Report. Glasgow, Clyde River Purification Board.

CRPB. 1990b. *Trace metals levels in Garnock Estuary waters: report on results for the survey of May, 1990.* Internal Report. Glasgow, Clyde River Purification Board.

CRPB. 1992. *Unpublished data for trace metals levels in the Garnock Estuary, 1992.* Glasgow, Clyde River Purification Board.

Forstner, U., & Wittmann, G.T.W. 1981. Metal transfer between solid and aqueous phases. *In: Metal pollution in the aquatic environment,* 197-270. Berlin, Springer-Verlag.

Long, E.R., & Morgan, L.G. 1990. The potential for biological effects of sediment sorbed contaminants tested in the National Status and Trends Program. *In: National Oceanic & Atmospheric Administration Technical Memorandum, NOS OMA 52.*

Mance, G. 1987. *Pollution threat of heavy metals in aquatic environments.* London, Elsevier.

Mance, G., Brown, V.M., & Yates, J. 1984. *Proposed environmental quality standards for List II substances in water: copper.* Medmenham, Water Research Centre. (Technical Report No. 210.)

NMAQC. 1994. *National Marine AQC Scheme: results for distribution 7.* Medmenham, Water Research Centre.

NCC. 1987. *Bogside Flats Site of Special Scientific Interest, Cunninghame District.* Balloch, Nature Conservancy Council.

O'Reilly Weise, S.B., Bubb, J.M., & Lester, J.N. 1995. The significance of sediment metal concentrations in two eroding Essex saltmarshes. *Marine Pollution Bulletin, 30 (3):* 190-199.

Persaud, R., Jaagumagi, R., & Hayton, A. 1989. *Development of provincial sediment quality guidelines.* Toronto, Ontario Ministry of the Environment.

Society of the Chemical Industry. 1980. Guidelines for classification of contaminated soils. Site investigations and materials problems. *In: Proceedings of the Conference on Reclamation of Contaminated Land, Eastbourne. October 1979.*

SETAC. 1993. *Guidance document on sediment toxicity tests and bioassays for freshwater and marine environments.* Proceedings of a workshop on sediment toxicity assessment at Renesse, Netherlands, ed. by I.R. Hill, P. Matthiessen & F. Heimbach. Society of Environmental Toxicology and Chemistry - Europe.

Webster, J., & Ridgway, I. 1994. The application of the equilibrium partitioning approach for establishing sediment quality criteria at two UK sea disposal sites. *Marine Pollution Bulletin, 28 (11):* 653-661.

Comparison of the influence of sediment and diet as sources of metals for diatoms and meiofauna

J. Figures, A.S. Hursthouse & J.E. Matthews

Levels of Cr, Fe, Mn, Ni and Zn were determined by ICP-AES and GFAAS in epipelic diatoms, meiofauna and oxic sediment sampled from Woodhall, a site within the Inner Clyde Estuary, Scotland.

The availability of a number of metals to epipelic diatoms and meiofauna was investigated by comparison with the total (*aqua regia* extracted) and bioavailable (acetic acid extracted) metal concentrations and the proportion of bioavailable metal for evidence of metal accumulation. Both total and bioavailable metal sediment concentrations strongly correlated with chromium, nickel and zinc tissue levels.

Accumulation of chromium and zinc by meiofauna from dietary sources was suggested by comparison with levels in the epipelic diatom fraction.

The results highlight the problems in assessing metal concentrations in environmental samples, but indicate that metal levels in food may be more important than availability of metals in sediments for the accumulation of some metals.

J. Figures*, Department of Biological Sciences and also Department of Chemistry and Chemical Engineering, University of Paisley, High Street, Paisley, PA1 2BE, UK.

A.S. Hursthouse, Department of Chemistry and Chemical Engineering, University of Paisley, High Street, Paisley, PA1 2BE, UK.

J.E. Matthews, Department of Biological Sciences, University of Paisley, High Street, Paisley, PA1 2BE, UK.

*To whom correspondence should be addressed

Introduction

The Clyde Estuary, Scotland (Figure 1) receives a high pollutant load from industrial, domestic and agricultural sources. The levels of metals in point source discharges, mussels and intertidal sediments are routinely monitored by the Clyde River Purification Board at particular sites within the lower reaches of the estuary and firth (Miller 1986, 1991). Less work has been done on the upper estuary, although recent studies by Hursthouse *et al.* (1994) showed elevated and variable levels of chromium in some intertidal areas, particularly within the White Cart Water, a major tributary to the Clyde.

Metal concentrations have been studied throughout the estuary but the work described here focuses on Woodhall Bay (NS 347742) on the south shore of the lower estuary, where sediment metal levels were found to be particularly high (Figures, Hursthouse & Matthews in press). The site is bounded on the western side by an area of reclaimed land and is further characterised by the presence of a sewage pipe and freshwater seepage.

This paper examines the importance of diet and sediment as sources of metal, through the measurement of total and bioavailable metal concentrations in sediments and ecologically relevant compartments of biota and aims to assess sediment-biota and biota-biota interactions. Metal levels were measured in sediments, epipelic diatoms and meiofauna. An outline of the ecological relevance of these compartments is given below.

Sediments

The action of sediments as both sinks for and sources of metals is affected by many complex natural processes but measured concentrations can often be shown to correlate with grain size and organic matter content. The measured metal content of sediments depends on the dissolution method employed and therefore results obtained are operationally defined. Complete dissolution involves the digestion of the clay and silicate fraction, but here the term 'total' has been used to describe the metal content released by leaching with *aqua regia*. Although a strong digestion procedure, it does not destroy the sediment matrix completely, but is more than adequate to release the majority of potentially mobile species in the sediment of
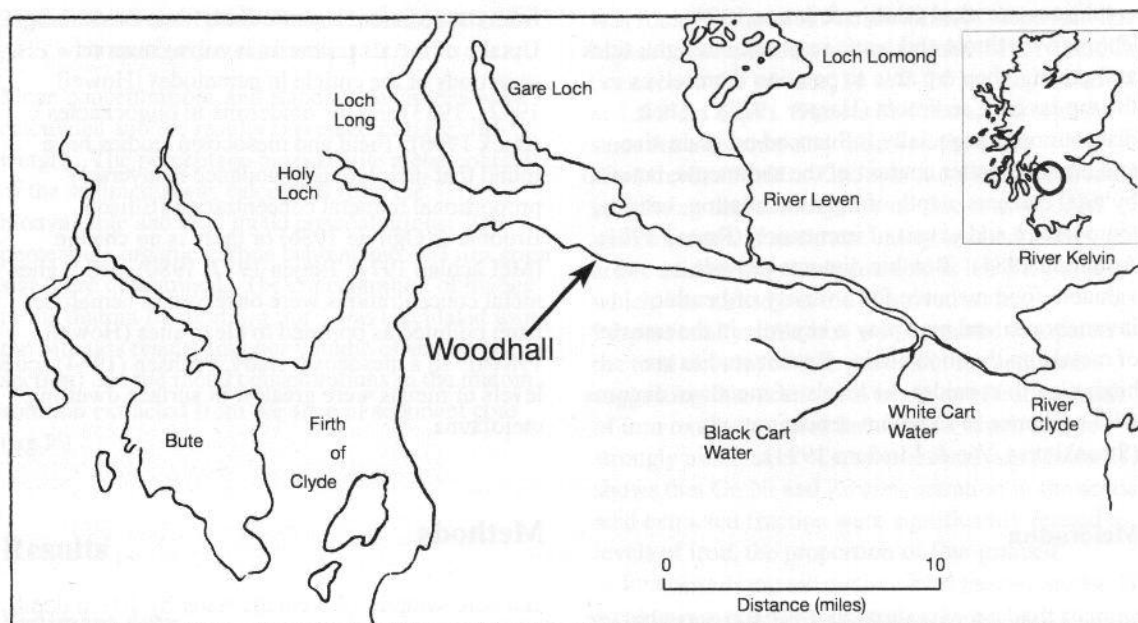
Figure 1. Map of the Firth and Estuary of Clyde highlighting the Woodhall sampling site.

significance in pollution studies. Other methods involve partial extraction, either in a single step or using a sequential procedure, targeting particular phases or forms of metals as an attempt to provide ecologically significant information. Extractants can solubilise elements from various reactive forms, including those adsorbed at particle surfaces (Fe/Mn oxides, clays, humic substances), present in amorphous Fe/Mn oxides, or associated with organic matter (living micro-organisms, freshly deposited detritus, refractory organic material). However, it must be stressed that partial extraction procedures are designed for use with oxic sediments and there are several limitations associated with their usage. Firstly, the results depend on the type of extractant used, the length of time the sediment is in contact with the reagent and the sediment to extractant ratio (Campbell & Tessier 1991). Also, following extraction and dissolution of particular phases, there is the potential for metals initially liberated by the extractant to be reabsorbed by exposed surfaces. Reagents used for extraction are unselective and sample preservation will greatly affect the chemical form of the metal in the sediment. Despite the debate as to the validity of this approach, it has been shown to provide useful information on metal behaviour (Hursthouse *et al.* 1991). Weakly acidic extractions (e.g. HCl, acetic acid, EDTA) are often used as an indication of the bioavailable fraction (Luoma & Bryan 1982; Weimin, Batley & Ahsanulla 1992). Acetic acid was used by Loring (1976) to remove elements held in carbonates, easily soluble amorphous compounds of Fe and Mn, loosely held in ion exchange and sorbed positions, and weakly attached to organic matter, but not those associated with Fe and Mn oxide minerals or silicate minerals.

Acetic acid has been used in several studies comparing the solubilising capability of various reagents. It was used by Agemain & Chau (1976) to dissolve the iron oxide phases, and Loring (1976) found that organically complexed copper was not appreciably extracted by acetic acid. It is generally considered a less rigorous leach than hydrochloric acid (Luoma & Bryan 1981).

Bioaccumulation

Trace levels of metals are required by all organisms and some organisms have additional needs, especially structural. Metals are taken up from solution or food by both active and passive processes via permeable surfaces (e.g. gills and alimentary tract). The relative rates of uptake and excretion are influenced by the permeability of the external surface, the type of food (detrital and planktonic particles are often metal-rich), method of capture and the efficiency of the osmoregulatory system. Accumulation of metals occurs when the net uptake exceeds excretion as external concentrations increase. Regulation involves maintaining the steady state between the rates of uptake and excretion despite increasing ambient levels. Metals taken into the organism may be detoxified and temporarily or permanently stored. Storage is achieved by the formation of metal-rich granules and the binding of metals to ligands with high metal affinities (Rainbow 1990) which are often proteins (e.g. metallothioneins).

Epipelic diatoms

These are the dominant photosynthetic organisms on mudflats and form dense populations where

67

conditions are ideal (Colijn & Jonge 1984). Through rhythmic and tactic responses to light, tides and gravity, they are able to position themselves in the top layer of sediment (Harper 1977). Their distribution is especially influenced by grain size and organic matter content of the sediments, but also by tidal currents, depth of light attenuation, salinity, temperature and extent of immersion (Round 1971; Admiraal 1984). Benthic diatoms provide a valuable food resource for a variety of benthic invertebrates and may play a key role in the transfer of metals up the food chain. Recent studies are beginning to consider the levels of metals in diatoms with reference to sediment concentrations (Stronkhorst, Vos & Misdorp 1994).

Meiofauna

This term is used here to describe the benthic animals that can pass through a 500 µm sieve but are retained by a 42 µm mesh. Most meiofauna are found within the top 2 cm of sediment, with the vertical distribution controlled by the depth of the redox boundary, the organic matter content, pore water content and temperature (Coull 1988; McLachlan, Erasmus & Furstenberg 1977). Horizontal distribution is related to salinity, wave action, tidal amplitude, desiccation and freshwater seepage (McLachlan 1980). The abundance and species composition is primarily determined by the grain size of the sediment (Smol *et al.* 1994). Meiofauna are potentially more advantageous than macrofauna as biological indicator organisms because of their small size, high densities, short generation time and completely benthic lifestyle (Somerfield, Gee & Warwick 1994) but separation

from the sediment is particularly time-consuming. Uptake of metals primarily involves mucous secretions of the cuticle in nematodes (Howell 1982a, 1983) and the epidermis in oligochaetes (Back 1990). Field and mesocosm studies have found that meiofaunal abundance is inversely proportional to metal concentration (Ellison, Broome & Ogilvie 1986) or there is no change (McLachlan 1977; Tietjen 1977, 1980), and higher metal concentrations were observed in nematodes from polluted as opposed to clean sites (Howell 1982b). In a mesocosm study, Frithsen (1984) found levels of metals were greatest in surface dwelling meiofauna.

Methods

Ten core samples (6.5 cm diameter by 10 cm depth) were taken from the upper, mid- and lower exposed shores for meiofaunal and diatom analysis. On return to the laboratory, the top 2.5 cm of the cores was sliced into five 0.5 cm sections. One core from each shore was used for sediment analysis, five for diatom and four for meiofauna. The individual core treatments are described in Table 1.

During meiofauna sediment dissolution two replicates were taken for each sample and a blank prepared to assess the purity of the reagents and check for contamination. Certified reference materials (sediments BEST-1 and BCSS-1, and tissue TORT-1) and in-house standard materials were also digested as a check on method reproducibility and accuracy. Analysis of Cr, Fe, Mn, Ni and Zn was performed using Perkin Elmer

Table 1. Methods used for the preparation and treatment of diatom, meiofauna and sediment core samples.

Sample	Preparation	Treatment
Sediment core (1 core)	Freeze dry Screen through 500 µm	Total metal: *Aqua regia* digestion on a hotplate (Harper *et al.* 1989) Bioavailable metal: leach for 6 h in 25% v/v acetic acid. Centrifuge at 2,500 rpm Loss on ignition: 600°C until constant weight Carbonate content: titration with HCl and NaOH (Hursthouse *et al.* 1991) Particle size: screen through 64 µm sieve
Epipelic diatoms (5 cores)	Constant illumination for 16 h & removal on lens tissue (Eaton & Moss 1966)	Counting/identification (1 core): Store at 4°C in Lugol's iodine/glycerol (Wetzel & Likens 1991) Biomass (1 core): chlorophyll extraction in acetone (Wetzel & Likens 1991) and calculation using monochromatic method (Lorenzen 1967) Metal analysis (3 cores): rinse lens tissue in 10‰ saline. Centrifuge solution at 3,500 rpm. Add 4% v/v nitric acid to residue. Sonicate and store at 4°C. Microwave digestion in teflon bombs using nitric acid
Meiofauna (4 cores)	Screen through 500 µm Elutriate each section for 20 min (McIntyre & Warwick 1984) Retain on 42 µm sieve	Counting/identification (1 core): store at 4°C in 4% v/v formalin. Metal analysis (3 cores): freeze-dry. Grind. Microwave digestion in teflon bombs using nitric acid. Centrifuge at 2,500 rpm

2100 GFAAS and Perkin Elmer Optima 3000 ICP-AES with appropriate standards.

Mean concentrations and standard deviations were calculated and the results expressed as $\mu g \ g^{-1}$ dry weight. The percentage bioavailable metal content of the sediments was calculated from the bioavailable and total metal concentrations. The percentage organic carbon content and <63 μm grain size were determined. The concentration of metals in the diatom fraction ($\mu g \ mg^{-1}$) was calculated using the biomass results (mg per volume of sediment section) and the metal concentrations in the diatom solution extracted from the slice of sediment core ($\mu g \ l^{-1}$).

Results

Sediment data

The concentration of total (*aqua regia* extracted) Cr, Ni and Zn increased from surface levels down the profile, whereas Fe and Mn declined from the surface to 1.5 cm and then increased slightly to 2.5 cm (Figure 2). The higher levels at the surface may be due to the formation of iron and manganese oxides, and the slight increase from midway down the core to the bottom to the association with the deposition of fine organically rich particles. The proportion of fine-grained sediment and organic matter also increased from surface levels (Figure 2f) and levels were much higher on the upper and mid-shores compared with the lower. Table 2 shows that all metals except Cr were significantly positively correlated with total Fe and Mn levels, grain size and organic matter (P≥0.01). The concentration of Ni and Zn may be directly related to the distribution of fine organically rich material, whereas chromium levels may be related to several metal accumulation factors.

On the upper and mid shore, the availability of metals was highest at the surface, whereas on the lower shore a greater proportion of metals was extracted from deeper core sections. Chemical partition revealed that 16-21% of the total Cr, 8-11.5% Fe, 27-42% Mn, 5-8.5% Ni and 48-78% Zn

was found in the acetic acid extracted fraction. The highest concentration of bioavailable Mn, Ni and Zn occurred at the surface, Fe at 2-2.5 cm depth and Cr at 1.5-2 cm depth. The ease of extraction was the same for all shores and followed the trend Zn>Mn>Cr>Fe>Ni. Zinc was most easily extracted suggesting that the majority of zinc is associated with fractions of sediment easily leached using acetic acid or that the acetic acid is leaching zinc which was already in the dissolved state. Proportionally, little iron was extracted compared to the total amount of iron present in the sediment suggesting that acetic acid is not an effective leach of iron oxides or other fractions to which iron is strongly associated. Correlation analysis (Table 2) shows that Cr, Ni and Zn concentration in the acetic acid extracted fraction were significantly related to levels of iron, the proportion of fine-grained sediment and organic matter. Manganese levels were only significantly correlated with total manganese suggesting acetic acid may be an effective leach of manganese oxides.

Diatom samples

The trend of metal concentration for diatom samples was the same for all shores (Fe>Mn>Zn>Cr>Ni) with the greatest diatom metal concentration found on the upper shore. The depth profiles for the upper and low shores were similar with levels decreasing from the surface down the profile, then increasing to near surface levels at 2.5 cm depth. For the mid-shore profile (Figure 3) metal concentrations were greatest just below the surface and then declined to zero at 2.5 cm depth. This was because no live diatoms were extracted from the bottom section.

Meiofauna

Nickel levels in the meiofauna profiles were similar for each tidal level with little change with depth. The manganese profile in Figure 4 markedly decreases from the high levels found at the surface, whereas iron levels remained steady to midway down the core and then declined slightly. Chromium and zinc profiles were similar and appear to follow the same trend in iron levels. Similar trends for each

Table 2. Correlation matrix of bioavailable and total concentrations of metals in the sediment with various metal-accumulating factors (n = 30).

Metal	[Bio Fe]	[Total Fe]	[Bio Mn]	[Total Mn]	% <63 μm	% organic carbon
Cr	J	J		J	J	J
Fe		J		J, X	J, X	J, X
Mn		X		J	X	X
Ni	J	J, X		J, X	J, X	J, X
Zn	J	J, X		J, X	J, X	J, X

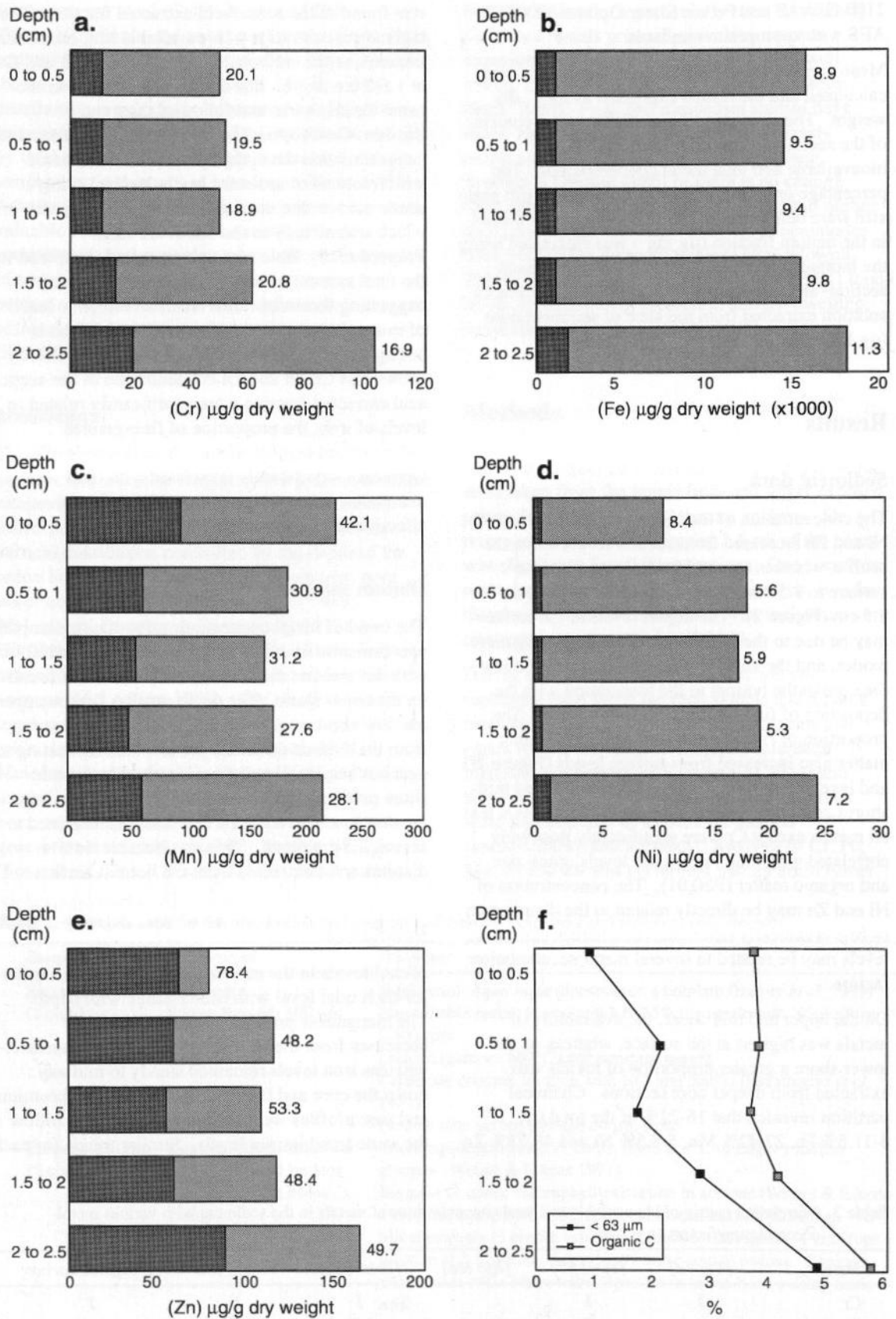Key: J = Acetic acid-extracted metal (P≥0.01); X = total metal (P≥0.01)

Figure 2. Total ■ and acetic acid extracted ▨ metal concentration (µg/g dry weight) and percentage extracted metal for the mid-shore: a = chromium, b = iron, c = manganese, d = nickel, e = zinc, and f = percentage organic carbon and fine grain (<63 µm diameter).
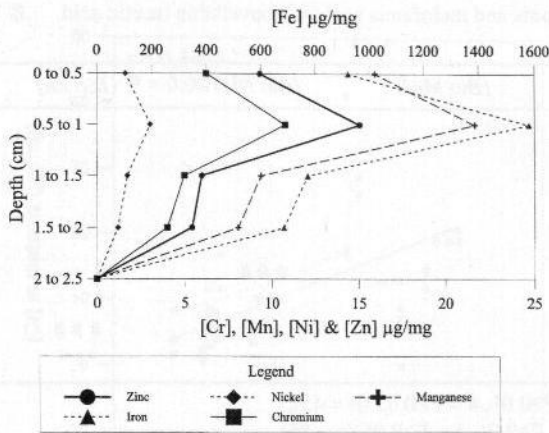
Figure 3. Depth profile of the diatom metal concentration for the mid-shore (µg/mg).
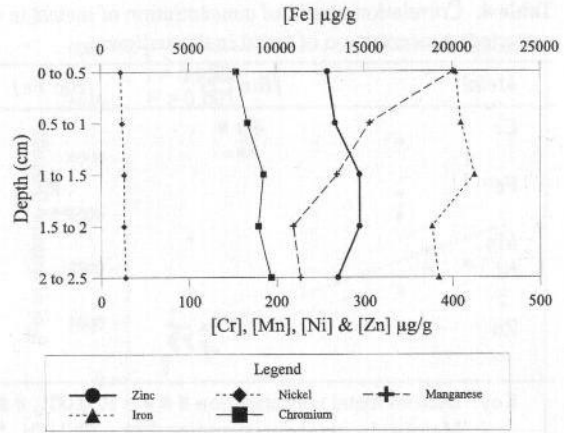
Figure 4. Depth profile of the meiofaunal metal concentration for the mid-shore (µg/g dry weight).

metal were shown by all metals on all shores. The lowest concentrations were found on the lower shore.

Statistical comparisons

Statistical techniques are frequently used to assess the importance of factors affecting metal accumulation in sediments or in the tissues of organisms. Relationships within datasets may be found whether or not cause and effect actually occur (Luoma & Bryan 1982). Using the data presented in the results section, the following hypotheses were tested :

Are metal concentrations in diatoms and meiofauna influenced by total metal concentrations in the sediment?

Table 3 shows that there is a significant positive relationship (P≥0.001) between the levels of metal in both diatoms and meiofauna and the total concentration of the same metal in the sediment. Figures 5a and 6a show the linear regression for chromium and iron for the diatom fraction, and

Figures 7a and 8a for meiofaunal chromium and manganese.

Do acetic acid extractable phases of metals in sediment correlate better than total metal concentrations in sediment with levels of metals in diatoms and meiofauna?

When the concentration of each metal in diatom or meiofauna is correlated with the bioavailable fraction of the same metal (Table 4), strong significant correlations were found for Cr, Ni and Zn and meiofauna iron and manganese (P≥0.001). Both diatom Fe and meiofauna Mn showed a significant correlation with bioavailable sediment concentrations of Fe and Mn respectively. Diatom Mn showed no correlation. Figures 5-8b show examples of these relationships.

Does the proportion of bioavailable metal in the sediment correlate better than the concentration of bioavailable metal?

The results of the correlation analysis (Table 5) suggest significant correlations exist between

Table 3. Correlation matrix of concentration of metals in diatoms and meiofauna against total (*aqua regia* extracted) concentration of metal in the sediment.

Metal	[Total Cr]	[Total Fe]	[Total Mn]	[Total Ni]	[Total Zn]
Cr	# # # ***				
Fe		# # # ***			
Mn			# # # ***		
Ni				# # # **	
Zn					# # # ***

Key: Diatom metal concentration # # # = P≥0.001, # # = P≥0.01, # = P≥0.05 (n = 45);
Meiofauna metal concentration *** = P≥0.001, ** = P≥0.01, * = P≥0.05 (n = 86)

Table 4. Correlation matrix of concentration of metals in diatoms and meiofauna against bioavailable (acetic acid extracted) concentration of metal in the sediment.

Metal	[Bio Cr]	[Bio Fe]	[Bio Mn]	[Bio Ni]	[Bio Zn]
Cr	# # # ***				
Fe		# ***			
Mn			***		
Ni				# # # **	
Zn					# # # ***

Key: Diatom metal concentration # # # = P≥0.001, # # = P≥0.01, # = P≥0.05 (n = 45);
Meiofauna metal concentration *** = P≥0.001, ** = P≥0.01, * = P≥0.05 (n = 86)

meiofauna and diatom Cr, diatom Fe and Zn, and meiofauna Mn with their respective percentage bioavailable metal. Tissue levels of Ni did not correlate with percentage bioavailable levels. Figures 5-8c show some of the results of the linear regression analysis.

Does the presence of metal-accumulating factors in the sediment affect metal bioavailability?

The total and bioavailable metal concentration were normalised separately to several metal-accumulating factors in the sediment (total concentration of Fe and Mn, and the proportion of fine grains and organic carbon). Correlation and linear regression analyses were then performed between these normalised datasets and the levels of the same metal in diatoms and meiofauna. Strong correlations (P≥0.001) were found for Cr in meiofauna, and meiofauna Zn (Table 6) and diatom Zn against bioavailable Zn normalised to iron and manganese (Table 7). The meiofauna Cr data is shown in Figure 9 and diatom Zn data in Figure 10.

Do meiofauna accumulate a substantial fraction of their metal burden from their diet, using epipelic diatoms as an example?

Sediment-dwelling meiofauna ingest a variety of food found in the sediment including bacteria, epipelic diatoms, other meiofauna and detrital material. However, only data for the epipelic diatom fraction were available for comparison. Table 8 shows that significant correlations were found for chromium and zinc (P≥0.01 and P≥0.001 respectively). The linear regressions are presented in Figure 11.

Discussion

Epipelic diatoms

Metal concentrations for epipelic algae decrease with depth (Figure 2) because the number of live diatoms decreases down the core. The metal levels associated with the diatom fraction were very low, but during conversion of the data to comparable units (μg mg^{-1}), any small differences in concentration were magnified greatly. Therefore the variation between samples also increased. Despite this, trends in metal concentration were clear and consistent for each metal. More diatoms were found on the upper shore because of the increased length of exposure time (i.e. more photosynthesis and more growth), and this was reflected in the biomass data.

Meiofauna

High levels of metals were recorded in the meiofaunal samples, often greater than those for the total sediment metal extracted using *aqua regia*.

Table 5. Correlation matrix of concentration of metals in diatoms and meiofauna against proportion of bioavailable (acetic acid extracted) metal in the sediment.

Metal	[% Bio Cr]	[% Bio Fe]	[% Bio Mn]	[% Bio Ni]	[% Bio Zn]
Cr	# ***				
Fe		# # #			
Mn			***		
Ni				*	
Zn					# #

Key: Diatom metal concentration # # # = P≥0.001, # # = P≥0.01, # = P≥0.05 (n = 45);
Meiofauna metal concentration *** = P≥0.001, ** = P≥0.01, * = P≥0.05 (n = 86)

Figure 5. Linear regression of the concentration of chromium in diatoms (µg/mg) against concentration of chromium from different leaches of sediment: a = total chromium (µg/g dry weight), b = bioavailable chromium (µg/g dry weight) and c = proportion bioavailable chromium (%).
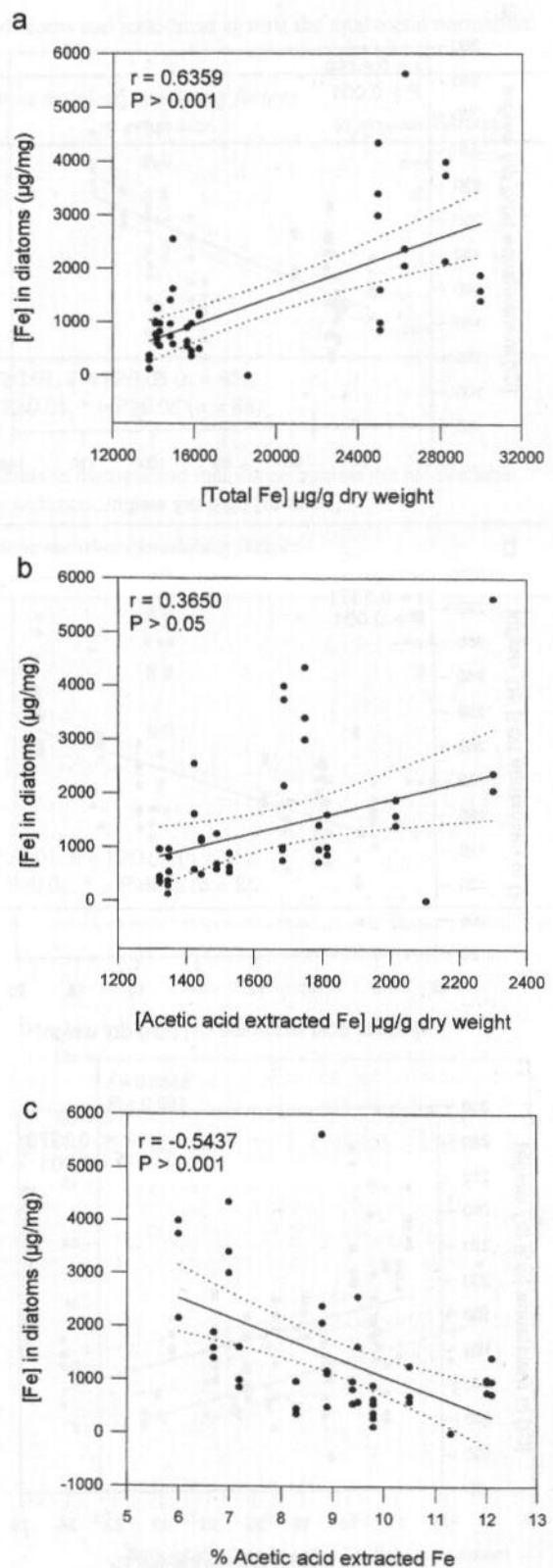
Figure 6. Linear regression of the concentration of iron in diatoms (µg/mg) against concentration of iron from different leaches of sediment: a = total iron (µg/g dry weight), b = bioavailable iron (mg/g dry weight) and c = proportion bioavailable iron (%).

Figure 7. Linear regression of the concentration of chromium in meiofauna (µg/g dry weight) against concentration of chromium from different leaches of sediment: a = total chromium (µg/g dry weight), b = bioavailable chromium (µg/g dry weight) and c = proportion bioavailable chromium (%).
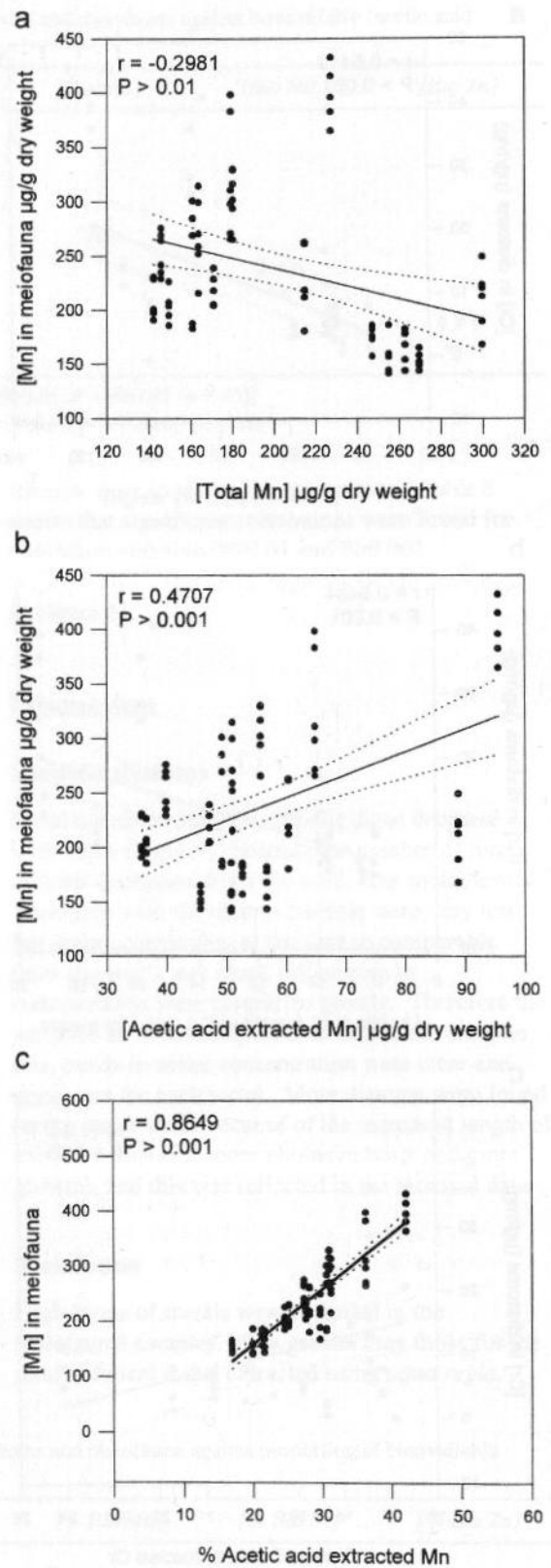
Figure 8. Linear regression of the concentration of manganese in meiofauna (µg/g dry weight) against concentration of manganese from different leaches of sediment: a = total manganese (µg/g dry weight), b = bioavailable manganese (µg/g dry weight) and c = proportion bioavailable manganese (%).

Table 6. Correlation matrix of concentration of total metals in diatoms and meiofauna against the total metal normalised to metal-accumulating factors in the sediment.

| Metal | Metal normalised to various metal-accumulating factors | | | |
	to iron	to manganese	to grain size	to organic carbon
Cr	***	***	***	***
Fe		**	##	#
Mn			***	
Ni		##	##	
			*	
Zn	#	#	#	
			***	***

Key: Diatom metal concentration # # # = P≥0.001, # # = P≥0.01, # = P≥0.05 (n = 45);
Meiofauna metal concentration *** = P≥0.001, ** = P≥0.01, * = P≥0.05 (n = 86)

Table 7. Correlation matrix of concentration of bioavailable metals in diatoms and meiofauna against the bioavailable metal normalised to metal-accumulating factors in the sediment.

| Metal | Metal normalised to various metal-accumulating factors | | | |
	to iron	to manganese	to grain size	to organic carbon
Cr			##	#
		***	***	***
Fe		##	##	#
Mn				
Ni		##	##	
			*	
Zn	###	###	#	***
			**	

Key: Diatom metal concentration # # # = P≥0.001, # # = P≥0.01, # = P≥0.05 (n = 45);
Meiofauna metal concentration *** = P≥0.001, ** = P≥0.01, * = P≥0.05 (n = 86)

Figure 9. Linear regression of the concentration of zinc in diatoms (µg/mg) against concentration of bioavailable zinc normalised to different metal-accumulating factors: a = iron and b = manganese.
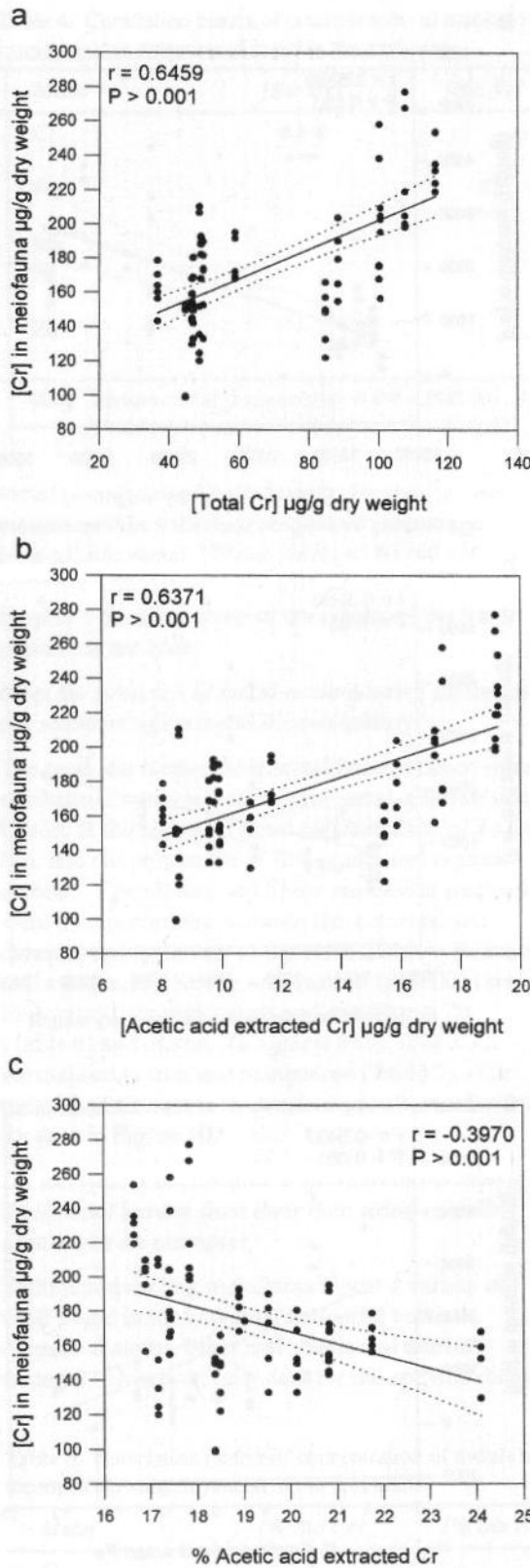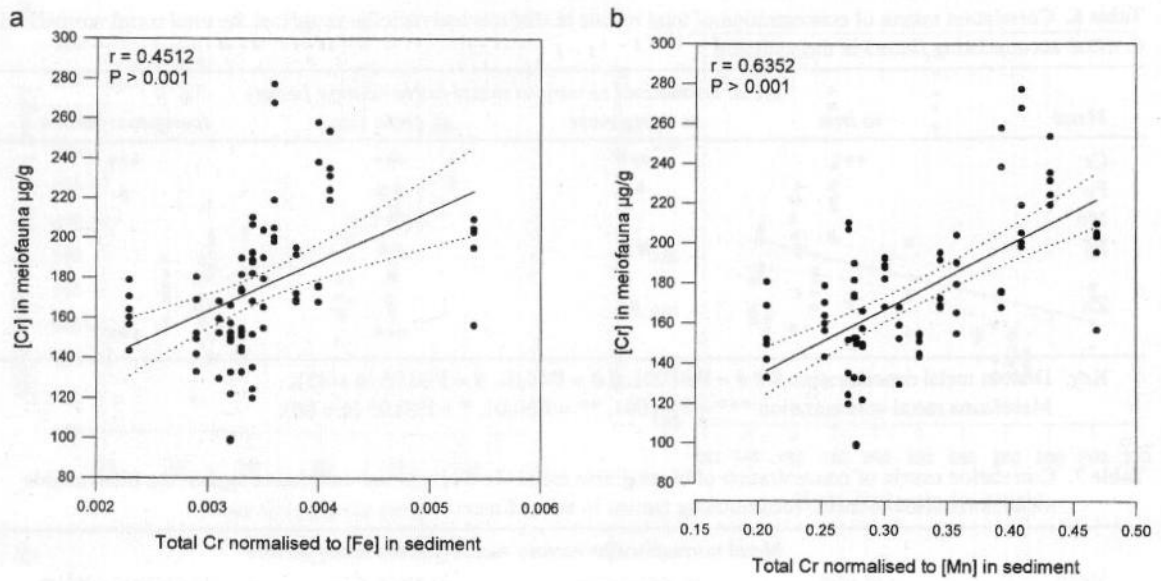
Figure 10. Linear regression of the concentration of chromium in meiofauna (µg/g dry weight) against concentration of total chromium normalised to different metal-accumulating factors: a = iron and b= manganese.

Table 8. Correlation matrix of concentration of metals in diatoms against metals in meiofauna (n=86).

Diatom			Meiofauna		
	Cr	Fe	Mn	Ni	Zn
Cr	**				
Fe		***			
Mn			*		
Ni				***	
Zn					***

Key: *** = P≥0.001, ** = P≥0.01, * = P≥0.05
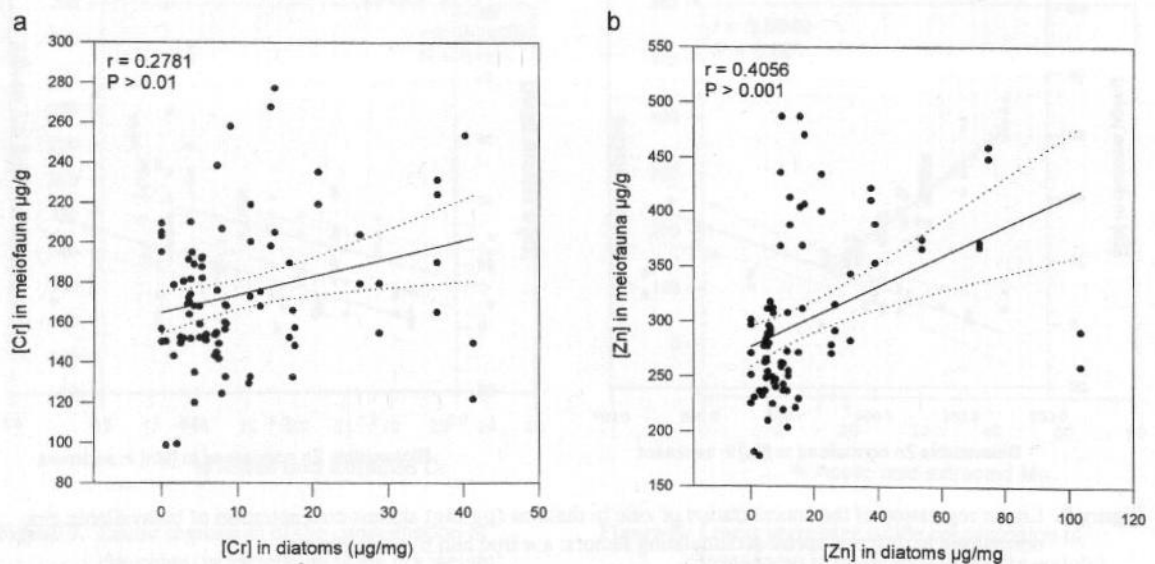
Figure 11. Linear regression of the concentration of metal in the diatom fraction (µg/mg) with that in the meiofaunal fraction (µg/g dry weight): a = chromium and b = zinc.

This reflects the presence of adsorbed and ingested sedimentary material and the greater proportion of finer sediments and organic matter in these samples as a consequence of the use of the elutriation method (this method not only separates organisms from the denser sediment, but very fine organic and inorganic particles are also carried along with the flow). This fine organically rich material provides sites for metal adsorption and the distribution of all four metals measured was correlated with these two factors. However, the organically contaminated meiofauna gives a realistic representation of food material for deposit feeders, suspension feeders and scavengers. Greater isolation of the meiofaunal fraction could be obtained by the use of several grades of sieves, and separation by hand of certain organisms (e.g. harpacticoid copepods and nematodes) but this would be more time-consuming. Hand separation would allow depuration of live meiofauna in clean saline water, prior to freeze-drying and grinding, to reduce ingested and adsorbed inorganic material. The trend in data associated with the meiofaunal fraction showed a decline in metal concentration with depth for most metals. Meiofauna are mainly found within the uppermost sediments, and therefore metal concentrations may reflect the presence of the meiofaunal community. This has been confirmed by counting and identification of meiofauna in the preserved samples. Manganese levels closely corresponded to percentage bioavailable manganese. This may represent accumulation of manganese, but it is more likely that manganese oxides, formed in the oxidised surface sediments, may have been included in the meiofaunal fraction and digested by nitric acid.

Sediment

Ideally sediment should be leached immediately following collection or within 24 hours during studies of the form of metal in the sediment, otherwise degradation of the samples may occur. However, this is not always possible due to the number of samples involved, so the samples are often stored or dried. During drying, the chemistry of the sediment is changed by oxidation or reduction and therefore the proportion of metals weakly held in the sediment is altered (Bartlett & James 1980; Kersten & Forstner 1987). The act of removing water also disturbs the equilibrium between different dissolved species, including trace metals, which become concentrated and crystallise in a variety of forms, often at the surface of mineral grains or hydrated ferruginous material (Hamilton 1980). Work by Thomson *et al.* (1980) found that wet storage at 4°C only preserved the sediment in its original state for 15 days and Campbell & Tessier (1991) found that both wet storage and drying will

greatly alter the partitioning of metals in sediment. Freezing will lyse cells and may free intracellular organic materials, along with any associated trace metals but it is an adequate method for storage prior to treatment with acetic acid (Thomson *et al.* 1980). Freeze-drying is preferable to oven-drying sediments because there is a lower risk of losing volatile elements and it provides a powdery material instead of a hard clay aggregate (Loring & Rantala 1992). However, a comparison of the efficiency of extraction of copper, manganese and zinc in sediment using acetic acid found that there was no significant difference between sediment dried at 25°C and 90°C compared with samples extracted within 24 hours of collection (Thomson *et al.* 1980). As the samples for this study were collected several months prior to extraction, freeze-drying was identified as a suitable method for long-term stable storage since it allowed both grain size and total metal content analyses (both based on a constant dry weight) and was an adequate method for acetic acid extraction.

Zinc was shown to be the easiest metal to extract and therefore potentially the most bioavailable. Statistical evidence indicates that Cr, Ni and Zn are partitioned among several competing substrates in the oxidised sediment. Bioavailable chromium, nickel and zinc were correlated with both total iron and acetic acid extracted iron, indicating a probable association with iron oxide grain coatings, a substrate more likely to be leached by the mild extractant (Agemain & Chau 1976). In contrast, a strong correlation with total manganese either suggests an association with a form of manganese not solubilised by acetic acid, or an artifact of the relationship of total manganese with other factors such as fine organically rich material. Bioavailable Cr, Ni and Zn all strongly relate to the proportion of fine, organically rich material which provides a large surface area over which metals can become sorbed. Only a small proportion of nickel is leached using acetic acid compared with the total nickel concentration, and this amount is similar throughout the core, which suggests that nickel is more strongly held by certain fractions in the sediment which may be non-anthropogenic in origin.

Statistical comparisons

As the concentration of Cr, Ni and Zn in diatoms and meiofauna were strongly related to both the total and bioavailable concentrations in the sediment, the weakly held Cr, Ni and Zn in the sediment must be an important source of metals for these organisms. This may also be true for meiofaunal iron concentrations. Generally, the proportion of acetic acid extracted metal showed little evidence of significant relationships with organism

concentrations. Figures 5-7c show some exceptions, however these were usually negative relationships, i.e. as the proportion of bioavailable concentration increased in the sediment there was no associated increase in tissue levels. Comparisons between normalised sediment metal data and tissue concentrations appeared to suggest some significant relationships. However, when the correlation coefficients from the normalised comparisons and those from comparisons with unnormalised data were made, no improvements in the strength of the relationship were seen. Therefore although metal weakly associated with the sediment may be of importance in affecting tissue concentration, other sources of metal may play an influential role. Comparisons between the levels of metals in diatoms and meiofauna to assess dietary intake of metals showed that there was a strong relationship between diatom chromium and zinc levels with those in meiofauna.

Conclusions

Measurable levels of the metals studied were found in epipelic diatoms and the meiofaunal fraction sampled from an intertidal bay. When these levels were compared with the total and bioavailable (acetic acid leached) chromium, nickel and zinc some strong correlations were observed.

This work highlights the problem in assessing metal concentrations in environmental samples, especially establishing the relationship between different chemical leaches and their comparison with tissue concentrations. In this work total sediment metal concentrations were most strongly related to tissue concentrations and this relationship did not improve with a more selective leach or by normalisation to metal-accumulating factors in the sediment. This contrasts with the work done on the accumulation of metals by macrofauna by the bioavailable metal fraction in sediment (Luoma & Bryan 1982). Comparisons between compartments in the food chain are necessary to try to understand the relationships between organisms and the impact their surroundings have on them. The comparisons made between different compartments with this data, although a fraction of those interactions found in an estuarine ecosystem, suggest the relationship between organisms and their food is equally important in the accumulation of chromium and zinc as sediment levels.

References

Admiraal, W.I.M. 1984. The ecology of sediment-inhabiting diatoms. *In: Progress in Phycological Research Volume 3*, ed. by F.E. Round & G. Chapman, 269-322. Biopress Ltd.

Agemian, H., & Chau, A.S.Y. 1976. Evaluation of extraction techniques for the determination of metals in aquatic sediments. *The Analyst, 101*: 761-767.

Back, H. 1990. Epidermal uptake of Pb, Cd, and Zn in tubificid worms. *Oecologia (Berlin), 85*: 226-232.

Bartlett, R., & James, B. 1980. Studying dried, stored soil samples - some pitfalls. *Soil Science Society of America, 44*: 721-724.

Campbell, P.G.C., & Tessier, A. 1991. Biological availability of metals in sediments: analytical approaches. *In: Heavy metals in the environment*, ed. by J.P. Vernet, 161-173. Amsterdam, Elsevier.

Colijn, F., & de Jonge, V.N. 1984. Primary production of microphytobenthos in the Ems-Dollard Estuary. *Marine Ecology Progress Series, 14*: 185-196.

Coull, B.C. 1988. Ecology of the marine meiofauna. *In: Introduction to the study of meiofauna*, ed. by R.P. Higgins & H. Thiel, 18-38. Washington, DC, Smithsonian Institution Press.

Eaton, J.W., & Moss, B. 1966. The estimation of numbers and pigment content in epipelic algal populations. *Limnology and Oceanography, 11*: 584-595.

Ellison, R.L., Broome, D., & Olgilvie, R. 1986. Foraminiferal response to heavy metal contamination in the Patapsco River and Baltimore Harbour, Maryland. *Marine Pollution Bulletin, 17*: 419-423.

Figures, J.E., Hursthouse, A.S., & Matthews, J.E. In press. *Environmental Geochemistry and Health*.

Frithsen, J.B. 1984. Metal incorporation by benthic fauna: relationships to sediment inventory. *Estuarine and Coastal Shelf Science, 19*: 523-539.

Hamilton, E.I. 1980. Analysis for trace elements. I. Sample treatment and laboratory quality control. *In: Applied soil trace elements*, ed. by B.E. Davies, 21-68. John Wiley and Sons Ltd.

Harper, D.J., Fileman, C.F., May, P.V., & Portman, J.E. 1989. *Aquatic environment protection, analytical methods No. 3: Methods for the determination of metals in soils, sediments and sewage sludge and plants by hydrochloric-nitric acid digestion with a note on the determination of the insoluble metal contents*. London, HMSO.

Harper, M.A. 1977. Movements. *In: The biology of diatoms*, ed. by D. Werner, 224-249. Oxford, Blackwell.

Howell, R. 1982a. The secretion of mucus by marine nematodes (*Enoplus* spp.): a possible mechanism influencing the uptake and loss of heavy metal pollutants. *Nematologia, 28*: 110-114.

Howell, R. 1982b. Levels of heavy metal pollutants in two species of marine nematodes. *Marine Pollution Bulletin, 13*: 396-398.

Howell, R. 1983. Heavy metals in marine nematodes: uptake, tissue distribution and loss of copper and zinc. *Marine Pollution Bulletin, 14*: 263-268.

Hursthouse, A.S., Baxter, M.S., Livens, F.R., & Duncan, H.J. 1991. Transfer of Sellafield-derived neptunium to and within the terrestrial environment. *Journal of Environmental Radioactivity, 14*: 147-174.

Hursthouse, A.S., Adamczyk, M., Adamczyk, L., & Smith, F.J. 1994. Inorganic and organic contaminants in intertidal sediments of the Clyde: preliminary observations of historical trends? *Marine Pollution Bulletin, 28*: 765-767.

Kersten, M., & Forstner, U. 1987. Effect of sample pretreatment on the reliability of solid speciation data of heavy metals - implications for the study of early diagenetic processes. *Marine Chemistry, 22*: 299-312.

Lorenzen, C.J. 1967. Determination of chlorophyll and phaeo-pigments: spectrophotometric equations. *Limnology and Oceanography, 12*: 343-346.

Loring, D.H. 1976. The distribution and partition of zinc, copper, and lead in the sediments of the Saguenay fjord. *Canadian Journal of Earth Science, 13*: 960-971.

Loring, D.H., & Rantala, R.T.T. 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Science Reviews, 32*: 235-285.

Luoma, S.N., & Bryan, G.W. 1981. A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. *The Science of the Total Environment, 17*: 165-196.

Luoma, S.N., & Bryan, G.W. 1982. A statistical study on environmental factors controlling concentration of heavy metals in the burrowing bivalve *Scrobicularia plana* and the polychaete *Nereis diversicolor*. *Estuarine and Coastal Shelf Science, 15*: 95-108.

McIntyre, A.D., & Warwick, R.M. 1984. Meiofauna techniques. *In: Methods for the study of the marine benthos*, ed. by N.A. Holme & A.D. McIntyre, 217-244. Oxford, Blackwell Scientific Publications.

McLachlan, A. 1977. Effects of ore dust on the physical and chemical features, and on the meiofauna and macrofauna, of a sandy beach. *Zoologica Africana, 12*: 73-88.

McLachlan, A. 1980. Intertidal zonation of macrofauna and stratification of meiofauna on high energy sandy beaches in the Eastern Cape, South Africa. *Transactions of the Royal Society of South Africa, 44*: 213-223.

McLachlan, A., Erasmus, T., & Furstenberg, J.P. 1977. Vertical and horizontal distribution of sublittoral meiofauna in Algoa Bay, South Africa. *Marine Biology, 40*: 355-364.

Miller, B.S. 1986. Trace metals in the common mussel *Mytilus edulis* (L.) in the Clyde Estuary. *Proceedings of the Royal Society of Edinburgh, 90B*: 377-391.

Miller, B.S. 1991. A decade of watching mussels: trend monitoring of cadmium in a contaminated UK estuary. *In: Heavy metals in the environment*, ed. by J.G. Farmer, 199-203. CEP Consultants Ltd.

Packer, D.M., Ireland, M.P., & Wootton, R.J. 1980. Cadmium, copper, lead, zinc and manganese in the polychaete *Arenicola marina* from sediments around the coast of Wales. *Environmental Pollution, 22A*: 309-321.

Rainbow, P.S. 1990. Heavy metals in marine invertebrates. *In: Heavy metals in the marine environment*, ed. by R.W. Furness & P.S. Rainbow, 67-80. CRC Press Inc.

Round, F.E. 1971. Benthic marine diatoms. *In: Oceanography and Marine Biology Annual Review Volume 9*, ed. by H. Barnes, 83-139. London, Allen & Unwin.

Schulz-Baldes, M. 1982. Animals as monitor organisms for heavy metals in the sea. An overview. *Decheniana Beihefte (Bonn), 26*: 43-54.

Smol, N., Willems, K.A., Govaere, J.C.R., & Sandee, A.J.J. 1994. Composition, distribution and biomass of meiobenthos in the Oosterschelde Estuary (SW Netherlands). *Hydrobiologia, 282/283*: 197-217.

Somerfield, P.J., Gee, J.M., & Warwick, R.M. 1994. Soft sediment meiofaunal community structure in relation to a long-term heavy metal gradient in the Fal Estuary system. *Marine Ecology Progress Series, 105*: 79-88.

Stronkhorst, J., Vos, P.C., & Misdorp, R. 1994. Trace metals, PCBs, and PAHs in benthic (epipelic) diatoms from intertidal sediments; a pilot study. *Bulletin of Environmental Contamination and Toxicology, 52*: 818-824.

Thompson, E.A., Luoma, S.N., Cain, D.J., & Johanson, C. 1980. The effect of sample storage on the extraction of Cu, Zn, Fe, Mn and organic material from oxidized estuarine sediments. *Water, Air and Soil Pollution, 14*: 313-317.

Tietjen, J.H. 1977. Population distribution and structure of the free-living nematodes of Long Island Sound. *Marine Biology, 43*: 123-136.

Tietjen, J.H. 1980. Population structure and species composition of the free-living nematodes inhabiting sands of the New York Bight apex. *Estuarine, Coastal and Marine Science, 10*: 61-73.

Wetzel, R.G., & Likens, G.E. 1991. *Limnological analysis*. New York, Springer Verlag.

Weimin, Y., Batley, G.E., & Ahsanulla, M. 1992. The ability of sediment extractants to measure the bioavailability of metals to three marine invertebrates. *The Science of the Total Environment, 125*: 67-84.

Classification of the Forth and Clyde Estuaries on the basis of trace metals levels in fucoid algae

B.S. Miller & J. Dobson

In 1977 an Estuaries Working Group was set up by the Department of the Environment (DoE) to develop a system for the classification of estuarine and coastal waters. The resulting scheme has been used throughout the UK since 1985. The scheme was simple to use, with points allocated according to the water quality as described by a range of parameters under the broad categories of aesthetic, chemical and biological condition. Each stretch of estuary was classified on the basis of the total scores awarded, and the waters described as class A (good quality), B (fair quality), C (poor quality) or D (bad quality).

As a result of reservations expressed by some River Purification Authorities (RPAs) on the sensitivity of the original scheme, it was revised in 1994 to operate on a default basis with each stretch of estuary classified according to the category for which water quality was the lowest. The classes A to D were retained, but the descriptions for water quality for these were changed to excellent, good, satisfactory and seriously polluted.

This paper describes the role of biomonitors in the estuary classification scheme, and shows how waters in the Forth and Clyde Estuaries were classified for the period 1982 to 1994 using the new scheme, by comparison of the trace metals levels found with standards set for fucoid algae. Attention is focused on copper. Interesting results were obtained for the classification of the two estuaries, in relation to the copper loadings and dissolved copper concentrations measured in estuary waters. The dangers of using the classification scheme to compare estuaries without full knowledge of their character was highlighted, especially in relation to the location of the algal collection sites relative to the major metals inputs.

Brian S. Miller*, Clyde River Purification Board, Rivers House, Murray Road, East Kilbride, Glasgow, G75 0LA, UK.

Judith Dobson, Forth River Purification Board, Clearwater House, Heriot-Watt Research Park, Avenue North, Riccarton, Edinburgh, EH14 4AP, UK.

*To whom correspondence should be addressed.

Introduction

The classification of the quality of Scotland's estuarine waters was first carried out in 1985 using the Estuary Classification Scheme devised by the Estuary Working Group (SDD 1987). In creating the classification scheme, the working party took into account the potential uses of estuaries, such as the passage of migratory fish, the water quality for resident fish, shellfish and wildlife, the maintenance of amenity in terms of the appearance of each estuary, the potential for activities such as sailing and fishing, and the needs of industry.

The Estuary Classification Scheme allowed the regulatory authorities responsible for the protection of water quality in Scotland - the River Purification Boards (RPBs) and Islands Councils - to classify estuary waters, with points awarded according to the aesthetic, biological and chemical quality of the waters. Sites in each estuary were chosen as representative of that part of the estuary, and the area was classified on the basis of the total points awarded, as shown in Table 1 (SOEnD 1992). The scheme was applied every five years, and the information published by the Scottish Office as part of the Water Quality Survey of Scotland (SOEnD 1992), which also reported on the biological and chemical classification of rivers, lochs, canals and coastal waters throughout Scotland. The water quality survey reports identified problem areas and assessed the effectiveness of measures taken to reduce or control pollution.

This paper describes the original Estuary Classification Scheme, and the changes made in revising the scheme to make it more sensitive and more objective. The procedure of classification on the basis of the trace metals levels in fucoid algae is described. Finally, the revised scheme is used to classify the Forth and Clyde estuaries for the period 1982 to 1994, for trace metals levels in fucoid algae.

Allocation of points in the original scheme

Points were allocated in the original scheme for sites chosen to represent specified areas in each estuary. The points were awarded according to the aesthetic, biological and chemical quality of the estuary waters, as shown in Table 2. The points total gave the description and classification for each part of the estuary, as in Table 1. The classifications for the Forth and Clyde Estuaries for 1990 are shown in Figures 1 and 2 (SOEnD 1992).

Table 1. Original Estuary Classification descriptions.

Classification	Number of points	Description
Class A	24-30	Good quality
Class B	16-23	Fair quality
Class C	9-15	Poor quality
Class D	0-8	Bad quality

Data from SOEnD (1992).

Revision of the scheme for greater sensitivity

Criticisms of the original scheme related to its subjectivity and lack of sensitivity. This can be demonstrated in relation to the number of points available for the absence of substantially elevated levels of persistent toxic or tainting substances in biota, with only four out of a total of 30 points

awarded for this category (see Table 2). As a result, while contaminated sites were awarded no points, an uncontaminated site was allocated only four points. The consequence was that the two sites with very different contaminant levels may have been classed similarly under the old scheme, because the class depended on the *total* number of points. This also meant that where pollution control measures had been applied to reduce discharges of toxic and persistent substances to improve water quality, this may not have been reflected by an improvement in the classification of that part of the estuary. This lack of sensitivity was regarded as unsatisfactory by some RPAs, so the Marine and Estuarine Sub-group of the Association of Directors and River Inspectors for Scotland (ADRIS) was charged with the task of proposing a suitable alternative. The new scheme was produced in 1994, with the points scoring system replaced by a default system, where each stretch of the estuary is classified not according to the total points scored, but rather on the basis of the parameter having the lowest category. The RPAs will initially operate the two schemes in parallel, to compare the estuary classifications obtained.

The new estuary classification scheme

In the new scheme each stretch of the estuary is still classified according to the water quality, as determined by its aesthetic, biological and chemical condition. The categories have been broadened to include more
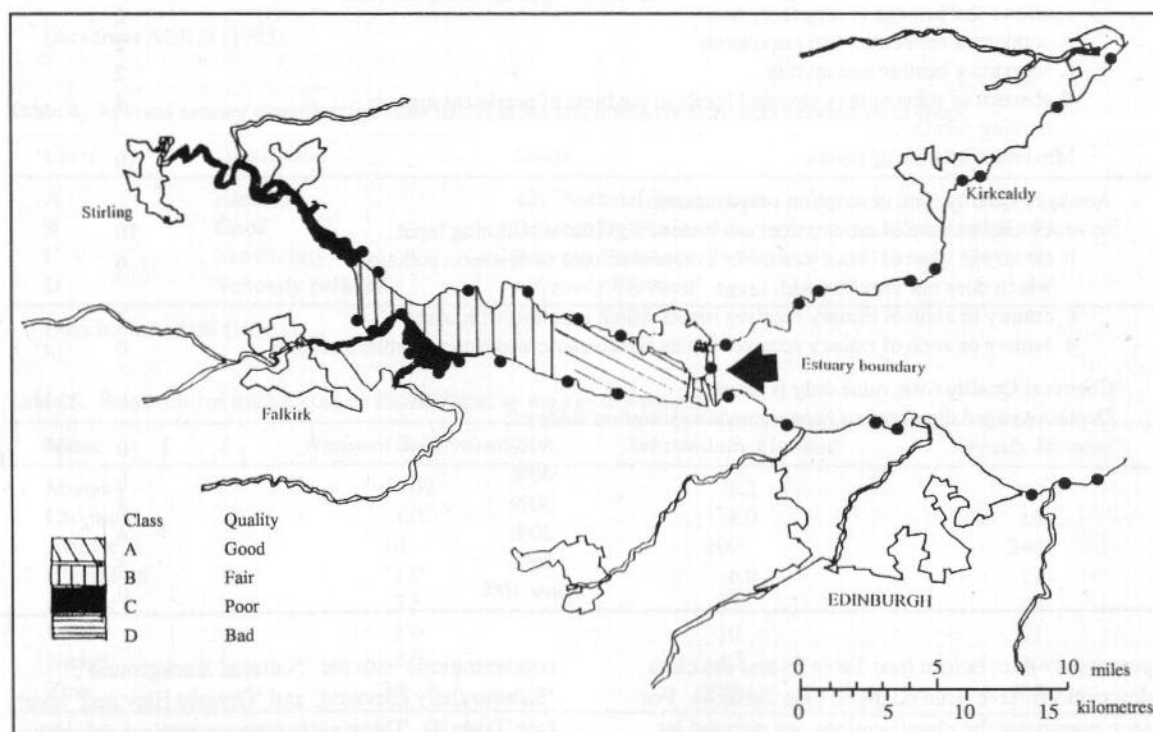
Figure 1. Forth Estuary classification for 1990 and algae collection sites.

Class	Quality
A	Good
B	Fair
C	Poor
D	Bad

Class	Quality
A	Good
B	Fair
C	Poor
D	Bad

⬅ :Major inputs

Estuary boundary

GLASGOW

| 0 | | 5 | | 10 | miles |
| 0 | 5 | 10 | 15 | kilometres |
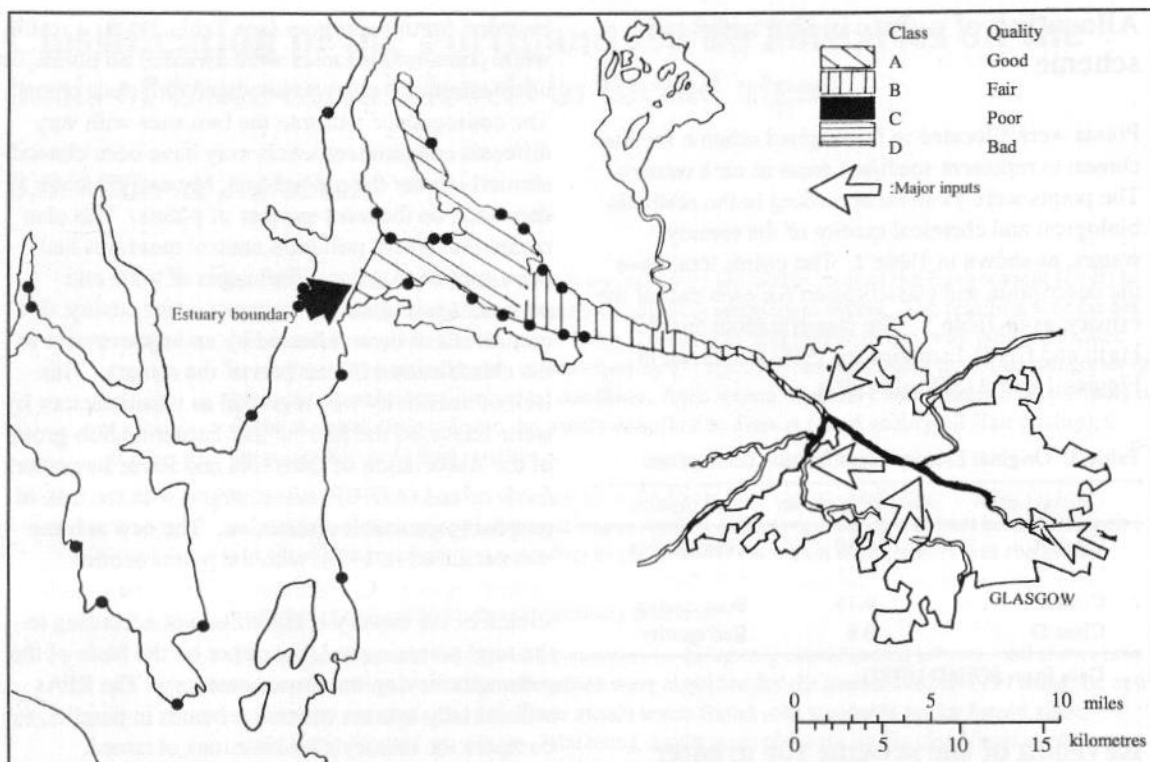
Figure 2. Clyde Estuary classification for 1990 and algae collection sites.

Table 2. Allocation of points for original Estuary Classification Scheme (SOEnD 1992).

Description	Points awarded if the estuary meets this description
Biological Quality (scores under a, b, c and d are summed)	
a. allows the passage of migratory fish	2
b. supports a residential fish population	2
c. supports a benthic community	2
d. absence of substantially elevated levels in the biota of persistent toxic or tainting substances	4
Maximum number of points	10
Aesthetic Quality (one description only is chosen)	
a. estuary or zone of estuary does not receive significant polluting input	10
b. estuary or zone of estuary receives a certain amount of aesthetic pollution which does not interfere with usage	6
c. estuary or zone of estuary receives inputs which interfere with usage	3
d. estuary or zone of estuary receives inputs which cause widespread public nuisance	0
Chemical Quality (one value only is chosen)	
Depth-averaged dissolved oxygen exceeds a saturation value of:	
60%	10
40%	6
30%	5
20%	4
10%	3
below 10%	0

parameters than before (see Table 3) and the class descriptions have been changed (see Table 4). For each parameter the classifications are decided by comparison of the measured environmental concentrations with the 'National Background', 'Substantially Elevated' and 'Grossly Elevated' levels (see Table 4). These were set as numerical values by the Estuary Working Group (SDD 1987). The levels

for trace metals in fucoid algae are shown in Table 5. Each estuary is classified according to the concentrations found. For example, if the lead concentration in algae from a particular site is below twice the 'National Background' level (i.e. below 2.0 mg kg⁻¹ dry weight), then that site is classified as A, and the water quality may be described as excellent. If the concentration found was between 2.0 and 10.0 mg kg⁻¹, than the site is classified as B, indicating good water quality. Since the new scheme is default-based, then if the waters were classified as C on the basis of another parameter, then the lower classification would determine the overall description applied in both these cases.

Derivation of standards for trace metals in fucoid algae

As stated, the numerical values for the 'National Background', 'Substantially Elevated' and 'Grossly Elevated' levels were set in the original scheme by the Estuary Working Group on the basis of a literature review, with most of the environmental concentrations measured in the early 1970s. As part of the revision of the scheme, these values were re-assessed for trace metals in fucoid algae on the basis of more recent environmental data gathered mainly by the Clyde and Forth RPBs, and by other monitoring authorities. Only two small changes were made on the basis of the more recent data, indicating the older work to be fairly robust. The exceptions were for cadmium and chromium for which the 'National Background' levels were revised upwards to 1.0 mg kg⁻¹ dry weight, from 0.6 and 0.8 mg kg⁻¹ respectively. Although these changes altered the levels upwards, they were justified by the increased reliability of the more recent data.

Table 3. Parameters included in the revised estuary classification scheme.

Water quality category	Parameter
Aesthetic condition	Presence or absence of petroleum residues, sewage derived solids or conspicuous or gross accumulations of other materials
Biological condition	Evidence of fish migration Evidence of presence or absence of resident fish populations Presence or absence of *Beggiatoa* mats Results of sediment bioassays Degree of imposex Levels of persistent substances in biota
Chemical condition	Depth-averaged dissolved oxygen levels Levels of UK 'Red List', List I and List II substances in waters and compliance with Environmental Quality Standards

Data from ADRIS (1995).

Table 4. Revised estuary classification class descriptions and levels for persistent substances in biota.

Class	Description	Levels
A	Excellent	<2x 'National Background'
B	Good	Between 2x 'National Background' and 'Substantially Elevated'
C	Satisfactory	Between 'Substantially Elevated' and 'Grossly Elevated'
D	Seriously polluted	>'Grossly Elevated'

Data from ADRIS (1995).

Table 5. Standards for trace metals in fucoid algae, as mg kg⁻¹ dry weight.

Metal	'National Background'	'Substantially Elevated'	'Grossly Elevated'
Mercury	0.02	0.2	0.4
Cadmium	1.0	8.0	16
Arsenic	10	100	240
Chromium	1.0	6.0	12
Copper	3.5	35	70
Lead	1.0	10	21
Nickel	4.0	40	80
Zinc	35	350	700

Data from ADRIS (1995).

The use of biomonitors

Biomonitors are organisms which accumulate contaminants in their tissues. These are analysed to identify the abundancies and bioavailabilities of contaminants such as trace metals and organochlorine compounds in the aqueous environment (Phillips & Rainbow 1993). This term is synonymous with that of 'biological monitors', which may be used for regular surveillance and to quantify the amount of a pollutant present in a given environment (Martin & Coughtrey 1982). Biomonitors have been incorporated into monitoring programmes for toxic, persistent and bio-accumulable substances such as trace metals and organochlorine compounds for many years, for example by regulatory authorities and research organisations in the UK (e.g. Burt et al. 1992; MAFF 1993). The use of mussels in particular has been widespread, owing to a number of factors including the call by Goldberg (1975) for a world-wide 'mussel-watch' programme as the first step in global marine monitoring. The Forth and Clyde River Purification Boards have used the 'mussel-watch' approach to monitor trace metals and organochlorine compounds since 1980 (Haig & Miller 1984; Miller 1986). Macrophytes such as fucoid algae also fulfil the criteria required for biomonitors (Phillips 1994), and have been used throughout the world in this role for many years (Black & Mitchell 1952; Butterworth, Lester & Nickless 1972; Preston et al. 1972; Romeril 1977; Seeliger & Edwards 1977; Melhuus et al. 1978; Cullinane & Whelan 1982; Barnett & Ashcroft 1985; Ronnberg et al. 1990).

Since biomonitors integrate contaminant concentrations with time, their tissue or body burdens reflect not only the levels in the surrounding waters, but also those concentrations which are bioavailable. A 'multiple organism' approach is often used for monitoring trace metals in the marine environment, since metals are present in both the soluble and particulate forms (Forstner & Wittmann 1981), and the fraction taken up by an organism is dependent on its feeding mechanism (Bryan et al. 1985). For example, mussels are filter-feeders, and their primary uptake route for trace metals is thought to be from particulates suspended in the overlying waters (WWA 1982). There is some debate as to the exact uptake route for metals by fucoid algae, but it is thought that dissolved metals are taken in by a passive mechanism, which is probably linked to their metabolism. It has also been suggested that fucoid algae may scavenge metals from particulate matter (Luoma, Bryan & Langston 1982).

The 'indicator potential' of a range of organisms for different trace metals has been assessed according to feeding mechanism (Bryan et al. 1985). It is wise to combine the use of both mussels and algae in a monitoring programme, since these vary in their indicator potential for different metals (Table 6). This approach has been adopted in the Estuary Classification Scheme, which has included both mussels and algae as biomonitors.

Sampling and analysis

Sampling of fucoid species was carried out at low tide by the Forth and Clyde RPBs in the respective estuaries, with several whole plants collected from the mid-tide position (see Figures 1 and 2 for sampling sites). In the Clyde, samples were mainly *Fucus spiralis* collected from rocks, and in the Forth, mainly *Fucus vesiculosus* from rocks or on mudflats. Plants were washed by the Forth RPB to remove mucous material covering the fronds. At both RPBs the plants were frozen then freeze-dried, then nitric acid digestion was carried out; at the Clyde RPB samples were heated on a sand bath while at the Forth RPB microwave digestion was applied. Quantification was by flame AAS at both laboratories, which regularly participate in national and international interlaboratory calibration exercises for the determination of trace metals in marine biota, such as the National Marine AQC Scheme and the Quasimeme programme.

Results

A large dataset for trace metals levels in *Fucus spiralis* from the Clyde Estuary and Firth and in *Fucus vesiculosus* from the Forth Estuary and Firth for the period 1982-94 has been examined. Typical results for metals in algae from the Forth Estuary sites for 1988 are shown in Table 7, and for the Clyde Estuary for the same year in Table 8.

Table 6. Indicator potential of mussels and algae for trace metals.

Species	Metals Fraction	Good	Moderate	Poor
Fucoid algae	Dissolved	As Cd Co Cu Ni Zn	Ag Hg Pb Se Sn	
Mytilus edulis	Particulate	Cd Cr Zn	Co Hg Ni Se Sn V	Ag As Cu Zn

Data from Bryan et al. (1985).

Table 7. Trace metals levels in *Fucus vesiculosus* from the Forth Estuary, 1988 (mg kg⁻¹ dry weight).

Site	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Limekilns	1.15	1.2	25.2	0.028	11.4	1.3	198
Ironmills Bay	0.48	3.1	17.3	0.043	8.0	2.4	123
Torry Bay	0.55	2.2	18.3	0.040	8.4	1.8	143
Culross	0.68	2.7	32.4	0.070	7.9	2.6	193
Kincardine	0.87	10.7	35.7	0.074	9.4	3.2	339
Skinflats	0.88	27.7	45.7	0.190	6.7	6.2	279
Grangemouth	0.91	24.7	44.9	0.073	7.8	8.1	285
Carriden	0.68	2.3	20.3	0.066	8.1	2.6	193
Blackness	0.82	2.1	26.5	0.033	9.2	1.6	162
Port Edgar	0.58	1.4	14.7	0.027	7.5	1.9	132

Table 8. Trace metals levels in *Fucus spiralis* from the Clyde Estuary, 1988 (mg kg⁻¹ dry weight).

Site	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Portkil Bay	1.11	<1.55	6.67	176	7.66	1.05	212
Culwatty Bay	1.27	<3.35	7.61	240	11.6	2.00	235
Gareloch, Shandon	0.85	<3.33	7.68	132	7.11	0.48	158
Craigendoran	1.10	6.60	9.60	328	4.44	3.36	175
Ardmore	1.05	1.57	11.5	256	6.61	4.21	208
Cardross	0.92	<3.35	12.3	254	4.00	2.00	172
Cardross	0.92	<3.35	12.3	254	4.00	2.00	172
Pillar Bank	1.19	10.1	14.3	403	5.00	<2.22	198

Classification of the Forth and Clyde Estuaries

In classifying the Forth and Clyde Estuaries on the basis of the trace metals levels found in fucoid algae, it is important to consider firstly the trace metals inputs to each estuary, and secondly the typical ranges for the concentrations of dissolved trace metals, since these are available for uptake by the algae. Both estuaries receive major inputs of contaminants of various types, arising from domestic and industrial wastes. The total trace metals loadings inputs for 1990 are summarised for each estuary in Table 9. Attention will be focused in this paper only on copper, the total loadings of which are almost identical to each estuary from sewage discharges and rivers inputs. However, the Forth Estuary receives copper directly from industrial discharges, whereas in the Clyde these are combined with sewage discharges.

Despite receiving higher loadings of copper, levels of dissolved copper in the Forth Estuary are lower than in the Clyde Estuary. In the Forth, levels are typically in the range 0.57 to 2.46 µg l⁻¹, with a mean value of about 1.23 µg l⁻¹, while in the Clyde, dissolved copper is generally in the range 1.23 to 6.27 µg l⁻¹, mean 2.71 µg l⁻¹. Factors which may contribute to this observation are examined later.

Classification of the Forth and Clyde Estuaries was carried out using the new scheme for the period 1982-94, for copper (see Figures 3 and 4). Despite the higher dissolved copper concentrations in Clyde Estuary waters, the algae sites were mainly classed as A and B, while those in the Forth Estuary were mainly B and C. This result was unexpected. The copper concentrations in fucoid algae from the two estuaries for the period 1982-94 are summarised in Figure 5. This confirmed that lower concentrations were found in algae from the Clyde Estuary, for copper.

Table 9. Total metals loadings to the Forth and Clyde estuaries, 1990.

Metal	Rivers		Industrial discharges		Sewage discharges		Total	
	Forth	Clyde	Forth	Clyde	Forth	Clyde	Forth	Clyde
Cd kg⁻¹	530	341	55	ns	125	29	710	370
Hg kg⁻¹	35	25	73	ns	19	8	127	33
Cu t⁻¹	22	22	14	ns	11	10	47	32
Pb t⁻¹	14	34	0.7	ns	7	7	22	41
Zn t⁻¹	75	76	21	ns	47	14	143	90

Note: data are for unfiltered effluent samples; ns indicates no significant direct industrial discharges (see text).
Source: unpublished data from Forth and Clyde RPBs.

Discussion

It has been shown that while copper inputs are slightly higher to the Forth Estuary (Table 9) and dissolved copper concentrations are generally higher in the Clyde Estuary (see above), the Clyde Estuary has a higher classification in the scheme. Other determining factors must be sought to explain this apparent anomaly. It is known that the Forth has a higher solids loading than the Clyde, which could explain the lower dissolved copper concentrations. It may be that the results presented support the theory that algae can scavenge metals from particulates (Luoma, Bryan & Langston 1982) since the Forth algae were collected from the mudflat areas whereas the Clyde algae were generally collected from rocky shores.

Another critical factor may be the location of the algae collection sites in each estuary relative to the positions of the major metals inputs. In the Forth Estuary, the major metals inputs are from around the Grangemouth area on the southern shore of the Estuary, and all of the algae collection sites are within 15 km of this major discharge (see Figure 1). In the Clyde Estuary, however, the discharges are more spread out, and are made to the upper reaches of the estuary more than 15 km from the nearest algae collection site (see Figure 2). Evidence to support this theory is provided by the classification of sites in the inner Firth of Forth just beyond the bridges, at about the same distance from the major metals inputs in the Forth Estuary as are the Clyde Estuary sites. These inner Firth of Forth sites have similar classification to the Clyde Estuary sites, for copper.

Fucoid algae are not found in the Clyde Estuary as far upstream as the major metals inputs. The main factor is likely to be the different salinity regimes in the two estuaries. The Clyde tends to be partially to strongly stratified whereas the Forth is more usually partially stratified or well-mixed. In the Forth, saline waters intrude much farther up the estuary, allowing fucoid algae to penetrate to well beyond the location of the major metals inputs, near Grangemouth. Another contributory factor may be the canalised nature of the Clyde Estuary compared with the more open Forth Estuary.

Conclusions

Application of the Estuary Classification Scheme to sites in the Forth and Clyde Estuaries on the basis of copper levels found in fucoid algae produced surprising results, in comparison to the metals loadings and dissolved concentrations found in the two estuaries. The observed results may be due to a combination of factors, including the different suspended solids loadings in the estuaries, the substrate from which the algae were collected, and the location of the algae collection sites in relation to the major metals discharges. This highlights a potential danger in applying the scheme for comparison of different estuaries without full knowledge of the discharge locations relative to the sampling sites, and of the other important characteristics of the estuary.

Future work

Future work may include examination of evidence for the scavenging of copper from particulates through comparison of concentrations of the metal in particulate materials, bed sediments and mussel populations in the two estuaries.
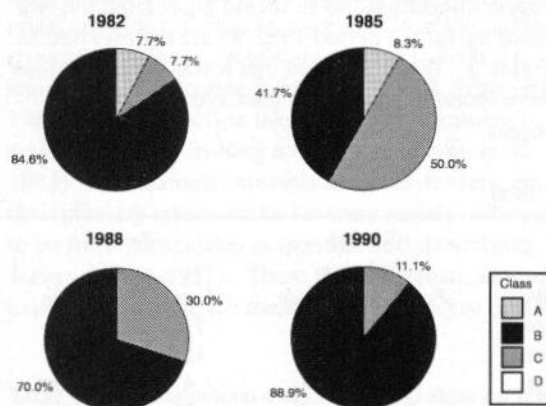

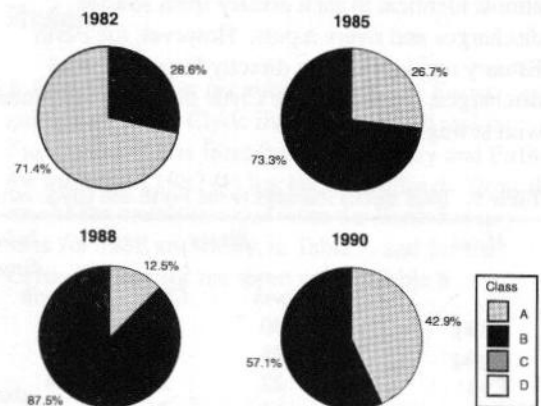**Figure 3.** Forth Estuary classificiation for copper levels in fucoid algae.

Figure 4. Clyde Estuary classificiation for copper levels in fucoid algae.
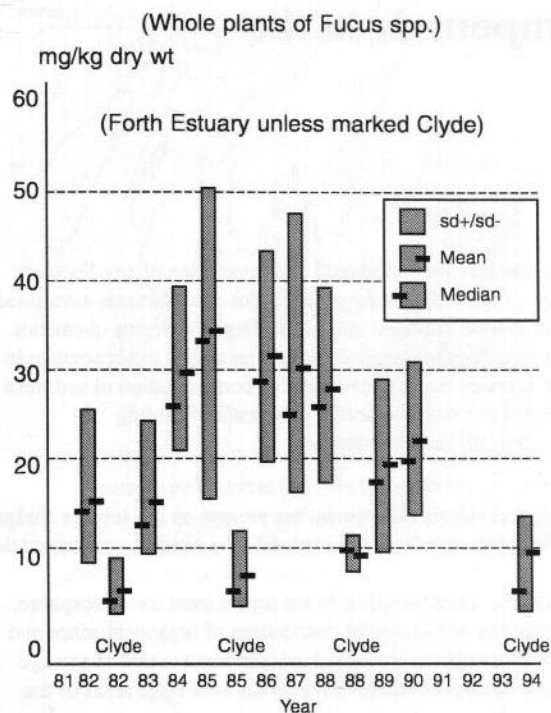
Figure 5. Copper levels in fucoid algae from the Forth and Clyde Estuaries, 1982-1994.

Acknowledgements

References

ADRIS. 1995. *ADRIS Estuary Classification Scheme.* Perth, ADRIS Marine and Estuary Sub-group.

Barnett, B.E., & Ashcroft, C.R. 1985. Heavy metals in *Fucus vesiculosus* in the Humber Estuary. *Environmental Pollution (Series B), 9*: 193-213.

Black, W.A.P., & Mitchell, R.L. 1952. Trace elements in the common brown algae and in sea water. *Journal of the Marine Biological Association of the UK, 30*: 575-584.

Bryan, G.W., Langston, W.J., Hummerstone, L.G., & Burt, G.R. 1985. *A guide to the assessment of heavy-metal contamination in estuaries using biological indicators.* Occasional Publication No. 4. Plymouth, Marine Biological Association of the UK.

Burt, G.R., Bryan, G.W., Langston, W.J., & Hummerstone, L.G. 1992. *Mapping the distribution of metal contamination in United Kingdom estuaries.* Final report on DoE contract PECD 7/7/280. Plymouth, Plymouth Marine Laboratory.

Butterworth, J., Lester, P., & Nickless, G. 1972. Distribution of heavy metals in the Severn Estuary. *Marine Pollution Bulletin, 3*: 72-74.

Cullinane, J.P., & Whelan, P.M. 1982. Copper, cadmium and zinc in seaweeds from the south coast of Ireland. *Marine Pollution Bulletin, 13 (6)*: 205-208.

Forstner, U., & Wittmann, G.T.W. 1981. *Metal pollution in the aquatic environment.* Berlin, Springer-Verlag.

Goldberg, E.D. 1975. The mussel watch - a first step in global marine monitoring. *Marine Pollution Bulletin, 6*: 111-113.

Haig, A.J.N., & Miller, B.S. 1984. Chemistry of the Firth of Clyde. *Analytical Proceedings, 21*: 116-118.

Luoma, S.N., Bryan, G.W., & Langston, W.J. 1982. Scavenging of heavy metals from particulates by brown seaweed. *Marine Pollution Bulletin, 13 (11)*: 394-396.

MAFF. 1993. *Monitoring and surveillance of non-radioactive contaminants in the aquatic environment and activities regulating the disposal of wastes at sea 1991.* Lowestoft, Directorate of Fisheries Research, Ministry of Agriculture, Fisheries and Foods. (Aquatic Environment Monitoring Report, No. 36.)

Martin, M.H., & Coughtrey, P.J. 1982. *Biological monitoring of heavy metal pollution: land and air.* London, Applied Science Publishers.

Melhuus, A., Seip, K.L., & Seip, H.M. 1978. A preliminary study of the use of benthic algae as biological indicators of heavy metal pollution in Sorfjorden, Norway. *Environmental Pollution, 15*: 101-107.

Miller, B.S. 1986. Trace metals in the common mussel *Mytilus edulis* (L.) in the Clyde Estuary. *Proceedings of the Royal Society of Edinburgh, 90B*: 377-391.

Phillips, D.J.H. 1994. Macrophytes as biomonitors of trace metals. *In: Biomonitoring of Coastal Waters and Estuaries,* ed. by K.J.M. Kramer. Florida, CRC Press.

Phillips, D.J.H., & Rainbow, P.S. 1993. *Biomonitoring of trace aquatic contaminants.* London, Elsevier.

Preston, A., Jeffries, D.F., Dutton, J.W.R., Harvey, B.R., & Steele, A.K. 1972. British Isles coastal waters: the concentrations of selected heavy metals in sea water, suspended matter and biological indicators - a pilot survey. *Environmental Pollution, 3*: 69-82.

Romeril, M.G. 1977. Heavy metal accumulation in the vicinity of a desalination plant. *Marine Pollution Bulletin, 8 (4)*: 84-87.

Ronnberg, O., Adjers, K., Ruokolahti, C., & Bondestam, M. 1990. *Fucus vesiculosus* as an indicator of heavy metal availability in a fish farm recipient in the Northern Baltic Sea. *Marine Pollution Bulletin, 21 (8)*: 388-392.

Scottish Development Department. 1987. *Water quality survey of Scotland 1985.* Edinburgh, HMSO.

Seeliger, U., & Edwards, P. 1977. Correlation coefficients and concentration factors of copper and lead in seawater and benthic algae. *Marine Pollution Bulletin, 8 (1)*: 16-19.

SOEnD. 1992. *Water Quality Survey of Scotland, 1990.* Edinburgh, The Scottish Office Environment Department Civil Engineering and Water Services.

WWA. 1982. *Investigations into the methodology of bioaccumulation studies.* (Tidal Waters Report No. TW 82/4/34.) Bridgend, Welsh Water Authority.

Persistent organochlorine compounds in the Firth of Clyde

A.G. Kelly & P.W. Balls

The Firth of Clyde borders the largest concentration of industry and population of any Scottish coastal water. The semi-enclosed nature of the firth has the potential for contaminants associated with such development to accumulate in marine sediment and biota. Organochlorine chemicals are of special concern by virtue of their toxicity, their persistence and an ability to accumulate in aquatic food chains. The present paper assesses the current degree of contamination of sediment and fish in the Firth of Clyde by such persistent organochlorine chemicals, including chlorobiphenyls, DDT and metabolites, dieldrin and chlordanes.

A north-south contaminant gradient is present in both sediment and biota. The greatest concentrations of organochlorines and faecal sterols in sediment are present on the sewage sludge disposal areas at Garroch Head. Fish from the vicinity of the disposal area similarly contained the maximal concentrations observed. Such concentrations are comparable to or exceed those previously found in United Kingdom waters. Quantification of the inputs from the atmosphere, rivers, sewerage and waste disposal in relation to this spatial distribution of organochlorines and faecal sterols in surficial sediment and biota, suggests that the dominant input is that of sewage sludge disposal in the north of the firth. The effect of this input extends over large areas of the firth.

A.G. Kelly & P.W. Balls*, Scottish Office Agriculture and Fisheries Department, Marine Laboratory, PO Box 101, Victoria Road, Aberdeen, AB9 8DB, UK.

*To whom correspondence should be addressed.

Introduction

The Firth of Clyde and the Clyde Estuary (Figure 1) are associated with the most industrialised and urbanised region of Scotland. Input of organic contaminants to these marine environments occur mainly from industrial discharges and from domestic discharges to the sewerage system. Associated with the latter is the disposal of sewage sludge off Garroch Head. Since the commencement of this operation in 1904, some 90 million tonnes of wet sludge have been dumped in the northern firth. The firth is separated from the neighbouring North Channel by the Great Sill, and by seasonal thermoclines. As a result only limited water exchange occurs, a flushing time of 3-4.5 months having been estimated (Baxter, Stenhouse & Drudarski 1980; Simpson & Rippeth 1993). Particle-bound contaminants such as lipophilic organics (e.g. McIntyre & Lester 1984) entering the firth may therefore tend to remain in the area and accumulate in sediment. Elevated levels of contaminants in the water column and sediment will lead to corresponding high levels in biota, through equilibrium partitioning and bio-concentration up the food chain (Jaffe 1991).

Previous studies of the distribution of organochlorine compounds in the firth are limited. Sediment data are confined mainly to the vicinity of the sewage sludge disposal areas. Two such areas exist, one in use until 1971, south of Garroch Head, and the current site some 4 km farther south. In both areas sea bed accumulation of sludge has occurred with concomitant elevation in sediment organic carbon and heavy metal concentrations, (Mackay, Halcrow & Thornton 1972; Halcrow, Mackay & Thornton 1973; Rodger, Davies & McHenery 1992a, b).

Studies of organochlorine contaminants in the sludge disposal areas suggest a similar distribution to that of organic carbon and heavy metals. Elevated concentrations of polychlorobiphenyls (CBs), were present in sediment at the former site to a depth of 20 cm (Halcrow, Mackay & Bogan 1974). One source of this material was an industrial release of CBs into the sewerage system (Waddington *et al.* 1973). The maximum concentration of 2,890 µg kg^{-1} Arochlor 1254 was present in the centre of the area. More widespread low-level contamination was also found. A more recent study (Kelly 1995) of the present disposal site revealed a lower maximum sediment chlorobiphenyl concentration of 515 µg kg^{-1} Arochlor 1254 in line with a decreasing concentration of CBs in sludge (Strathclyde Regional Council). Accumulations of dieldrin, DDT compounds, hexachlorobenzene, lindane, and polychloroaminodiphenylethers (PADS), were also observed. Using sediment core data, the study by
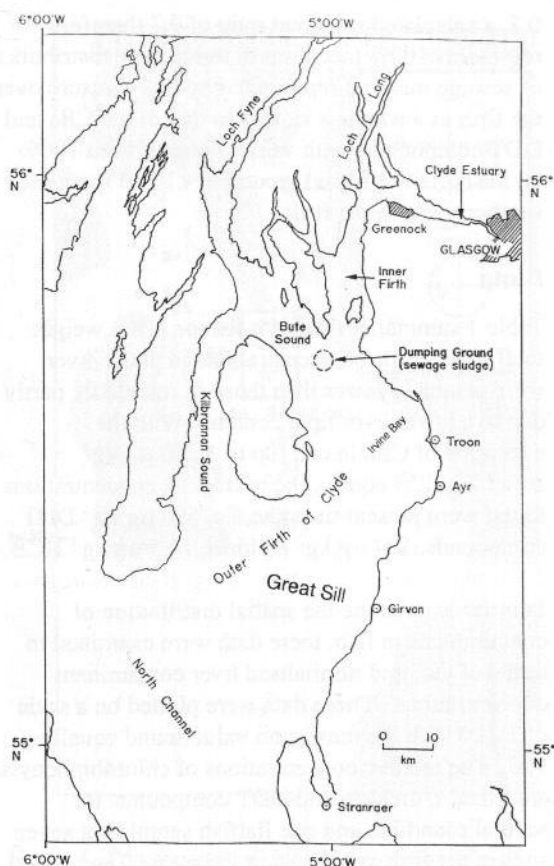
Figure 1. Location map of the Firth of Clyde indicating major settlements and the Garroch Head sewage sludge dumping ground.

Kelly demonstrated that the concentration of these compounds is unlikely to decrease in sub-surface sediment, as little mixing occurs and most are resistant to degradation in the sedimentary environment. A recent report (Tyler *et al.* 1994) on levels of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), in sediment in UK estuaries found 287-4,670 pg g^{-1} PCDDs and 100-1,540 pg g^{-1} PCDFs in the Clyde Estuary. These concentrations were considered to be above expected baseline values, and were exceeded only in the Dee Estuary.

That levels of organochlorine contaminants in the Firth of Clyde are elevated in comparison with other Scottish waters has been demonstrated by studies of fish and shellfish. The firth was highlighted by the 1977 'mussel-watch' survey of Scottish waters (Cowan 1981). Levels of dieldrin, chlorobiphenyls, DDTs and lindane in *Mytilus edulis* fell within the upper decile of values found. Further surveys in 1981 and 1982 confirmed sites in the firth as 'hotspots' for dieldrin, DDT and chlorobiphenyls, but indicated a downwards trend in concentrations (Haig & Miller 1984). As these compounds are no longer used industrially, this downwards trend may indicate a declining input. Such a decline in ambient

levels is indicated by analytical measurements of their content in Glasgow sewage sludge (Strathclyde Regional Council). Recently, levels of chlorobiphenyls, DDT and dieldrin in cod and herring from the Firth of Clyde were shown to be significantly higher than those in fish from the Firth of Forth and the northern North Sea (Kelly & Campbell 1994a). A comprehensive study of organochlorine contaminants in fish and shellfish from all Scottish fishing areas identified the Firth of Clyde as the area most contaminated by chlorobiphenyls, DDT compounds, lindane and dieldrin, with levels comparable to or exceeding those found in other UK and European offshore areas (Kelly & Campbell 1994b).

This present work reports results of a survey of organochlorine contaminants in sediment and fish extending over the entire area of the Firth of Clyde, the primary objective being to determine the spatial distribution of such contaminants. A further aim is to use such data to rank known input sources in order of greatest effect on the environment of the firth. To this end sterols of faecal origin measured in the sediment were utilised as tracers of one of the major inputs to the firth, that of sewage. Full details of the sediment work are given elsewhere (Kelly & Campbell 1995).

Methods

Sediment samples were collected from FRV Scotia in January 1989. Grab samples were obtained with a Day Grab and the top 5 cm removed. Subsequently, the sediment was stored in a glass jar and frozen at -20°C. The sediment was freeze-dried and roughly ground in a mortar and pestle. Sub-samples were taken for trace organic analysis and organic carbon (OC) determination. For trace organic analysis sediment (5-20 g) was placed in pre-extracted cellulose thimbles and extracted for four hours with dichloromethane. Clean-up and gas chromatograph (GC) instrument conditions have been previously reported (Kelly 1995). GC calibration was by the internal standard method using a five point calibration. Data collection and analysis were performed by the VG Minichrom system.

Fish and shellfish were obtained in May 1990 by FRV *Clupea*. Sampling and analysis were by previously reported methodology (Kelly & Campbell 1994a).

Results

Sediment

The concentrations of selected organochlorine

contaminants in the top 5 cm of sediment has been plotted in Figure 2 (CBs as the sum of the seven congeners IUPAC Nos. 28, 52, 101, 118, 138, 153 and 180) and Figure 3 ΣDDT. Figure 4 shows the distribution of CBs normalised to the OC content. The full data set is given elsewhere (Kelly & Campbell 1995).

The spatial distribution of CBs and DDT compounds is similar, with mean concentrations highest at the former and present sludge disposal grounds, i.e. 218 µg kg⁻¹ and 87 µg kg⁻¹ CBs and 175 µg kg⁻¹ and 55 µg kg⁻¹ DDT compounds respectively. Elevated concentrations extend north-west into Bute Sound and north into the inner firth. Over the outer firth as a whole, north-south and west-east concentration gradients are apparent. Lowest concentrations of 0.5 µg kg⁻¹ CBs and 1 µg kg⁻¹ DDT compounds are present at the most southerly site.

The concentrations of coprostanol (a sterol of faecal origin) in surface sediments are plotted in Figure 5. The estimated contribution of faecal sterols to total sediment sterols is also plotted in Figure 5. This figure is derived by determining the ratio of coprostanol and epi-coprostanol to the sum of these and cholesterol, stigmasterol and ß-sitosterol, sterols of natural origin. The value of this ratio in sludge is

0.7, a calculated sediment ratio of 0.7 therefore represents 100% faecal sterol input. The distribution of sewage material represented by this measure over the firth as a whole is similar to that of the CBs and DDT compounds, with values ranging from 100% on the current disposal ground to <1% at the most southerly site in the firth.

Biota

Table 1 summarises data for fish on a wet weight total tissue basis. Concentrations in plaice liver were generally lower than those in roundfish, partly due to a lower liver lipid content. With the exception of CBs in cod (up to 5,200 µg kg⁻¹ Arochlor 1254 equiv), the maximum concentrations found were present in saithe, i.e. 598 µg kg⁻¹ DDT compounds, 104 µg kg⁻¹ dieldrin, 13.5 µg kg⁻¹ HCB, 5.1 µg kg⁻¹ lindane and 100 µg kg⁻¹ total chlordanes. In order to examine the spatial distribution of contaminants in fish, these data were examined in terms of the lipid normalised liver contaminant concentrations. These data were plotted on a scale of 1-100 with the maximum value found equalling 100. The relative concentrations of chlorobiphenyls, chlordanes, dieldrin and DDT compounds for several roundfish and one flatfish sampled at seven sites in the firth are shown in Figure 6. The results reflect the general distribution found in sediment, suggesting a north-south concentration gradient of
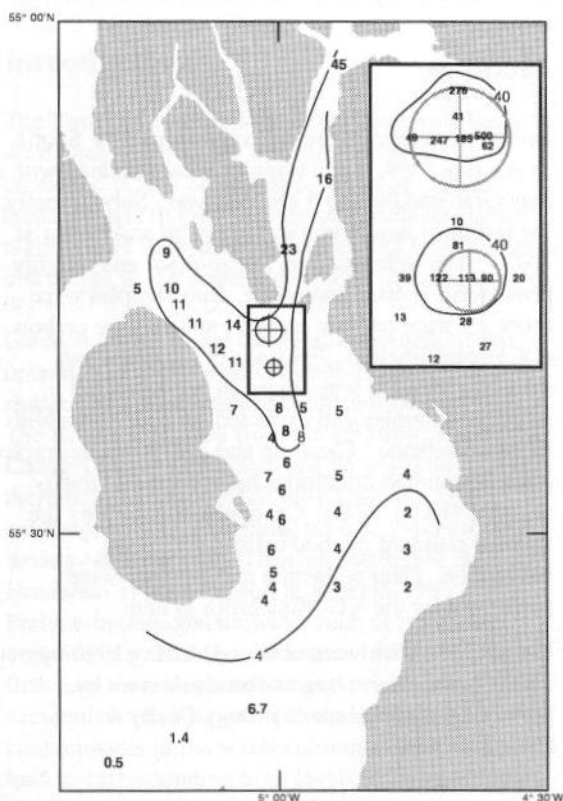

Figure 2. Concentration of chlorobiphenyls in surficial sediment as sum of congeners IUPAC Nos. 23, 52, 101, 118, 138, 153 and 180 (µg kg⁻¹ dry weight).

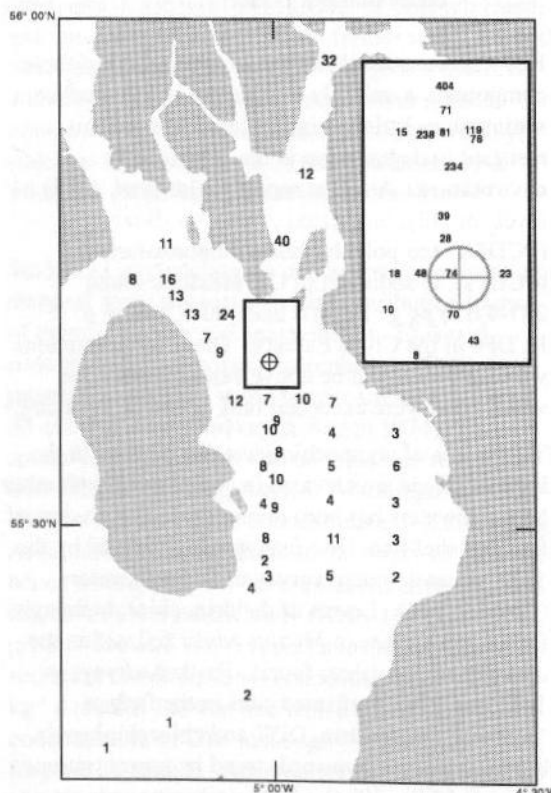**Figure 3.** Concentration of ADDT in surficial sediment (µg kg⁻¹ dry weight).
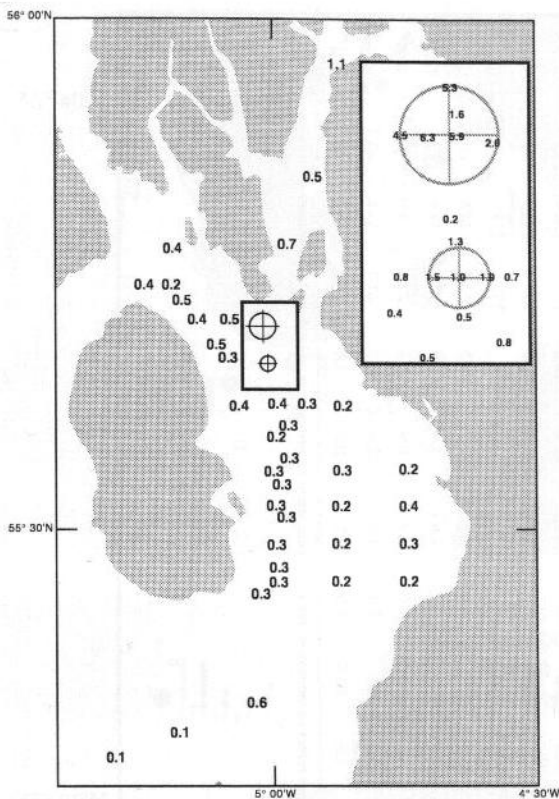
Figure 4. Concentration of chlorobiphenyls in surficial sediment as sum of congeners IUPAC Nos. 28, 52, 101, 118, 138, 153 and 180 in surficial sediment normalised to sediment organic carbon (mg kg⁻¹ organic carbon dry weight).

Figure 5. Concentration of coprastanol in surficial sediment (figures µg kg⁻¹ dry weight) and percentage sewage input (contours). Percentage sewage input is the ration of coprostanol and epicoprastanol to the sum of these plus cholesterol, stigmasterol and -sitosterol. The ratio is expressed as a percentage of the value (0.7) found in sludge. Therefore 100% suggests that sediment organic matrix is entirely sludge derived.

organochlorine contaminants in certain fish species. Highest concentrations are generally in the north of the firth at the Garroch Head, Ardrossan Bay and Irvine Bay sites, and lowest at the most southerly site in the North Channel. Haddock and whiting show the smallest differences between sites, cod and plaice the largest, reaching a maximum of a factor of 17 for chlorobiphenyls in cod liver.

Discussion

Sediment

The complete interpretation of the sediment data is given elsewhere (Kelly & Campbell 1995), only the important conclusions will be included here.

The spatial distribution of contaminants in sediment presents a consistent picture. A distinct north-south gradient confirms that the major input occurs in the north of the firth with subsequent transport of material around the firth, and (excluding the sludge disposal areas), predominant deposition of particulates in the deeper waters of the firth (e.g. Bute Sound). The north of the firth is dominated by the 'hotspots' of the sludge disposal sites and the higher contaminant concentrations at the mouth of

the Clyde Estuary. These data suggest that these are the two major sources of input to the firth with the third possible source, that from the eastern shore of the firth, being of minor importance.

In considering these distributions, account must be taken of the influence of both sediment chemistry and hydrographic factors. In an equilibrated system the concentration of lipophilic compounds such as coprostanol, DDT and chlorobiphenyls associated with particulate material will be directly proportional to the organic carbon content of that material (Karickhoff 1981). Sediment chemistry will thereby greatly influence contaminant distribution. But in environmental systems an equilibrated state is often not reached, desorption of contaminants from particles being kinetically limited (Karickhoff & Morris 1985). The sediment concentration of contaminants may then reflect that of the input.

To examine whether such equilibration is important in Clyde sediments the data for CBs has been

Table 1. Concentration of organochlorines in liver of fish from the Firth of Clyde ($\mu g\ kg^{-1}$ wet weight).

	Location	Sampling date	No. of fish/ pools	Length (cm)	% Lipid	CB28	CB52	CB101	CB118	CB153	CB138	CB180	Arochlor 1254 EQ	HCB	G-HCH	Total Chlordanes	Dieldrin	4,4'- DDE	4,4'- DDD	4,4'- DDT	SUM DDTs
Fish liver																					
Cod	55°41N 05°00W	18/05/90	20/4	26-35	29.4	43.3	66.9	190	254	633	466	427	5,200	<1	<1	51.1	99.2	267	177	16.6	499
sd						(17.7)	(24.1)	(13.8)	(49.6)	(141)	(160)	(182)	0.00			(6.0)	(35.7)	(28.5)	(60.6)	(6.8)	
Cod	55°31N 04°53W	20/05/90	8/1	22-30	23.2	5.2	17.4	70.7	133.6	435	295	207	2,910	4.1	1.7	31.0	37.8	197	70.4	8.1	291
Cod	55°06N 05°30W	20/05/90	10/1	48-53	47.2	3.6	6.0	17.2	25.4	75.9	53.8	24.2	515	6.9	4.5	23.9	30.7	46.4	26.7	6.3	83.3
Whiting	55°37N 04°43W	22/05/90	5/1	24-26	52.6	10.8	35.1	114	115	355	267	143	2,600	10.0	3.7	32.1	55.5	231	139	34.0	422
Whiting	55°36N 04°48W	19/05/90	5/1	23-26	37.4	6.9	19.7	59.3	84.4	271	196	119	1,890	5.7	4.0	58.3	51.4	232	191	43.1	495
Whiting	55°06N 05°30W	20/05/90	10/1	26-35	36.2	5.5	9.8	20.4	38.6	103	94.0	46.6	795	5.7	4.2	41.9	48.8	94.3	112	27.5	249
Haddock	55°41N 05°00W	18/05/90	10/1	24-28	42.8	11.0	20.7	42.9	59.3	165	119	80.2	1,240	4.6	3.9	19.1	52.5	64.1	97.3	14.6	193
Haddock	55°06N 05°30W	20/05/90	10/1	23-28	32.8	6.1	9.1	29.2	50.9	147	108	49.5	999	5.2	2.3	15.6	25.6	98.7	69.2	24.9	196
Hake	55°41N 05°00W	18/05/90	10/1	32-42	53.3	5.4	17.5	43.0	43.7	124	93.9	53.8	952	6.2	<0.1	13.0	35.8	90.3	60.3	16.8	181
Hake	55°37N 04°53W	22/05/90	5/1	29-42	50.0	8.4	33.9	96.3	89.8	253	198	114	1,980	6.9	5.0	56.6	100	149	214	36.1	445
Hake	55°36N 04°48W	19/05/90	6/1	35-39	67.6	9.9	30.0	69.7	64.5	170	139	71.6	1,390	11.8	<0.1	19.9	67.7	129	110	33.3	294
Hake	55°31N 04°53W	19/05/90	6/1	36-52	57.6	6.4	23.0	58.7	62.2	181	132	76.7	1,350	10.3	<0.1	36.7	12.9	136	112	13.8	292
Hake	55°24N 05°17W	20/05/90	10/1	33-55	54.4	6.7	22.0	58.8	64	171	138	72.6	1,330	9.7	<0.1	21.8	10.8	135	156	13.2	329
Saithe	55°41N 04°59W	18/05/90	10/1	31-35	24.3	19.2	46.3	127	106	341	290	120	2,620	7.9	3.7	88.9	81.6	259	297	10.9	598
Saithe	55°33N 04°55W	21/05/90	10/1	31-37	45.2	22.5	50.7	114	95.2	270	222	98.8	2,180	13.5	5.1	100	104	252	258	41.0	593
Plaice	55°41N 05°01W	20/05/90	18/1		22.2	11.7	14.8	23.0	23.9	72.1	46.1	38.1	574	3.6	2.0	6.6	27.3	32.2	25.8	<0.5	64.8
Plaice	55°37N 04°53W	20/05/90	25/1		15.9	3.1	3.1	7.7	9.8	38.5	26.9	18.1	268	1.9	1.6	1.4	10.9	27.2	17.6	<0.2	48.6
Plaice	55°36N 04°48W	20/05/90	25/1		11.0	2.5	2.5	4.5	7.5	24.6	16.3	9.8	169	1.4	0.9	0.9	7.2	22.8	9.9	<0.2	34.8
Plaice	55°25N 05°10W	20/05/90	25/1		30.0	23.0	34.6	39.7	32.3	86.9	55.2	42.6	785	7.4	3.5	11.6	40.7	47.7	33.8	<0.2	88.6
Plaice	55°06N 05°30W	20/05/90	4/1		12.3	2.9	1.3	2.2	3.0	7.1	5.8	2.6	61.9	1.6	1.5	0.9	3.4	7.9	3.7	<0.5	12.5

The figure for an Arochlor 1254 equivalent is calculated as 2.5 times the sum of the seven listed chlorobiphenyl congeners. Total chlordanes refers to the sum of cis-chlordane, trans-chlordane, cis-chlordene, trans-chlordene, trans-nonachlor, heptachlor, oxychlordane and heptachlor epoxide.
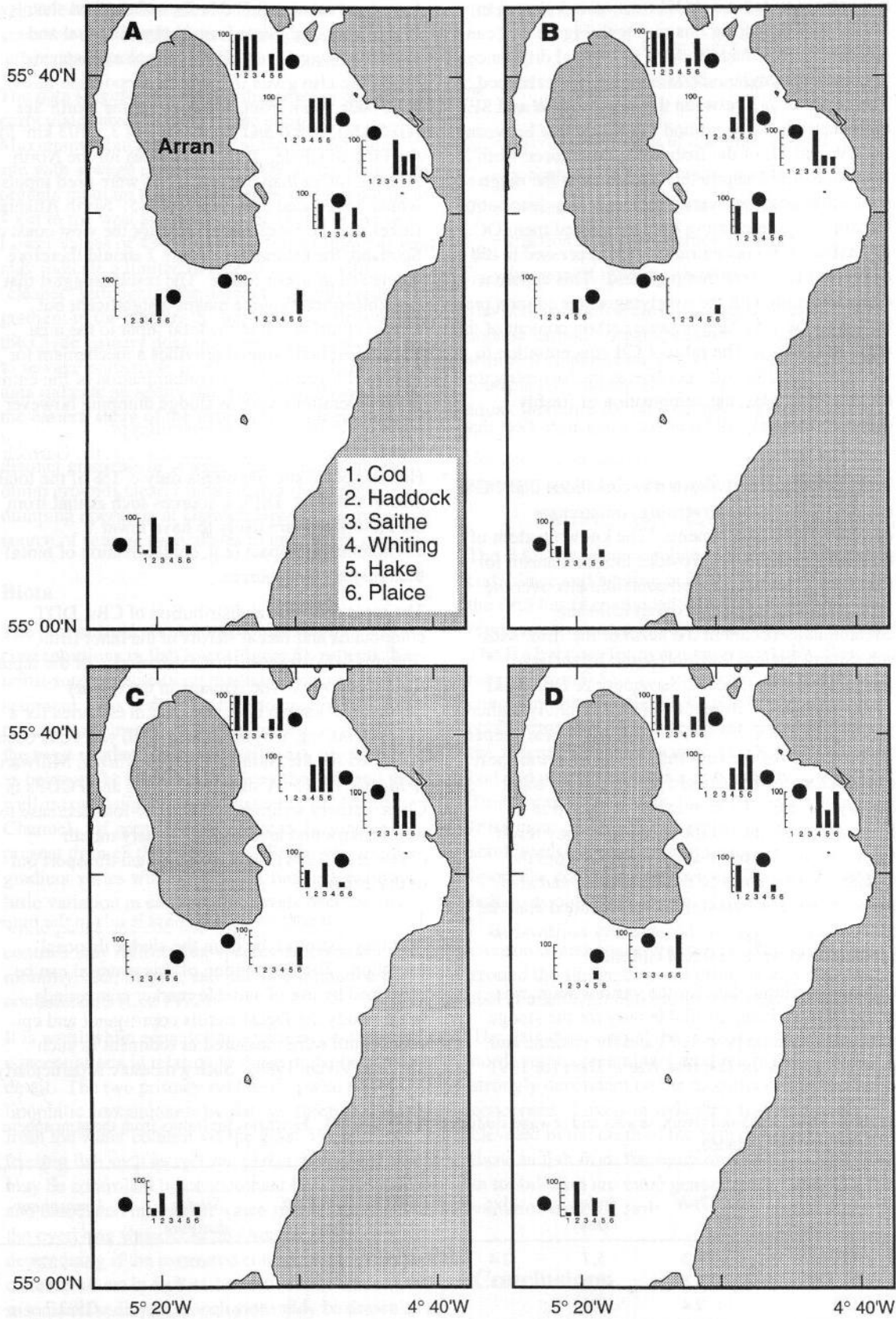
Figure 6. Relative concentration of organochlorine contaminants in fish from the Firth of Clyde. Data have been normalised to tissue lipid content: (a) Chlorobiphenyls as an Arochlor 1254 equivalent; (b) total chlordanes; (c) dieldrin; (d) sum of 4,4'-DDT, DDD and DDE.

normalised to sediment OC content and plotted in Figure 4. Comparing this plot with Figure 2, it can be seen that the magnitude of the spatial differences in chlorobiphenyl concentration has been reduced. The factor of 2-3 between the extreme NW and SE has been reduced to around 1.5, while that between the SW and SE of the firth has been reduced from 2 to around 1.3. Despite this reduction in the range of concentrations, the overall pattern of the distribution remains. It is interesting to note that sediment OC normalised CB concentrations are depressed in the centre of the current dump ground. This apparent disequilibrium with the overlying water column may be due to the very high organic carbon content of the sediment (12%). The ratio of CB concentration to OC content is likely to increase as the less refractory material degrades, the composition of freshly dumped material will however primarily reflect that of sludge itself.

From the discussion above it is concluded that OC is not the major factor governing contaminant concentrations in sediments. The known pattern of residual current flows provides the mechanism for transport of particle-bound contaminants over the firth. The major input of organochlorine contaminants occurs in the north of the firth, with subsequent limited transport south by surface residual currents (Baxter, Stenhouse & Drudarski 1986; Simpson & Rippeth 1993). Generally higher levels of organochlorine contaminants in the deeper western areas of the firth may result from transport of particulates by westward flowing deep-water density currents. Contaminated sediment in Inchmarnoch Water to the north-west may result from westward movement of material from the sludge disposal areas or the inner firth, and also from northwards transport of resuspended material in the Arran Trough by the generally northwards-moving deep water residual currents.

Quantitative input data for the various sources is rather limited, being available only for the sludge disposal operation post-1973 and for riverine and sewage input in the last few years. Data for 1991 have been tabulated (Table 2), and confirm that major inputs originate from sludge disposal and from the River Clyde. Estimates of atmospheric inputs are also given in Table 2. Deposition rates have been taken from estimates for the North Sea (GESAMP 1989) and use an area of 3×10^3 km^2 for the Firth of Clyde. If flux estimates for the North Atlantic rather than the North Sea were used inputs would be reduced by a factor of 2-5. North Atlantic fluxes may be more appropriate for the west coast of Scotland, the estimates in Table 2 should therefore be viewed as upper limits. The results suggest that the atmospheric source makes a significant but diffuse contribution to the total input to the area. The atmospheric source provides a mechanism for low level organochlorine contamination of the entire firth. Operations such as sludge dumping however introduce relatively large quantities of organochlorines to localised areas, e.g. the Garroch Head disposal site represents only c. 1% of the total area of the firth. Diffuse sources such as that from the atmosphere are likely to have lower environmental impact (e.g. contamination of biota) than major point sources.

The measured spatial distribution of CBs, DDT compounds and faecal sterols in the inner firth (Figures 2-5), suggests that the majority of the input from the River Clyde remains in the estuary. Sediment is known to be retained in estuaries for a long period, e.g. a cycling time of 20 years has been estimated for the Humber Estuary (Turner, Millward & Morris 1991). A study of PCDDs and PCDFs in Clyde Estuary sediment found a 10-fold decrease to near background levels at the estuary mouth (Tyler et al. 1994) suggesting limited transport out of the estuary.

The major impact on contaminant levels in the outer firth may therefore be from the sludge disposal operation. The distribution of this material can be examined by use of suitable marker compounds. In this study the faecal sterols coprostanol and epi-coprostanol were measured in sediment as such markers (Vivian 1986). Such a measure is particularly

Table 2. Input (kg) from rivers, sewers and sewage sludge dumping in 1991. Estimates for inputs from the atmosphere are also included.

	Clyde	Irvine Bay	Ayr	Girvan	Total	Sludge dumping	Atmosphere
		Rivers and sewers[a]					
HCH	33.5	5.7	2.4	0.9	42.5	<0.5	54-222*
CBs	5.8	0.3	0.1	0.1	6.3	11.7	9.9-20.4
HCB	2.4	0.4			2.8		0.9-2.7
Dieldrin	0.2	0.3			0.5	<2.7	3.6-6.0
DDT	2.2	0.5			2.7	<5	0.5-5.1**
DDD	0.3	0.6			0.9	<5	
DDE	0.7	0.6			1.3	<5	

*HCH; **DDT; [a]Clyde River Purification Board (pers. comm.)

valuable being independent of sediment OC content, grain size or accumulation rate, and thus accurately reflects the distribution of sewage particulates.

The data (Figure 5) confirms that sewage-derived particulates are present over the entire firth. Maximum input levels occur at the present dump site with sewage constituting 100% of the sediment organic input up to 2 km, and 60% of the input up to 4 km to the west and south of the centre of the site. Lower values of 43-66% on the former dump ground may indicate a limited degree of mixing with 'cleaner' sediment. The decreasing northwards gradient in the inner firth confirms that outflow from the Clyde Estuary does not contribute substantially to sewage particulate levels in the outer firth. These data indicate an additional input from Irvine Bay on the eastern shore of the firth, with sediment input levels of over 40% sewage in this area, but the distinct gradients of sewage input centred on the dump grounds clearly indicate that the sludge dumping operation at Garroch Head is the major source of sewage particulates to the firth in general.

Biota

The plot of lipid normalised contaminant concentrations in fish liver (Figure 6), reflects the north-south contaminant gradient observed in sediment. It is perhaps not surprising that the lowest contaminant levels are mainly present in fish from the most southerly site. This site may be considered as being at the boundary between the firth and the well-mixed 'offshore type' waters of the North Channel. Of greater significance is the gradient present through the other sites. Sensitivity to this gradient varies with species, i.e. haddock exhibits little variation in contaminant levels over the firth, while plaice and cod show large variation. This contrast may reflect inter-species differences in mobility, diet, habitat, and rate of elimination of contaminants (Lee 1992).

It is worthwhile considering sediment contaminant concentrations in relation to those in the fish in more detail. The two primary routes of uptake of lipophilic contaminants by fish are through diet and from the water column via the gills. For bottom-feeding fish such as cod and plaice, both these routes may be controlled by contaminant levels in sediment and associated interstitial water, rather than that in the overlying water column (Adams 1987). By determining if the measured contaminant concentrations in fish in the firth reflect those in the associated sediment, conclusions may be drawn as to the influence of that sediment on the 'local' fish populations. One means of examining this relationship is by the 'fugacity' approach. This considers the thermodynamic equilibrium of a chemical between a source (sediment) and a sink

(fish) (Mackay & Paterson 1981) so at equilibrium:

$$c_{oc} . C_s / f_{oc} = c_{lip} . C_f / f_{lip}$$

c_{oc} = activity coefficient of chemical in organic carbon

c_{lip} = activity coefficient of chemical in lipid

C_s = concentration of chemical in sediment

C_f = concentration of chemical in fish liver

f_{oc} = fraction of organic carbon in sediment

f_{lip} = fraction of lipid in fish liver

The activity coefficients of a chemical in sediment organic carbon, (organic carbon content controls sediment contaminant levels), and fish lipid, (lipid controls fish contaminant levels) are considered equal, therefore the ratio of lipid normalised tissue levels to organic carbon normalised sediment levels (termed the bioaccumulation factor, BAF) should approximate to 1.0 if an equilibrium exists.

$$BAF = c_{oc} / c_{lip} . ((C_f / f_{lip}) / (C_s / f_{oc}))$$

The BAF has been calculated for chlorobiphenyls in cod, plaice and whiting in Table 3. For this exercise, the firth has been divided into three areas and representative sediment CB concentrations assumed. The BAF values for plaice are remarkably close to 1, ranging from 0.5 to 2.2, suggesting that the concentration of chlorobiphenyls in plaice is in equilibrium with that in sediment, possibly due to the sedentary habit of plaice. Single high values for cod and whiting indicate a non-equilibrium state. This is most likely to be due to movement of fish from more contaminated northern waters southwards. As rates of elimination of very lipophilic contaminants such as CBs are low, with half-lives of months to years (e.g. Mackay & Hughes 1984), even limited exposure to high environmental concentrations such as are present around the sludge disposal grounds may dominate fish contaminant burdens for considerable periods.

The data thus suggest that the effect on fish of the north-south contaminant gradient in sediment is strongly dependent on the mobility of the species concerned. Levels in sedentary fish are greatly elevated in the north of the firth in comparison with those in fish from the south of the firth, whilst levels in mobile fish are more generally elevated with less variation over the firth.

Conclusions

This study suggests that, in addition to the previously recognised effects within the disposal areas, dumping of sewage sludge is the major contributor to elevated levels of organochlorine pollutants over the Firth of Clyde generally.

Table 3. Bioaccumulation factor (BAF) of chlorobiphenyls for several fish species in the Firth of Clyde. BAF is the ratio of the lipid normalised concentration of CBs in fish liver to organic carbon normalised CB concentration in sediment.

Fish species	Sample position	Fish tissue lipid content (%)	Fish CBs (ICES 7) µg kg⁻¹ wet wt	Fish CBs (ICES 7) µg kg⁻¹ lipid	Sediment CBs (ICES 7) µg kg⁻¹ OC	BAF (lipid)
Cod	North firth	29.4	2,081	7,079	2,000	3.5
	Mid firth	23.2	1,164	5,019	300	16.7
	North channel	47.2	206	437	100	4.4
Plaice	North firth	22.2	230	1,036	2,000	0.5
	North firth	30.0	314	1,048	2,000	0.5
	Mid-firth	15.9	107	674	300	2.2
	Mid-firth	11.0	68	615	300	2.0
	North channel	12.3	25	202	100	2.0
Whiting	North firth	52.6	1,040	1,977	2,000	1.0
	North firth	37.4	757	2,024	2,000	1.0
	North channel	36.2	318	878	100	8.8

(The Fish CBs columns headers read: Fish CBs (ICES 7) $\mu g\ kg^{-1}$ wet wt; Fish CBs (ICES 7) $\mu g\ kg^{-1}$ lipid; Sediment CBs (ICES 7) $\mu g\ kg^{-1}$ OC)

This input has produced a distinct north-south contamination gradient, with contaminant levels in sediment in the north of the outer firth around the sewage sludge disposal grounds exceeding those in the inner firth and lower Clyde Estuary. Residual currents in the firth have transported particle bound contaminants input in the north, to the deeper depositional basins in the west and north-west. This distribution pattern of chlorobiphenyls and DDT compounds is likely to be reproduced by other as yet unmeasured lipophilic contaminants present in sludge.

Contaminant levels in fish on the whole reflect those in sediment with a north-south gradient. However, there is some evidence that very high contaminant concentrations in the sludge disposal areas have a more widespread effect on fish. In more distant mobile fish populations, a generalised raising of contaminant concentrations may result. This is of long-term importance both for aquatic life and for fisheries in the Clyde. As contaminant concentrations in the sludge disposal areas are unlikely to decline in the future (Kelly 1995) the proposed cessation of sludge dumping in 1998 may not result in an immediate reduction of contaminant levels in the Firth of Clyde. The effect of such changes in input on contaminant levels in the firth is being monitored by SOAFD. Currently an annual sampling of plaice in the northern part of the firth is undertaken, utilising a sampling strategy designed to detect temporal trends. Further sampling of sediment and biota in accord with the United Kingdom National Marine Monitoring Plan is also underway.

Acknowledgement

References

Adams, W.J. 1987. Bioavailability of neutral lipophilic organic chemicals contained on sediment: a review. *In: Fate and effects of sediment-bound chemicals in aquatic systems,* ed. by K.L. Dickson, A.W. Maki & W.A. Brungs. Pergamon Press.

Baxter, M.S., Stenhouse, M.J., & Drndarski, N. 1980. Fossil carbon in coastal sediments. *Nature, 287*: 35-36.

Cowan, A.A. 1981. Organochlorine compounds in mussels from Scottish coastal waters. *Environmental Pollution, Series B, 2*: 129-143.

GESAMP. 1989. *The atmospheric input of trace species to the world ocean.* Reports and Studies No. 38.

Haig, A.J.N., & Miller, B.S. 1984. Chemistry of the Firth of Clyde. *Analytical Proceedings, 21*: 116-118.

Halcrow, W.M., Mackay, D.W., & Thornton, I. 1973. Distribution of trace metals and fauna in the Firth of Clyde. *Journal of the Marine Biological Association of the UK, 53*: 721-739.

Halcrow, W., Mackay, O.W., & Bogan, J. 1974. PCB levels in Clyde marine sediments and fauna. *Marine Pollution Bulletin, 5*: 134-136.

Jaffe, R. 1991. Fate of organic pollutants in aquatic environments: a review. *Environmental Pollution, 69*: 237-257.

Karickhoff, S.W. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere, 10*: 833-846.

Karickhoff, S.W., & Morris, K.R. 1985. Sorption dynamics of hydrophobic pollutants in sediment suspensions. *Environmental Toxicology and Chemistry, 4*: 69-479.

Kelly, A.G. 1995. Accumulation and persistence of chlorobiphenyls, organochlorine pesticides and faecal sterols at the Garroch Head sewage sludge disposal site, Firth of Clyde. *Environmental Pollution, 88*: 207-217.

Kelly, A.G., & Campbell, L.A. 1994a. Organochlorine contaminants in liver of cod (*Gadus morhua*) and muscle of herring (*Clupea harengus*) from Scottish waters. *Marine Pollution Bulletin, 28*: 10-108.

Kelly, A.G., & Campbell, D. 1994b. *Persistent organochlorine contaminants in fish and shellfish from Scottish waters*. Aberdeen, SOAFD. (Scottish Fisheries Research Report, No. 54.)

Kelly, A.G., & Campbell, L.A. 1995. Persistent organochlorine contaminants in the Firth of Clyde in relation to sewage sludge input. *Marine Environmental Research, 41*: 99-132.

Lee, H. 1992. Models, muddles, and mud: predicting bioaccumulation of sediment-associated pollutants. *In: Sediment Toxicity Assessment*, ed. by G. Allen Burton, Jr.

McIntyre, A.E., & Lester, J.N. 1984. Occurrence and distribution of persistent organochlorine compounds in UK sewage sludges. *Water, Air and Soil Pollution, 23*: 397-415.

Mackay, D.W., Halcrow, W., & Thornton, I. 1972. Sludge dumping in the Firth of Clyde. *Marine Pollution Bulletin, 3*: 7-11.

Mackay, D., & Paterson, S. 1981. Calculating fugacity. *Environmental Science and Technology, 15*: 1,006-1,014.

Mackay, D., & Hughes, A.I. 1984. Three-parameter equation describing the uptake of organic compounds by fish. *Environmental Science and Technology, 18*: 439-444.

Rodger, G.K., Davies, I.M., & Topping, G. 1992a. Retention of trace metals contaminants in the sediment at an accumulating sewage sludge disposal site. *Water Research, 26*: 111-120.

Rodger, G.K., Davies, I.M., & McHenery, J. 1992b. Effects of sewage sludge disposal at the Garroch Head dump site, Firth of Clyde, Scotland. *Science of the Total Environment, 119*: 133-156.

Simpson, J.H., & Rippeth, T.P. 1993. The Clyde sea: a model of the seasonal cycle of stratification and mixing. *Estuarine, Coastal and Shelf Science, 37*: 129-144.

Turner, A., Millward, G.E., & Morris, A.W. 1991. Particulate metals in five major North Sea estuaries. *Estuarine, Coastal and Shelf Science, 32*: 325-346.

Tyler, A.O., Millward, G.E., Jones, P.H., & Turner, A. 1994. Polychlorinated dibenzo-para-dioxins and polychlorinated dibenzofurans in sediments from UK estuaries. *Estuarine, Coastal and Shelf Science, 39*: 1-13.

Vivian, C.M.G. 1986. Tracers of sewage sludge in the marine environment, a review. *Science of the Total Environment, 53*: 5-40.

Waddington, J.I., Best, G.A., Dawson, J.P., & Lithgow, T. 1973. PCBs in the Firth of Clyde. *Marine Pollution Bulletin, 4*: 26-28.

The application of the 'mussel-watch' concept to the identification of temporal and spatial trends in contamination of the Clyde Sea area by PCBs

B.S. Miller & D.J. Pirie

The Clyde Estuary receives a relatively high contaminant load derived from the domestic and industrial wastes of half of Scotland's population. Previous studies on levels of organochlorine compounds in mussels from Scottish waters have highlighted the Clyde as a contaminated 'hot-spot' area.

As regulatory authority for the area, the Clyde River Purification Board initiated in 1980 a 'mussel-watch' programme to monitor concentrations of these organochlorine compounds, and of other toxic, persistent substances such as trace metals. The data gathered have allowed the assessment of temporal and spatial trends in concentrations of these substances in mussels from the Clyde Sea Area. The Clyde RPB has also used the data to fulfil its obligations under EC Directives on the disposal of dangerous substances to the aquatic environment, and on the quality of water required for shellfish growing.

This paper focuses on concentrations of polychlorinated biphenyls (PCBs) in mussels collected over a 14-year period from shores throughout the Clyde Sea area. Spatial and temporal trends are assessed, and the data are compared to concentrations found in other areas in the UK and in continental Europe, to set the Clyde results in context.

B.S. Miller & D.J. Pirie*, Clyde River Purification Board, Rivers House, Murray Road, East Kilbride, Glasgow, G75 0LA, UK.

*To whom correspondence should be addressed.

Introduction

It was relatively recently in 1975 that a world-wide 'mussel-watch' survey was proposed, as a first step in the global marine monitoring of persistent, toxic and bioaccumulated pollutants, such as trace metals, organochlorine pesticides and polychlorinated biphenyl (PCB) residues (Goldberg 1975).

The Clyde River Purification Board (CRPB) started its own 'mussel-watch' surveys in 1980, with multiple aims:

- to assess whether 'hotspots' identified in the 1970s by other workers (Davies & Pirie 1980; Cowan 1981) still existed;

- to establish spatial and temporal trends in contaminant levels;

- to provide data for trace metals and organochlorine compounds to fulfil the CRPB's requirements as the regulatory authority for the Clyde Sea area in respect of UK and international legislation; and

- to set Clyde Sea area contaminant levels in context with those of other similar industrialised areas.

Polychlorinated biphenyls (PCBs) are a family of 209 organochlorine compounds which were widely used in transformer oils and capacitors because of their low solubility and ability to withstand high temperatures. PCBs have been manufactured in the UK since 1954, and were implicated in the deaths of thousands of seabirds in the Irish Sea in 1969 (Waddington *et al.* 1973). Despite restrictions in the sale of PCBs in the late 1970s, high levels were found in Clyde Sea area mussels at that time (Cowan 1981). More recent studies have shown elevated PCBs concentrations in fish (Kelly & Campbell 1994), sediments (Kelly 1995) and otter scats (Mason *et al.* 1992) from the Clyde Sea area. There is persuasive evidence for toxicological effects from PCBs in certain ecosystems, ranging from phytoplankton to marine mammals (Phillips 1994) and it is apparent that PCBs are ubiquitous environmental contaminants capable of impairing physiological processes such as reproduction, embryonic development and vitamin-related control systems in a variety of organisms (Brouwer 1991).

In view of the nature of PCBs and their effects, we have examined the concentrations in mussels collected by the Clyde RPB between 1981 and 1994 from 57 sites in the Clyde Sea area (see Figure 1). Data are presented for animals collected during the annual 'mussel-watch' survey and for other surveys
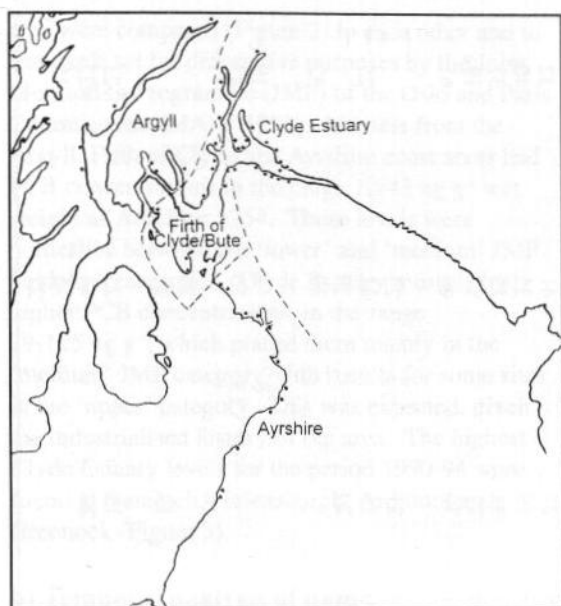
Figure 1. CRPB mussel collection sites in the Clyde Sea area.

in respect of the EC Shellfish-growing Waters Directive (EEC 1979). The 'mussel-watch' survey mainly includes sites in the relatively contaminated Clyde Estuary and along the Ayrshire coast and forms part of the Clyde RPB's monitoring programme for 'Red List' substances (DoE 1988). The EC Shellfish Directive survey covers mainly uncontaminated sites in more remote areas. The data are submitted annually to the Scottish Office by the Clyde RPB as part of its obligations under the EC Dangerous Substances Directive (EEC 1976) and Oslo and Paris Commissions (North Sea Task Force 1993).

Sampling

Sampling was carried out according to international guidelines which have been described elsewhere (Miller 1986). In summary, batches of 25 mussels in the size range 40-60 mm were collected from rocks at the mid-tide level, returned to the laboratory within 3 hours and depurated for 24 hours in sea water from the collection site, to clean out particulate material from the gut. The mussels were frozen at -18°C, then freeze-dried and stored for analysis.

Analysis

The techniques used for the analysis of organochlorine compounds in mussels have changed over the 14-year period for which data are reported. The Clyde RPB has always sought to use the best

available methods, together with the latest technology, and has participated in various national and international inter-laboratory exercises over the years, including Aquacheck, the National Marine AQC Scheme (MPMMG 1994) and the Quasimeme programme (Wells & de Boer 1994).

In summary, mussel tissues were analysed from 1981 to 1988 by chemical drying, solvent extraction adsorption chromatography clean-up and gas chromatography with ^{63}Ni electron capture detection (GC/ECD) (Wells & Johnstone 1977). Quantification was carried out by comparison of peak heights with Arochlor 1254 standards (Haig & Miller 1984). After 1988, mussels were freeze-dried and lightly macerated, then sub-samples of tissue were soxhlet extracted with 50% hexane in methyl tert butyl ether (MTBE). The extracts were concentrated then cleaned-up using aminopropyl and alumina adsorption chromatography prior to silica gel fractionation of the PCBs and organochlorine pesticides (HMSO 1985, 1992). The extracts were analysed by capillary GC with ^{63}Ni ECD. Quantification was by comparison of peak heights with those for individual PCB congener standards for the 'ICES 7' congeners (i.e. CBs 28, 52, 101, 118, 138, 153 and 180) (Duinker, Schulz & Petrich 1988), and against internal standards.

Results

The whole dataset is shown in Table 1, as ng g^{-1} wet weight as Arochlor 1254. Comparison of 1988-94 data with that for previous years was facilitated by conversion of the sum of the 'ICES 7' congeners to Arochlor 1254. This was carried out on the basis of the percentage contribution of the 'ICES 7' congeners in Arochlor 1254 (Schulz, Gert & Duinker 1989).

Discussion

The data set for all 57 sites for the 14-year period was large and complex, so this was split into four geographical areas and two temporal groups for ease of spatial and temporal analysis. Spatially the Clyde Sea area was split into four areas: Argyll, the Clyde Estuary, the Firth of Clyde (including Bute) and the Ayrshire coast (see Figure 1). Temporal analysis was carried out by comparison of the data over the 14-year period.

a) Spatial analysis of data

Spatial analysis was carried out only for data for the period 1990-94, in order to focus on the current contamination levels. PCB concentrations for each

Table 1. PCB Concentrations in mussels from the Clyde Sea Area, 1981-1994 (ng/g wet weight as Arochlor 1254).

Sampling site	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
Argyll														
Loch Fyne, River Fyne Mouth										7	11	23	6	14
Loch Fyne, Loch Gair										13	18	17	13	12
Loch Fyne, Whitehouse Bay										11	22	15	17	17
Loch Riddon, Ardachuple		39								21	30	28	29	22
Kyles of Bute, Colintraive										36		32	40	35
Clyde Estuary														
Loch Long, Ardentinny									16	24	31	57	36	32
Loch Long, Ardgartan									18	26	21	22	64	30
Loch Goil, Cuilmuich									19	28	13	25	38	40
Kilcreggan			114	55	66	203			20	28		71		49
Portkil Bay 1	120	80	75	108	141	86	136	58	36	52		38		86
Portkil Bay 2	351	86	147	87	104	131	125	108				58		124
Gareloch, Shandon 1	194	87	87	86	68	141	115	86						
Gareloch, Shandon 2	155	79	152		91	78	166	56						
Helensburgh					93	111	138		20	28		28		116
Craigendoran					96	109	182		23	34		35		81
Ardmore	168	117	84	139	67	77	82	66	25	37		46		80
Cardross			76					28				45		29
Pillar Bank						75	99	72	23	33				
Woodhall								34	19	27		41		32
Port Glasgow							286	33	13	19		35		40
Greenock (Garvel Point)								41	31	44		15		37
Greenock, Esplanade								67	54	77		92		119
Gourock	204	61	105	75	26	77	114	21	21	30		44		61
Firth of Clyde/Kyle of Bute														
Holy Loch, Kilmun	223	113	145	105	48	100	59	62	14	21		25		25
Dunoon, East	151	75					97		10	15		41		
Dunoon, West					82		79	33	14	20		30		32
Lunderston Bay												30		
Ayrshire														
Seamill, Boydston										5	8	8		19
Seamill, Bell Stane											13	20		43
Stevenston Point					37	65		17		6				
Garnock Estuary		67	67			48						25		25
Irvine Mouth	93	50	50	39	28	43		14		19		21		21
Barassie					48			187						
Troon, South	80	78	78	41	70	86	78			19		25		23
Ayr, Newton	172	156	156			143				20		44		22
Ayr, Greenan								29				15		15
Girvan, Curragh	<10	33			28	26	53	66				22		

area were compared (Figure 2) to each other and to standards set for descriptive purposes by the Joint Monitoring Programme (JMP) of the Oslo and Paris Commissions (MAFF 1993). Mussels from the Argyll, Firth of Clyde and Ayrshire coast areas had PCB concentrations in the range 12-43 ng g⁻¹ wet weight as Arochlor 1254. These levels were borderline between the 'lower' and 'medium' JMP guideline categories. Clyde Estuary mussels had higher PCB concentrations, in the range 29-125 ng g⁻¹, which placed them mainly in the 'medium' JMP category, with results for some sites in the 'upper' category. This was expected, given the industrialised history of the area. The highest Clyde Estuary levels for the period 1990-94 were found at Gareloch, Helensburgh, Ardmore and Greenock (Figure 3).

b) Temporal analysis of data

The studies of Cowan (1981) identified the Clyde Estuary as a 'hotspot' for PCBs in mussels during the 1970s. This was originally thought to be due to a localised release of PCBs from transformer oils (Waddington et al. 1973), or because of the industrialised history of the area. However, recent evidence has suggested that the picture may have been more complicated, since mussel body burdens reflect both past and present exposure to PCBs, and atmospheric inputs have also been identified as

important (Harrad et al. 1994). Data presented here for the Clyde Sea area were first split into the four geographical areas outlined above. The PCB concentrations were transformed into the natural log values to 'normalise' the data. Linear regression techniques were then applied to the annual means of the transformed data to identify temporal trends (Figure 4). Significant reductions in the mean concentrations (p<0.01) were identified in the Clyde Estuary, Firth of Clyde and Ayrshire coast areas. No such trend was evident in Argyll, where concentrations remained low over the period. Non-parametric statistical analysis of the data was also carried out to assess the magnitude of the reduction in actual PCB concentrations over a decade. Comparison of 1991-94 data with 1981-84 data indicated a five-fold reduction in mussels from the Firth of Clyde and Ayrshire coast areas. An approximate two-fold reduction was observed in Clyde Estuary mussels over the same period. This smaller reduction was due to the apparent increases in PCB concentrations observed at some Clyde Estuary sites in 1992 and 1994 (Figure 4). The authors have no evidence of point sources of PCBs in this area, and the trend is being investigated.

c) Future trends

Although PCBs were first manufactured in the UK in 1954 and their use restricted in the 1970s, the flux of PCBs into the UK environment is still high, and has been estimated as 19 t year⁻¹ to land, and 44-46 t year⁻¹ to the atmosphere (Harrad et al. 1994). This implies that PCBs will continue to circulate throughout the environment for many years, and environmental levels are unlikely to decline in the near future (Phillips 1994). As a result it is likely that in the future, PCBs concentrations in Clyde Sea area mussels will fall only slowly with time.

It is more difficult to predict future changes with time for mussels in the Clyde Estuary itself. Clyde Estuary sediments are known to be contaminated by PCBs, and will remain so for some years to come, so there is a high probability that a gradual release of PCBs due to weathering and dredging will continue to affect local mussels. In addition, while the major source of PCB inputs to the atmosphere is volatilisation from soils (88%), other activities highlighted as important sources (Harrad et al. 1994) take place in the Clyde Estuary. These include leaks from transformers and large capacitors (9.1%), the production of refuse-derived fuel (2.2%), the recovery of contaminated scrap metal (0.5%), and volatilisation from sewage sludge-amended land (0.2%). Inputs from these sources and any future trends will be monitored by continued application of the 'mussel-watch' approach by the Clyde RPB.
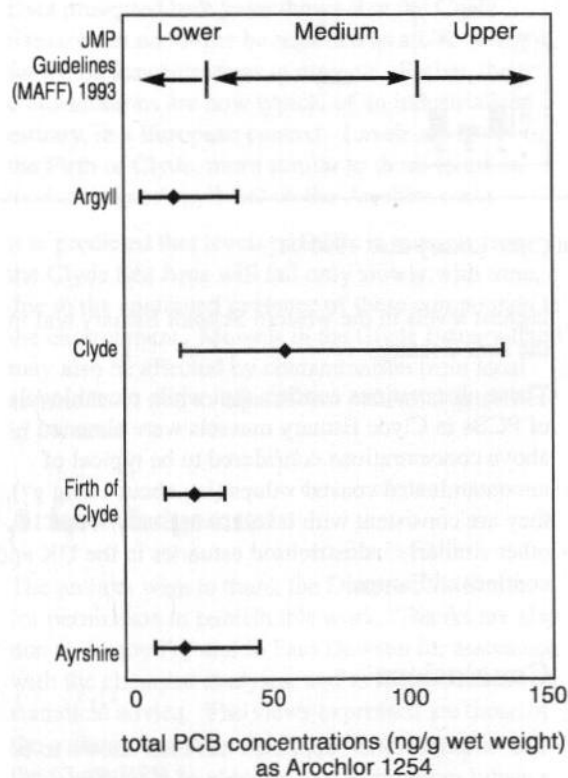

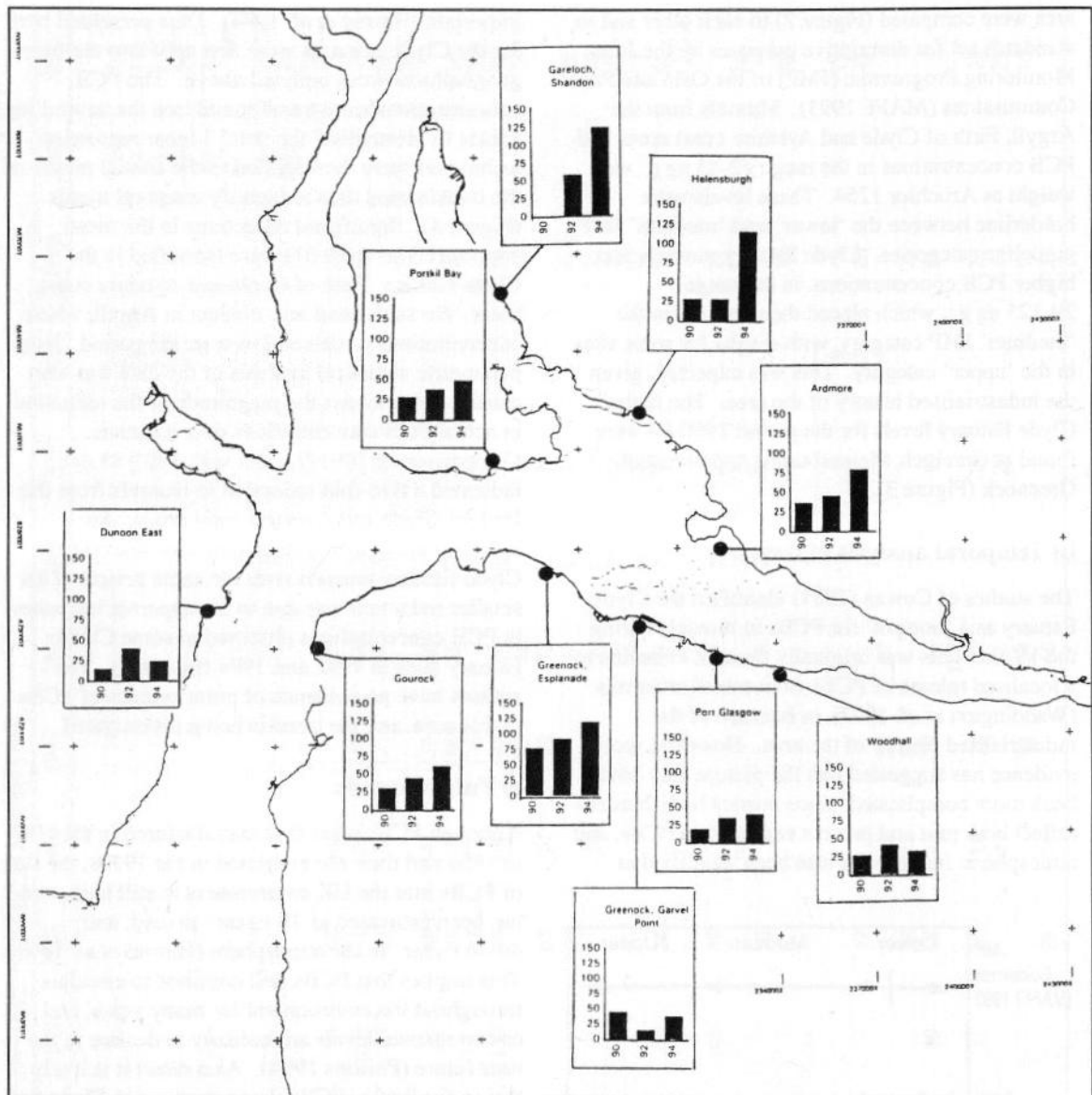**Figure 2.** Spatial trends (mean, min & max) for 1990-94 data and comparison to standards.

Figure 3. PCBs concentrations (ng g^{-1} wet weight) at selected Clyde Estuary sites, 1990-94.

d) Clyde Estuary PCB concentrations set in context

Comparison of Clyde Estuary PCB levels with those for other UK areas was not easy, due to the relative lack of recent data for mussels collected from estuarine or coastal sites. A survey was carried out by the Ministry of Agriculture, Fisheries and Foods (MAFF) of PCB concentrations in mussels from the east coast of England in 1990 (MAFF 1993). Results ranged from <1 ng g^{-1} for sites in rural areas such as at Berwick and in the Wash at King's Lynn, to higher levels of 35 ng g^{-1} and 95 ng g^{-1} for more industrialised sites in the Humber and Thames Estuaries. The 1993 North Sea Quality Status Report (North Sea Task Force 1993) indicated PCB concentrations in mussels from sites around the North Sea to be in the range 5-283 ng g^{-1}, with the highest levels in the western Scheldt Estuary and in the Ems Estuary.

These observations confirm that while recent levels of PCBs in Clyde Estuary mussels were elevated above concentrations considered to be typical of uncontaminated coastal values (i.e. about 10 ng g^{-1}), they are consistent with levels commonly found in other similarly industrialised estuaries in the UK and continental Europe.

Conclusions

The 'mussel-watch' approach has been shown to be a useful monitoring tool, capable of identifying spatial and temporal trends for PCB concentrations in mussels. Levels for the Clyde Sea area have been
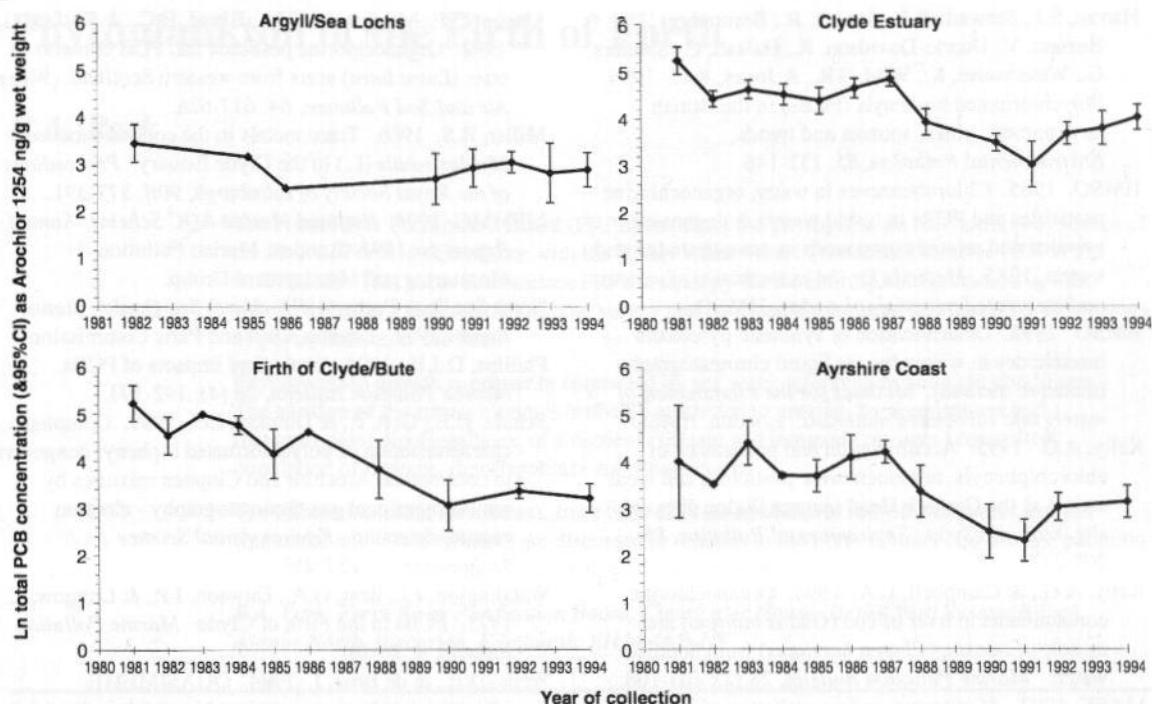
Figure 4. Trends in PCB concentrations with time for each area.

compared spatially and temporally, to standards applied in an international context and to concentrations found in other UK and European estuaries.

Data presented here have shown that the Clyde Estuary can no longer be regarded as a UK 'hotspot' for PCBs concentrations in mussels. Rather, the concentrations are now typical of an industrialised estuary, in a European context. Levels are lower in the Firth of Clyde, more similar to those found in mussels from Argyll and on the Ayrshire coast.

It is predicted that levels of PCBs in mussels from the Clyde Sea Area will fall only slowly with time, due to the continued presence of these compounds in the environment. Mussels in the Clyde Estuary itself may also be affected by contamination from local sediments or due to inputs from industrial activities in the area.

Acknowledgements

References

Brouwer, A. 1991. *In: The role of enzymes in regulating the toxicity of xenobiotics*, ed. by C.H. Walters. Reading, University of Reading.

Cowan, A.A. 1981. Organochlorine compounds in mussels from Scottish coastal waters. *Environmental Pollution (Series B)*, 2: 129-143.

Davies, I.M., & Pirie, J.M. 1980. Evaluation of a 'Mussel Watch' project for heavy metals in Scottish coastal waters. *Marine Biology*, 57: 87-93.

DoE. 1988. North Sea Conference, The Hague, 1987. *Inputs of dangerous substances to waters: proposals for a unified system of control*. London, Department of the Environment.

Duinker, J.C., Schulz, D.E., & Petrich, G. 1988. Selection of chlorinated biphenyl congeners for analysis in environmental samples. *Marine Pollution Bulletin*, 19 (1): 19-25.

EEC. 1976. *Council Directive on Pollution Caused by Certain Dangerous Substances Discharged to the Aquatic Environment of the Community*. Brussels, EEC. European Economic Community Report 76/464/EEC.

EEC. 1979. *Council Directive on the Quality Required of Shellfish Waters*. Luxembourg, EEC. European Economic Community Report 79/923/EEC.

Goldberg, E.D. 1975. The Mussel Watch - A first step in global marine monitoring. *Marine Pollution Bulletin*, 6: 111-113.

Haig, A.J.N., & Miller, B.S. 1984. Chemistry of the Firth of Clyde. *Analytical Proceedings*, 21: 116-118.

Harrad, S.J., Stewart, A.P., Alcock, R., Boumphrey, R., Burnett, V., Duarte-Davidson, R., Halsall, C., Sanders, G., Waterhouse, K., Wild, S.R., & Jones, K.C. 1994. Polychlorinated biphenyls (PCBs) in the British environment: sinks, sources and trends. *Environmental Pollution, 85:* 131-146.

HMSO. 1985. Chlorobenzenes in water, organochlorine pesticides and PCBs in turbid waters, halogenated solvents and related compounds in sewage sludge and waters, 1985. *Methods for the examination of waters and associated materials.* London, HMSO.

HMSO. 1992. Determination of synthetic pyrethroid insecticides in waters by gas liquid chromatography (tentative method). *Methods for the examination of waters and associated materials.* London, HMSO.

Kelly, A.G. 1995. Accumulation and persistence of chlorobiphenyls, organochlorine pesticides and fecal sterols at the Garroch Head sewage sludge disposal site, Firth of Clyde. *Environmental Pollution, 88:* 207-217.

Kelly, A.G., & Campbell, L.A. 1994. Organochlorine contaminants in liver of cod (*Gadus morhua*) and muscle of herring (*Clupea harengus*) from Scottish waters. *Marine Pollution Bulletin, 28 (2):* 103-108.

MAFF. 1993. *Monitoring and surveillance of non-radioactive contaminants in the aquatic environment and activities regulating the disposal of wastes at sea, 1991.* Lowestoft, Directorate of Fisheries Research, Ministry of Agriculture, Fisheries and Foods. (Aquatic Environment Monitoring Report No. 36.)

Mason, C.F., Macdonald, S.M., Bland, H.C., & Ratford, J. 1992. Organochlorine pesticide and PCB contents in otter (*Lutra lutra*) scats from western Scotland. *Water, Air and Soil Pollution, 64:* 617-626.

Miller, B.S. 1986. Trace metals in the common mussel *Mytilus edulis* (L.) in the Clyde Estuary. *Proceedings of the Royal Society of Edinburgh, 90B,* 377-391.

MPMMG. 1994. *National Marine AQC Scheme: Annual Report for 1993.* London, Marine Pollution Monitoring and Management Group.

North Sea Task Force. 1993. *North Sea Quality Status Report 1993.* London, Oslo and Paris Commissions.

Phillips, D.J.H. 1994. Ecological impacts of PCBs. *Marine Pollution Bulletin, 28 (4):* 192-193.

Schulz, D.E., Gert, P., & Duinker, J.C. 1989. Complete characterisation of polychlorinated biphenyl congeners in commercial Arochlor and Clophen mixtures by multidimensional gas chromatography - electron capture detection. *Environmental Science & Technology, 23:* 852-859.

Waddington, J.I., Best, G.A., Dawson, J.P., & Lithgow, T. 1973. PCBs in the Firth of Clyde. *Marine Pollution Bulletin, 4:* 26-28.

Wells, D.E., & de Boer, J. 1994. QUASIMEME laboratory performance study: chlorobiphenyls in fish oil and standard solutions. *Marine Pollution Bulletin, 29 (4-5):* 174-184.

Wells, D.E., & Johnstone, S.J. 1977. Methods for the separation of organochlorine residues before gas-liquid chromatographic analysis. *Journal of Chromatography, 140:* 17-28.