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HEAVY METAL TRANSPORTATION BY PHYTOPLANKTON IN TIDAL WATERS

Development of a mathematical model

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Abstract

The ability to model the association of heavy metals and phytoplankton within an estuarine and coastal water system would further improve the understanding of the heavy metal budgets of such systems and the environmental effects. This report describes the development of a mathematical model to predict heavy metal transport by phytoplankton and follows on from a literature review undertaken during 1985/6.

The phytoplankton biomass is the smallest of the three heavy metal reservoirs, sediment and water being the other two. Seasonal variations in the species composition and the size of the algal population are such that phytoplankton accumulation and transport of heavy metals is only of importance during the spring and summer when blooms are apparent. However at such times the phytoplankton readily adsorb metals from the water and are transported with water and then as algae die, sometimes catastrophically following a bloom, the detrital material falls to the bed transferring the adsorbed metals to the sediment reservoir.

As a preliminary phase it was thought necessary to develop a mathematical model which simulates the growth of one 'representative' phytoplankton species and the uptake and transport of one metal. Reliable data on the uptake of zinc by natural phytoplankton populations is available from laboratory experiments carried out by Davies.

Since the timescale for the growth of an algal bloom is many days the model described in this report is a tide-averaged, two-layer, 2-dimensional model. The model was applied to Liverpool Bay using residuals taken from a finer gridded 2D-2 layer tidal model developed to predict the transport and adsorption onto sediment of heavy metals.

CONTENTS

1 INTRODUCTION

Heavy metals enter estuaries and coastal waters by various routes including fresh water and sewage discharges, the disposal of sewage sludge, industrial discharges, mining activities and subsequent metal refining, precipitation and from the sea. The potential dangers in the uncontrolled discharge of effluents containing high levels of heavy metals to the estuarine and marine environments were demonstrated by the mercury poisoning which occurred at Minamata in Japan (12). In order to remove or minimise such dangers it is necessary to gain a knowledge of the source of heavy metal inputs and to understand the processes which govern the transport and accumulation of metals in the marine environment.

The control of Pollution Act 1974 placed the responsibility for the control of polluting discharges to the estuarine environment upon the Water Authorities in England and Wales. If controls are to be set to limit the ultimate concentrations of heavy metals in the estuarine and coastal waters it is necessary to be able to predict the transport and accumulation of metals. Figure 1 illustrates some of the metal pathways in aquatic ecosystems.

Phytoplankton are known to accumulate certain heavy metals. Transport of phytoplankton by tidal and residual currents in surface waters and the settling of detrital material must therefore by considered in any realistic prediction of heavy metal transport.

This report describes the development of a prototype mathematical model to predict heavy metal transport by phytoplankton and follows on from a literature review undertaken during 1985/6 (Ref 1). The model was

applied to Liverpool Bay and preliminary results are included in this report. Specialist advice on the biological aspects of the work was given by Dr A Davies of the Marine Biological Association at Plymouth.

2 HEAVY METALS IN THE MARINE ENVIRONMENT

2.1 The fate of heavy metals within the estuarine environment

Heavy metals differ from many contaminants in that they are normal constituents of the marine environment, and therefore traces at least are always found in marine organisms. Probably the most important feature which distinguishes the heavy metals from other toxic pollutants is that they are not biogradable, and having entered the environment their potential toxicity is controlled to a great extent by biological and geochemical factors.

The fate of heavy metals such as lead, zinc, cadmium and mercury in the estuarine environment is of extreme importance due to their impact on the ecosystem. This is especially true in urban estuaries where the inputs are diffuse and include municipal and industrial discharges, urban runoff, atmospheric contributions and the presence of harbour facilities with heavy ship traffic. The metals in such an environment can be accommodated in three basic reservoirs: water, sediment and biota. The importance of the biota reservoir is quite evident as organisms in the estuary can be adversely affected and human health hazards can arise through consumption of the contaminated organisms.

The biota reservoir however, is small compared to the water, which in turn is much smaller than the sediment reservoir. Even so, despite the phytoplankton representing a small reservoir for metals in relative terms, the dismissal of their influence on the heavy metal budget of an estuarine system could lead to significant errors, due to the concentration effect of the phytoplankton.

2.2 Biological availability of metals

The organic constituents of sewage sludge generally bind metals in such a way that renders them biologically unavailable. This may occur through chelation of the metals by organic compounds or by simple adsorption. A high organic content in the sediments usually ensures that the metals are firmly fixed on the suspended sediments and are not freely available to the marine biota in the water column. Davies (Ref 2) has suggested the mass of dissolved metal in an active environment is a good approximation to the mass of metal biologically available.

2.3 Concentration of metals by phytoplankton

Detailed laboratory experiments have been undertaken by a number of investigators in an attempt to understand the mechanism of uptake of the metals by the phytoplankton. Two mechanisms of uptake are generally known to occur, adsorption onto the external surface of the cell walls and absorption whereby the phytoplankton take up metals from solution through

their cell walls against a concentration gradient. The combined effect results in considerable accumulation of heavy metals by the phytoplankton, as shown by the concentration factors in Table 1.

There are large differences in the concentration factors for different metals. The ability of planktonic algae to accumulate metals is generally in the order: mercury, lead, cadmium (Ref 9) or mercury, silver, zinc, cadmium (Ref 10). Some differences in the accumulation of metals by diatoms and flagellates has also been observed with flagellates having a greater ability to accumulate metals.

2.4 Adsorption of zinc by phytoplankton

Data relating to the adsorption of zinc by natural phytoplankton assemblages is available from the work of Davies and Sleep (Ref 4). The results indicated that the metal:chlorophyll a ratios could be related to the metal concentrations in the water by an equation of the same form as the Langmuir adsorption isotherm.

$$z = \frac{z_{max} \cdot c}{(k+c)}$$

where

z is metal/chlorophyll a ratio

z_{max} is the maximum metal/chlorophyll a ratio

c is the metal concentration in solution (µg/l)

k is the metal concentration in water when phytoplankton cells reach half saturation (µg metal/l)

The values of z_{max} and k obtained for several experiments are given in Table 2.

The actual rate of metal uptake varies according to species and ambient conditions with an equilibrium being reached in a period ranging from a few minutes to a few hours.

2.5 Transport by tidal and residual currents

It is necessary to relate the accumulation of heavy metals by phytoplankton to overall metal transport and cycling in an estuarine system. Such biological mobilisation may result from the uptake of the metal by an organism followed by its release into the water column on the death and decay of an organism, after the physical movement of the organism out of the system by tidal and residual currents. Alternatively the death and subsequent settlement of an organism may transfer metal from the water column to the bed.

Concentrations of metals are generally highest in nearshore waters where elevated nutrient concentrations can support high levels of phytoplankton. Seasonal variations in the species composition and size of the algal population are such that phytoplankton accumulation and transport of heavy metal in UK coastal waters is only of importance during the spring and summer. At this time algal blooms occur and the phytoplankton readily adsorb metals from the water and are transported by tidal and residual currents. As the algae die, sometimes catastrophically following a bloom, the detrital material falls to the bed transferring the adsorbed metal from the water column to the bed sediment.

3 MATHEMATICAL MODEL

In order to model effectively the transport of metals by phytoplankton it is necessary to model water movement (and hence transport), phytoplankton growth and decay and the adsorption of metal. The timescale for the development and decay of an algal bloom is many days. Ideally model simulations should cover the whole of the period when phytoplankton are likely to play a significant role in metal transport; this would entail simulations covering several months and necessitates the use of a tide averaged model if the computation time is not to become excessive.

It was decided to estimate residual discharges from an existing pilot two layer 2-dimensional model (TIDEFLOW 2D2L) of Liverpool Bay (Ref 11) which had been developed to simulate the transport and adsorption onto mud of heavy metals. The TIDEFLOW-2D2L model had approximately 10,000 computational elements and used a timestep of a few seconds to simulate a period of a few, repeating, tidal cycles.

Liverpool Bay and the Mersey estuary were divided into 54 segments, (Figs 2-4), each being an integral number of elements of the TIDEFLOW-2D2L model. In areas where the water depth was greater than 7m, all of Liverpool Bay and the Mersey downstream of the narrows, the model had 2 layers with the lower, bed hugging, layer having a depth of 7m. Tidal residual flows from TIDEFLOW-2D2L were used to specify the residual flows for the present model, TIDEMEAN-2D2L. Some adjustment was necessary to ensure conservation since although TIDEFLOW-2D2L had been run to dynamic equilibrium the small but inevitable discrepancies in residual flows would have given rise to problems when applied to a period of several months.

3.1 Two layer transport

The transport model used the stored residuals and dispersive discharges from TIDEFLOW-2D2L and was based on the equations describing the conservation of mass

Surface layer

$$\frac{\partial}{\partial t}(V.C) + \frac{\partial}{\partial x}(Q_x.C) + \frac{\partial}{\partial y}(Q_y.C) - Q_z.C$$

$$- \frac{\partial}{\partial x}(QD_x.C) - \frac{\partial}{\partial y}(QD_y.C) - \frac{\partial}{\partial z}(QD_z.C) = \sum S \quad (1)$$

Bed layer

$$\frac{\partial}{\partial t}(V.C) + \frac{\partial}{\partial x}(Q_x.C) + \frac{\partial}{\partial y}(Q_y.C) + Q_z.C$$

$$- \frac{\partial}{\partial y}(QD_x.C) - \frac{\partial}{\partial z}(QD_y.C) - \frac{\partial}{\partial x}(QD_z.C) = \sum S \quad (2)$$

where C = concentration (kg/m^3)

Q_x, Q_y, Q_z = residual discharges in x, y and z directions (m^3/s)

QD_x, QD_y, QD_z = dispersive discharges in x, y and z directions (m^3/s)

$\sum S$ = net effect of all loadings, source and sink terms simulated.

3.2 Adsorption of zinc

In order to ensure conservation the equations governing the conservation of mass of metal adsorbed/absorbed by phytoplankton need to be solved in terms of the total concentration of 'algal metal'

$$C = C_p . C_{mp}$$

where C_p is concentration of algal carbon (kg/m^3)

C_{mp} is metal/algal carbon ratio

Algal carbon is used here as the measure of phytoplankton since this is the parameter used to model primary productivity.

The source/sink term for zinc adsorbed by phytoplankton is

$$S = \frac{V(Z - C_{mp})}{Dt} \qquad \text{if } C_{mp} < Z$$

$$S = 0 \qquad \text{otherwise}$$

where $Z = \frac{Z_{max} . C_m}{K + C_m}$

Z is equilibrium zinc/algal carbon ratio

Z_{max} is maximum zinc/algal carbon ratio

C_m is concentration of dissolved zinc (kg/m^3)

K is dissolved zinc concentration when phytoplankton cells reach half saturation (kg/m^3)

3.3 Primary productivity

Productivity is calculated from the temperature dependent maximum productivity for the species of phytoplankton considered. The maximum productivity is then modified to take account of the limiting effects of nitrate concentrations using Michaelis-Menten relationships.

$$PROD = P_{MAX}(T).\mu_1.\min(\mu_2, \mu_3, \mu_4)$$

where

$P_{MAX}(T)$ is maximum productivity for species

$P_{MAX}(T) = \exp(2.30259m\ T + c)$ where m and c are constants

μ_1 is limitation due to light intensity (1)

$$\mu_1 = \frac{e}{k_3(b_2-b_1)} \left[\exp\left(-\frac{I}{Im} e^{-k_3 b_2}\right) - \exp\left(-\frac{I}{Im} e^{-k_3 b_1}\right)\right]$$

b_2 is depth of bottom face of element from the water surface (m)

b_1 is depth of top face of element from the water surface (m)

Im is light intensity required for maximum productivity

k_3 is an equivalent extinction coefficient which takes account of turbidity in the overlying water

μ_2 is limitation due to nitrate concentration

$$\mu_2 = \frac{C_N}{C_N + MON}$$

Where C_N is nitrate concentration

MON is nitrate concentration which would permit 50% of maximum productivity.

3.4 Respiration

Losses due to respiration are calculated as a function of temperature as

$$RESP = RP_{10} \cdot Q_{10}^{(T - 10)} \cdot Cp$$

RP_{10} is respiration rate at 10°C

Q_{10} is the rate of increase of respiration for 10°C rise in temperature.

3.5 Mortality of phytoplankton

Phytoplankton losses due to natural mortality, grazing by zooplankton etc are treated in the model as a single mortality factor

$$INAK = M_p \cdot C_p$$

where M_p is the mortality of phytoplankton (d^{-1})

4 APPLICATION TO LIVERPOOL BAY

In order to test the methodology described in Section 3 a model of Liverpool Bay was set up to simulate tide averaged flows during summer conditions.

4.1 Tide averaged flows

The tide averaged residual flows used to drive the model were obtained from a previous two layer 2 dimensional model of Liverpool Bay. The general

pattern of flows is illustrated in Figure 4. The need to adjust the residual flows to ensure conservation resulted in a few local eddies being produced which may not be realistic.

4.2 Nutrient and metal loadings

The inputs of zinc into Liverpool Bay were taken from a previous study of the transport of heavy metals and adsorption onto mud particles (Ref 11) and are shown in Figure 6.

The only nutrient modelled was nitrogen and inputs of ammoniacal and oxidised nitrogen were provided by Dr P C Head of North West Water Authority and are shown in Table 3. The nitrogen available for phytoplankton growth was considered to be the sum of ammoniacal and oxidised nitrogen.

4.3 Preliminary results

Model simulations of phytoplankton production in Liverpool Bay over a period of 30 days were in fair agreement with observed levels (Figs 7, 8). The zinc adsorbed by the phytoplankton mass is lost through mortality and grazing by phytoplankton and the resulting detritus settles to the bed.

The model indicated that with an assumed mortality rate of 10% per day the equivalent of approximately 50 tonnes of chlorophyll a was deposited onto the bed of Liverpool Bay. The maximum concentration of zinc adsorbed onto the phytoplankton was 0.35g Zn/g Chl*a* so that about 17 tonnes of zinc (or 10% of the input of dissolved zinc) was transferred to the bed via phytoplankton. This figure is only an indication since the model was sensitive to residual flow patterns which of necessity were approximate. It is

thought however that these preliminary results indicate that phytoplankton can play a significant, although not major, role in the transport of metals.

DISCUSSION AND CONCLUSIONS

A mathematical modelling method was developed to simulate the uptake and transport of heavy metal by phytoplankton in tidal waters. The adsorption of metals was described by a Langmuir adsorption isotherm based on laboratory experiments by Davies (1979, 1980).

The theory, in the form of partial differential equations and empirical relationships was formulated to describe the transport of dissolved and adsorbed metal, nitrate, and the growth, transport, settling and mortality of phytoplankton in a residual coastal current.

The methodology was tested by setting up a pilot model of part of the Irish Sea. The transport model was driven by results from an earlier pilot model of Liverpool Bay.

The model simulated fairly well an algal bloom in the near shore, nutrient rich waters and demonstrated the uptake of dissolved zinc discharged into Liverpool Bay. The phytoplankton, with the adsorbed metals, were carried northward with the residual coastal current, which also carried dissolved metal out of Liverpool Bay. However, the dead phytoplankton settled to the bed thereby providing a pathway for dissolved metals to enter the benthal layer.

If required, it should be possible to use the method to simulate the transport of metals by phytoplankton in any part of the UK coastal waters if the residual currents are predicted with sufficient accuracy.

ACKNOWLEDGEMENTS

Dr A G Davies of the Marine Biological Association at Plymouth acted as specialist adviser for this study and contributed much useful input.

REFERENCE

1. Murray G E and Maskell J M, 1986. Heavy metal transport by phytoplankton in tidal waters - a literature review. Hydraulics Research Report No.SR87.

2. Driver P A, 1986. The practicality of modelling the transport of metals by phytoplankton in Liverpool Bay. Atkins Research and Development report to Hydraulics Research.

3. Davies A G, 1978. Pollution studies with marine plankton. Part II Heavy metals. Adv. Marine Biology, Vol 15, 1978, pp381-508.

4. Davies A G and Sleep J A, 1979. Inhibition of carbon fixation as a function of zinc uptake by natural phytoplankton assemblages. J Mar Biol. Ass. Uk, 59 pp937-949.

5. Davies A G and Sleep J A, 1980. Copper inhibition of carbon fixation in coastal phytoplankton assemblages. J. Mar. Biol. Ass. Uk, 60, pp841-850.

6. Davies A G, 1983. The effects of heavy metals upon natural marine phytoplankton populations. Progress in Phycological Research, Vol 2, ppl13-145.

7. Schulz-Baldes M and Lewis R A, 1976. Lead uptake in two marine phytoplankton organisms. Biological Bulletin, 150, ppl18-127.

8. Hardsteat-Romeo M and Gnaosia-Barelli M, 1980. Effect of complexation of natural phytoplankton exudates on the accumulation of cadmium and copper by Haptophyceae crycospaera elongata. Marine Biology, 59, pp79-84.

9. Jennet J C, Smith J E and Hassett J M, 1983. Factors influencing metal accumulation by algae. US EPA Research Report 377 pp83-149.

10. Fisher N S, Bohe M and Teyssie J C, 1984. Accumulation and toxicity of Cd, Zn, Ag and Hg in four marine phytoplankters. Marine Ecology (Progress Series) 18. pp201-213.

11. Rodger J G and Odd NVM, 1985. Sludge Disposal in coastal waters, mathematical modelling of the transport of heavy metals in Liverpool Bay. Hydraulics Research Report No. SR70.

12. Takeuchi, T. Biological reactions and pathological changes in human beings and animals caused by organic mercury contamination. In Environmental Mercury contamination (Ed R Hartung and B D Dinman). Ann Arbor Science Publishers, 1972, pp247-249.

TABLES.

TABLE 1

Metal Concentration Factors

Organisms	Type	Habitat	Metal Type	Concentration factor	Basis	Researcher
			ARSENIC			
Phytoplankton	Assorted	Lake Michigan	Ecological	1.5×10^3	Wet	Copeland & Ayers (1972)
			CADMIUM			
Prasinecladus subasia	green flagellated	lab culture (Marine)	Stable isotope	6.7×10^3	Dry	Kerfoot & Jacobs (1976)
Phaeodactylum tricornutum & Chaeotoceras ssp	Diatoms	Marine	Stable isotope	4×10^3	Dry	Kerfoot & Jacobs (1976)
			COPPER			
Phytoplankton	Assorted	Lake Michigan	Ecological	1.2×10^3	Dry	Copeland & Ayers (1972)
Phytoplankton	Assorted	Monterey Bay	Ecological	2.8×10^3	Dry	Martin & Knauer (1972)
Scenedesmus	green colonial	Lab culture	Stable isotope	$3.7\text{-}4.0 \times 10^3$	Dry	Stokes (1975)
			LEAD			
Phaeodactylum tricornutum	Diatom	Lab culture (Marine)	Stable isotope	2×10^3	Dry	Schulz-Baldes & Lewin (1976)
Platymonas subcordiformis	green flagellated	Lab culture (Marine)	Stable isotope	1×10^3	Dry	Schulz-Baldes & Lewin (1976)
			MERCURY			
Phytoplankton	Assorted	Lake Michigan	Ecological	5.9×10^3	Wet	Copeland & Ayers (1972)
Phytoplankton	Assorted	Monterey Bay	Ecological	2.2×10^2	Wet	Knauer & Martin (1972)
Phaeodactylum tricornutum	Diatom	Lab culture (Marine)	Radio isotope	1.3×10^4	Wet	Hannon et al (1973)
			NICKEL			
Phytoplankton	Assorted	Monterey Bay	Ecological	5.7×10^2	Dry	Knauer & Martin (1972)
			ZINC			
Phytoplankton	Assorted	Monterey Bay	Ecological	5.5×10^3	Dry	Martin & Knauer (1972)

TABLE 2

Adsorption rates for Zinc (after Davies)

Sample	Z_{max} $(\frac{\mu g\ Metal}{\mu g\ Chl\ \underline{a}})$	K (μg metal/ℓ)
a	0.42	14.7
b	0.28	11.4
c	0.40	19.4

TABLE 3

Nitrogen inputs to Liverpool Bay

Model Segment number	NH_3 (Kg N d^{-1})	NO_3 (Kg N d^{-1})
5	34	630
17	240	-
18	530	2135
25	1575	4450
31	7450	16675
43	410	3100
44	1250	3390
45	1130	6150
46	1400	-
47	20250	-
48	1400	-
49	6330	4900
50	560	800
51	5000	4900
52	19000	12000
53	8	75

FIGURES.

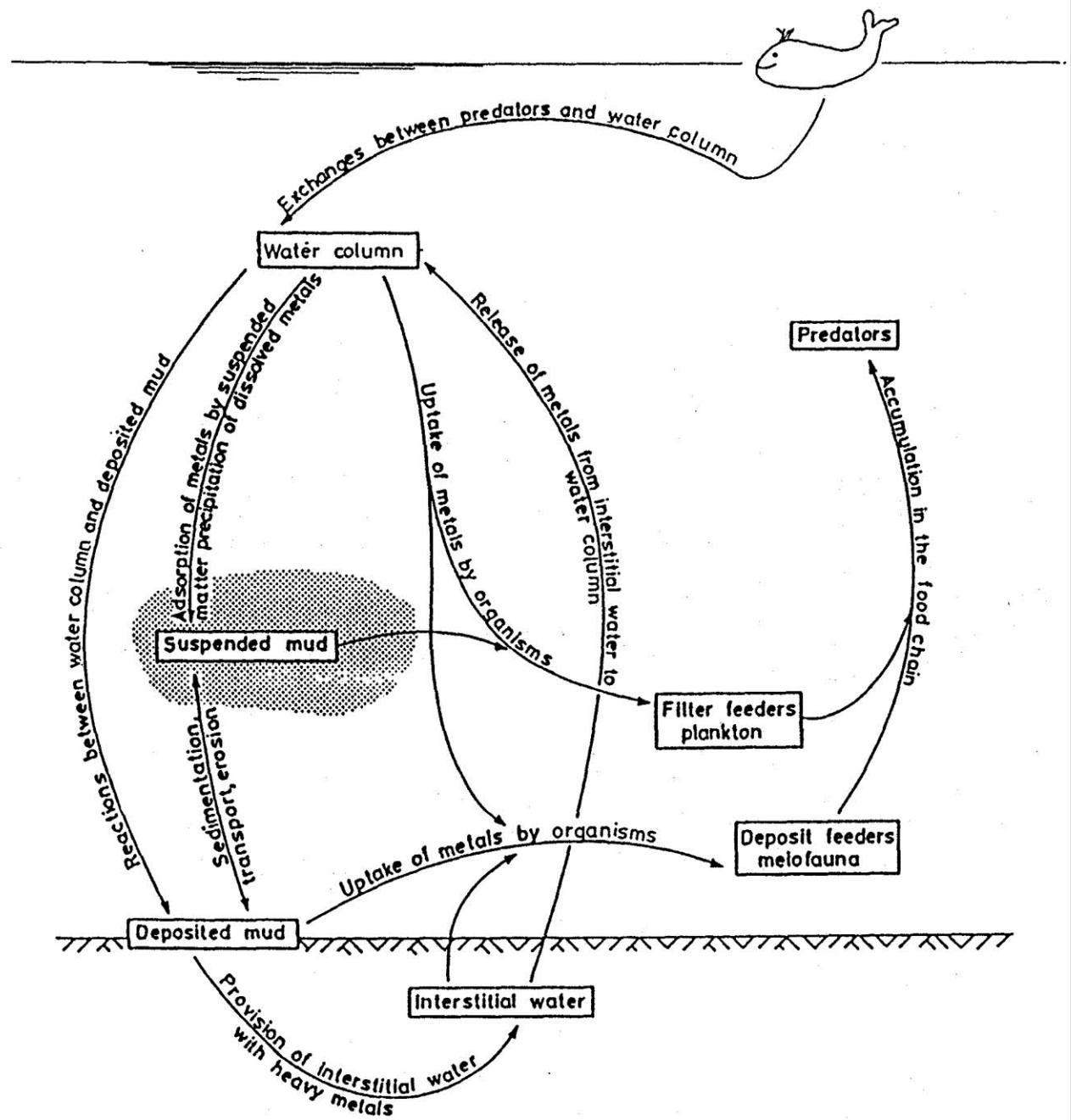


Fig 1 Pathways of metals in aquatic ecosystems

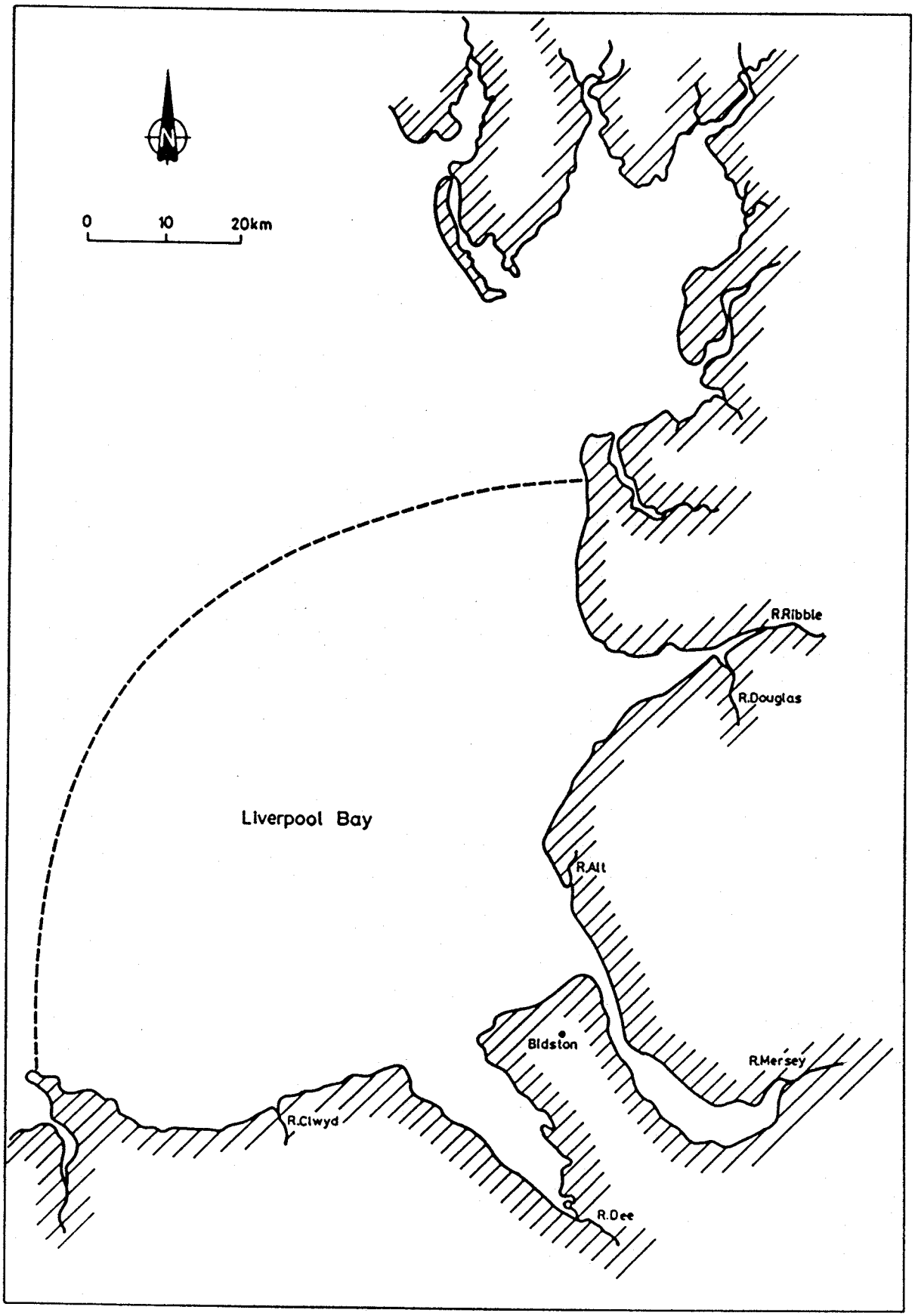


Fig 2 Defined limits of Liverpool Bay

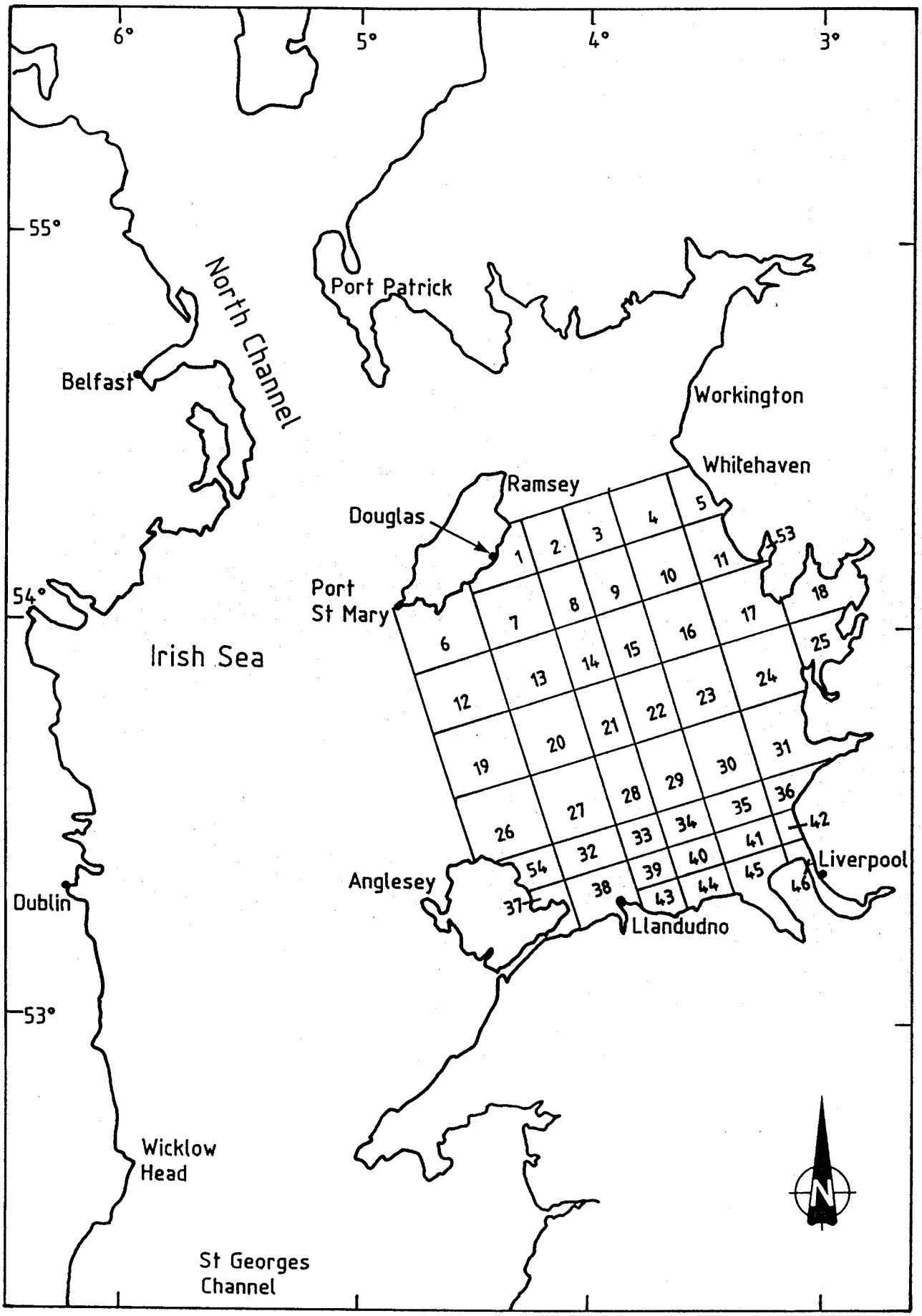


Fig 3a Model schematisation - Eastern Irish Sea and Liverpool Bay

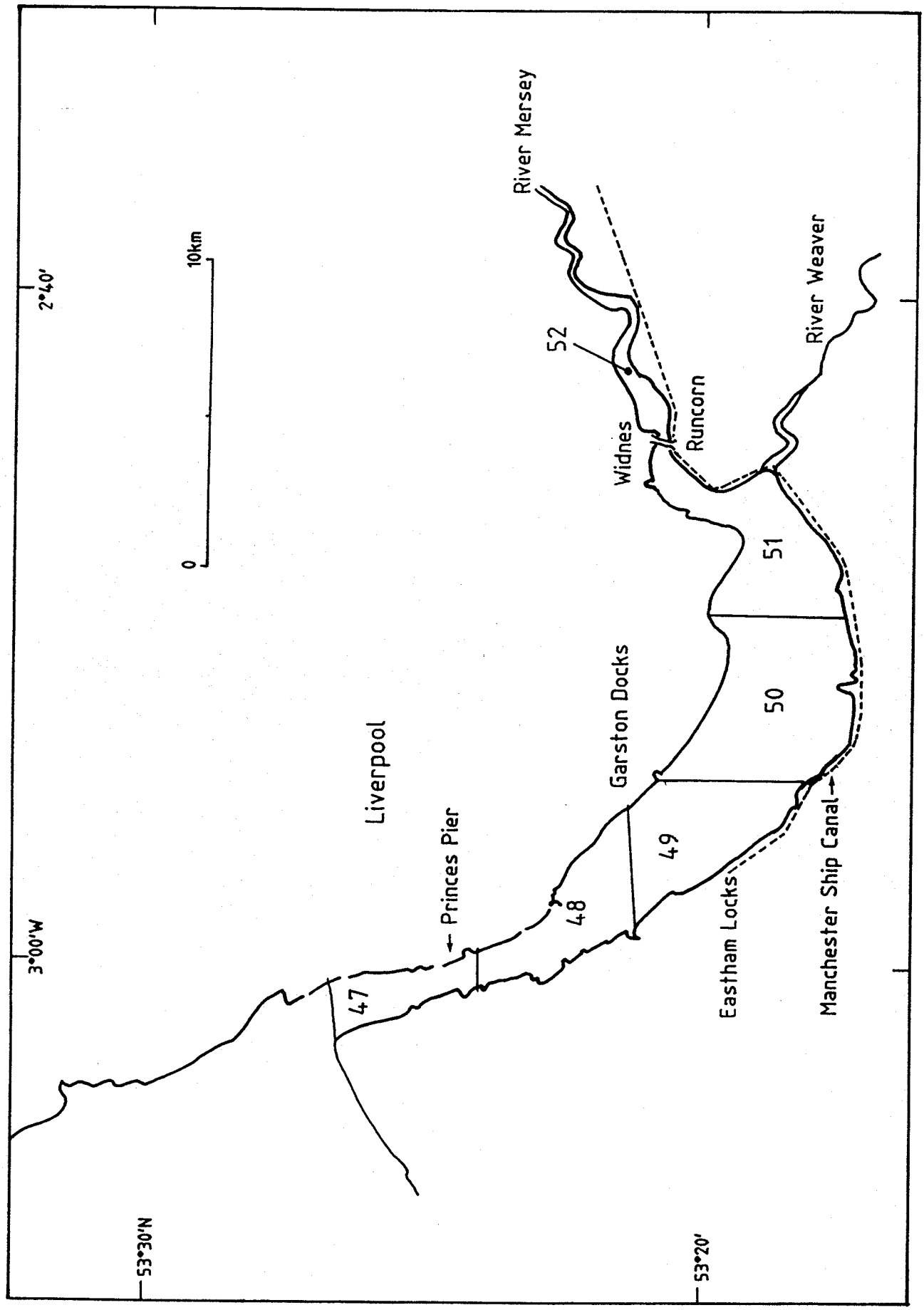


Fig 3b Model schematisation - Mersey Estuary

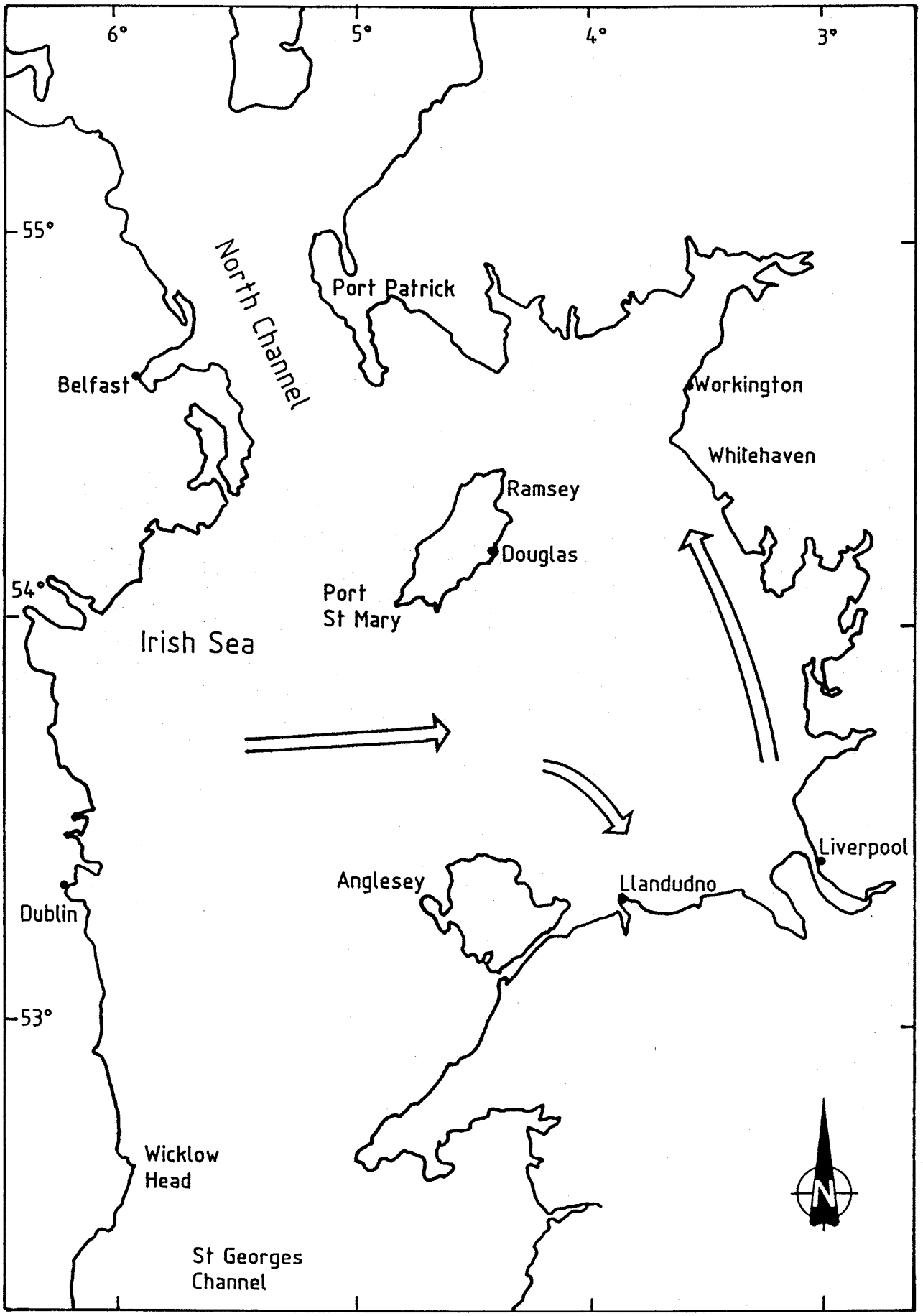


Fig 4 Tide averaged residual flow patterns

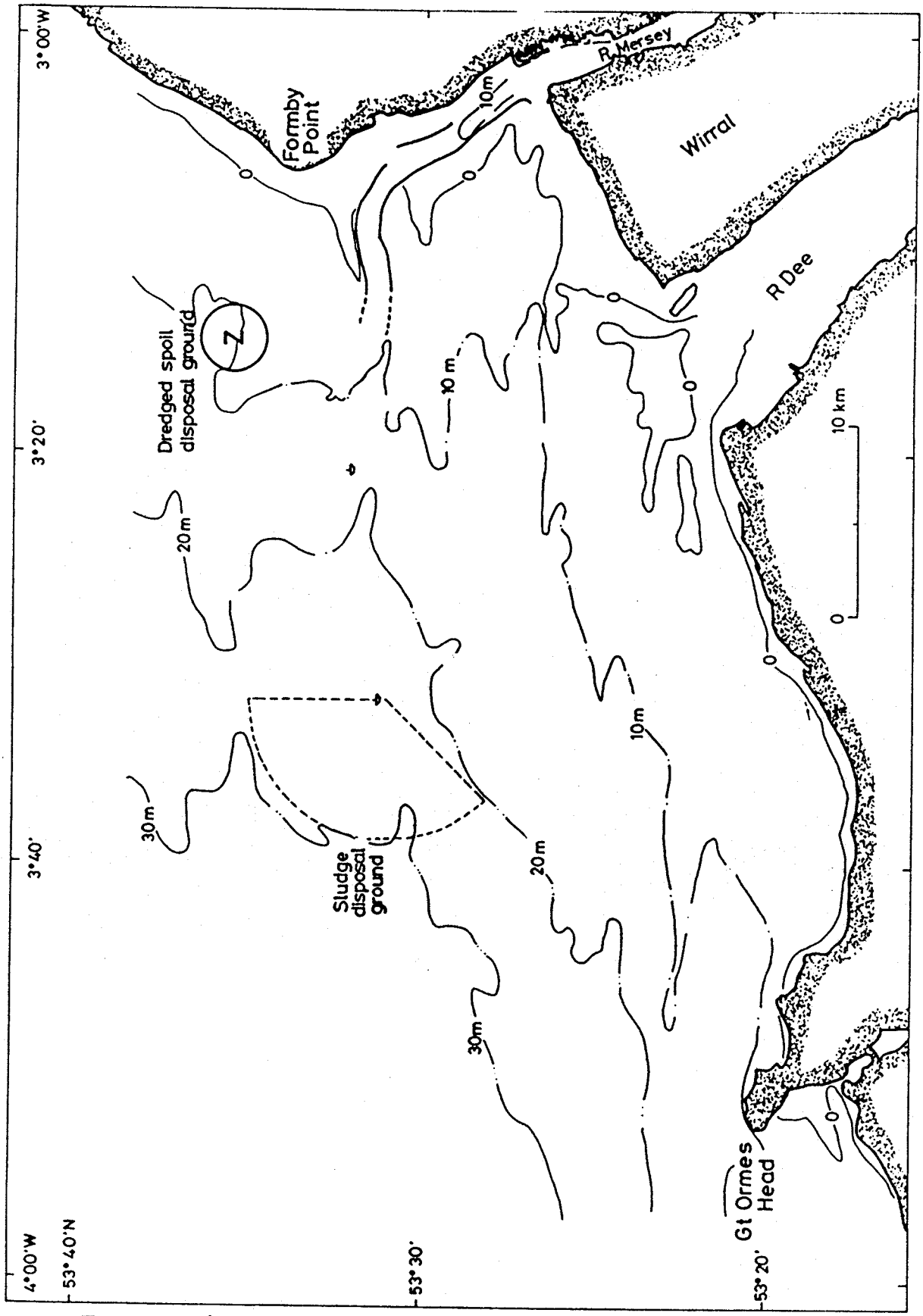


Fig 5 Location of sewage sludge and dredged spoil disposal grounds

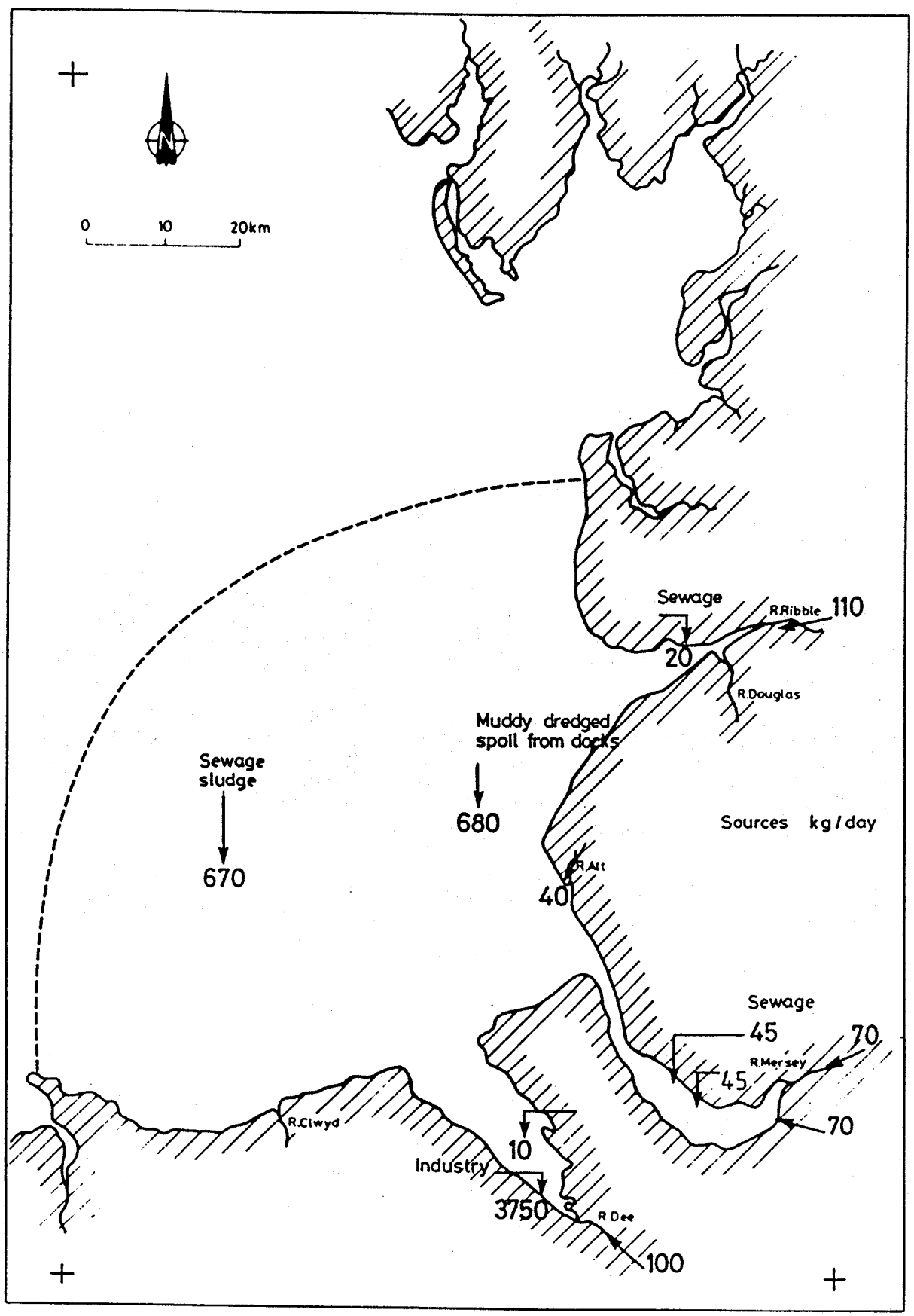


Fig 6 Prescribed sources of zinc

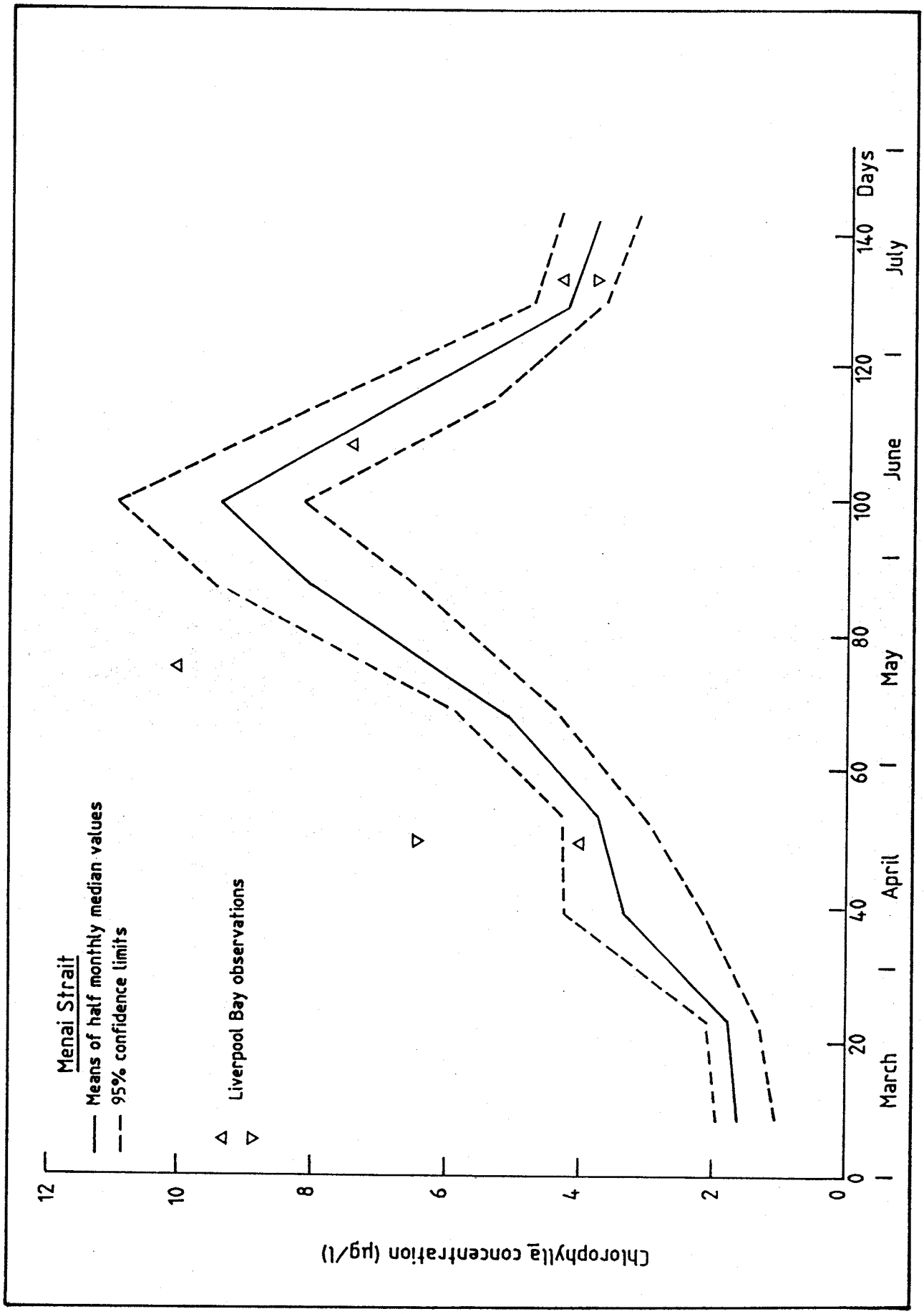
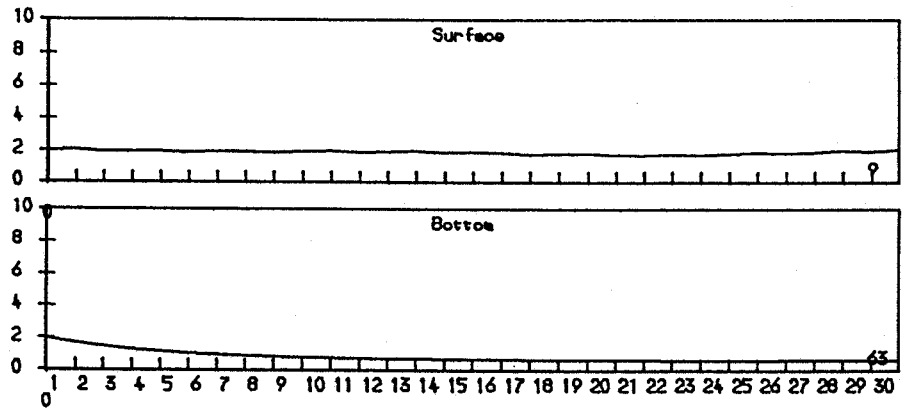
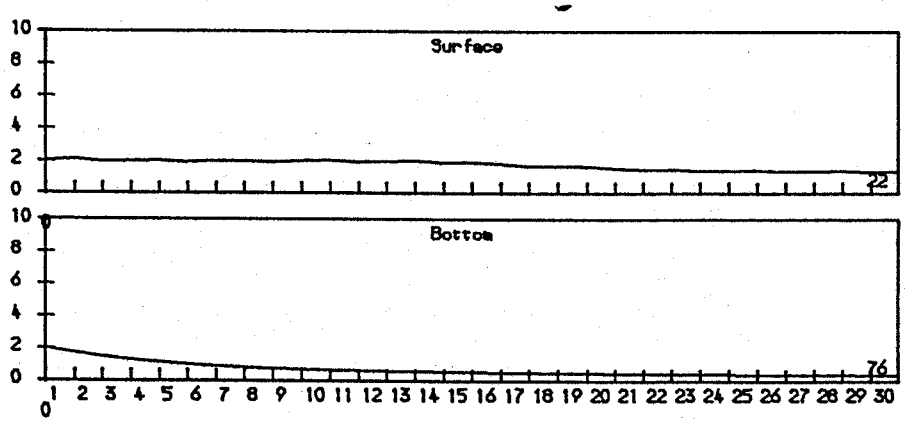


Fig 7 Observed variation of chlorophyll a in Liverpool Bay





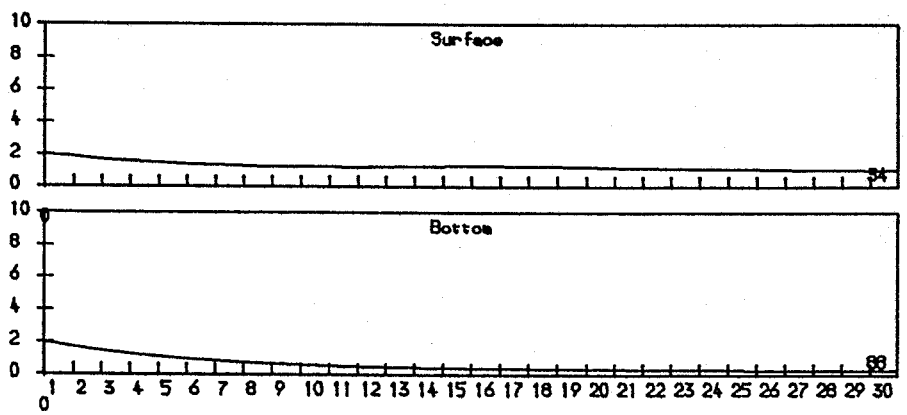


Fig 8a Simulated variation of Chlorophyll a segments 9, 22 and 34

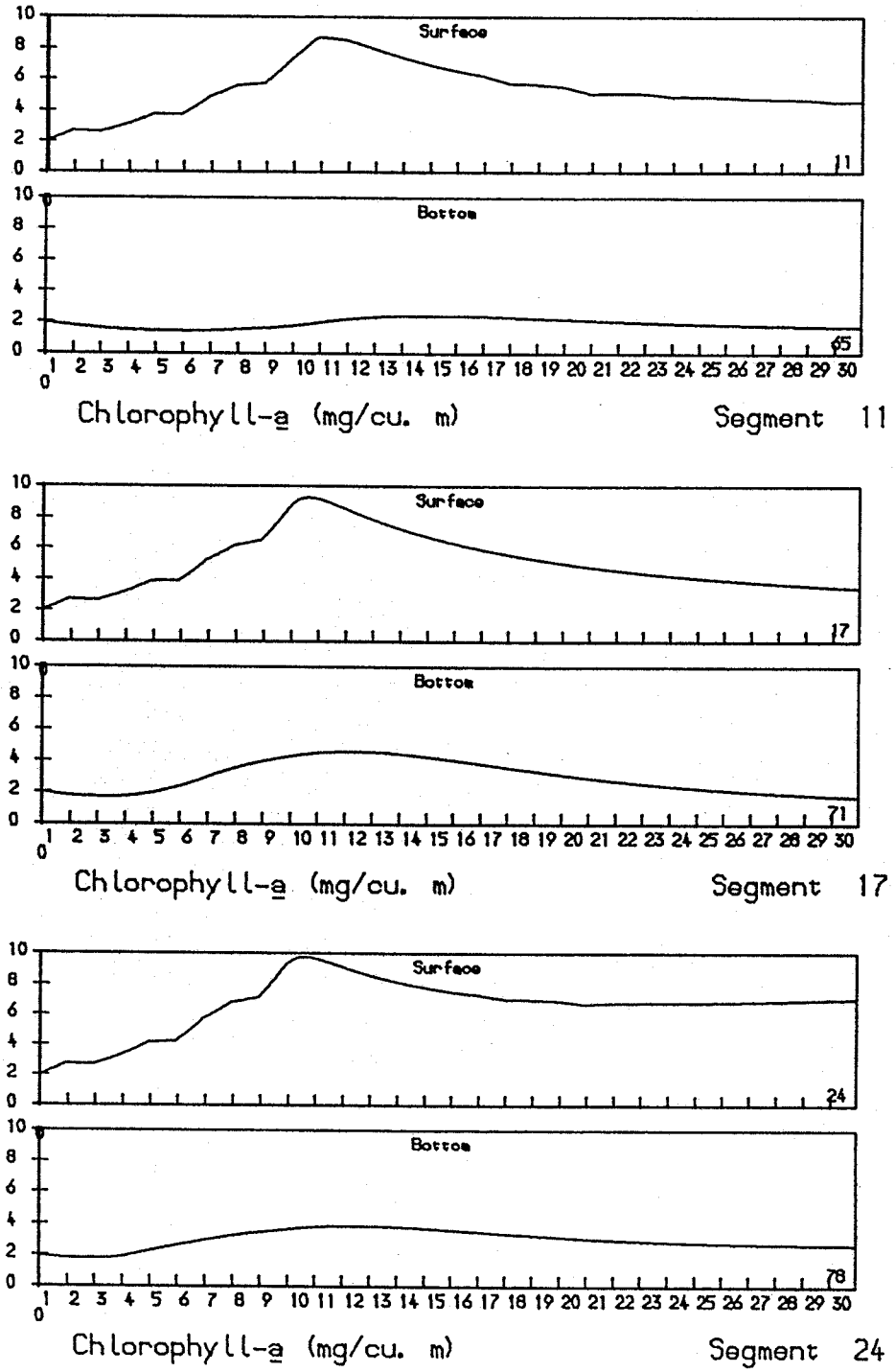
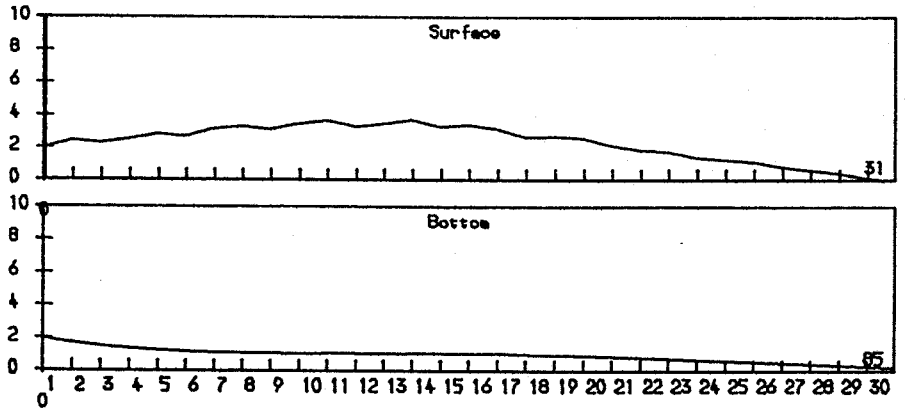
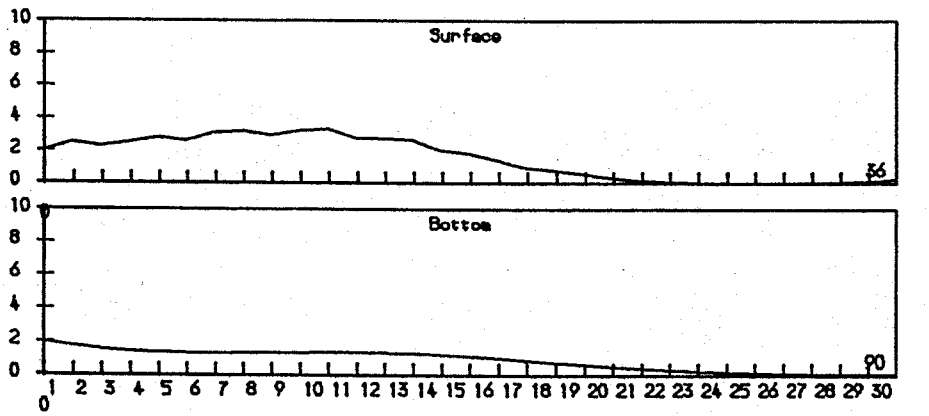


Fig 8b Simulated variation of Chlorophyll a segments 11, 17 and 24





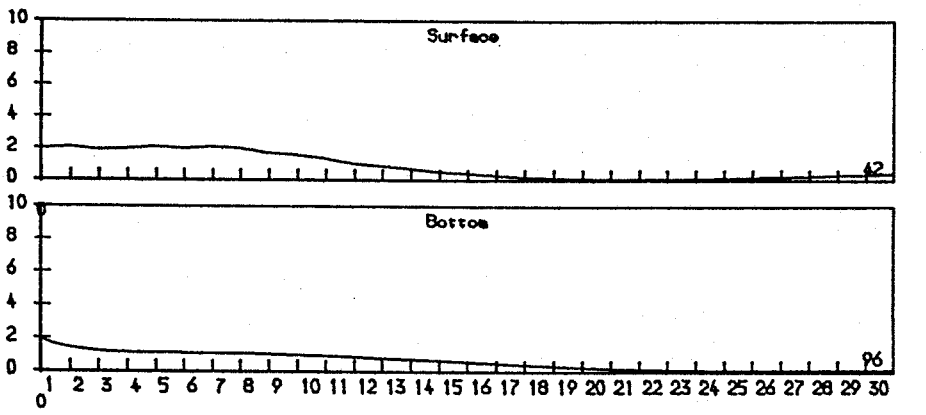
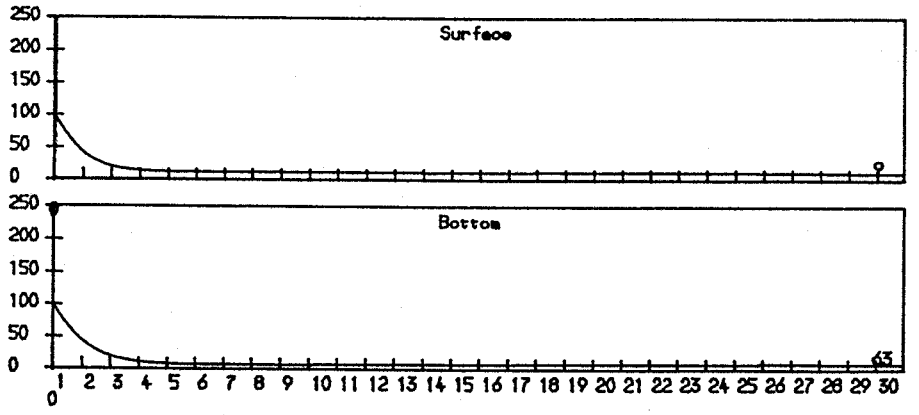
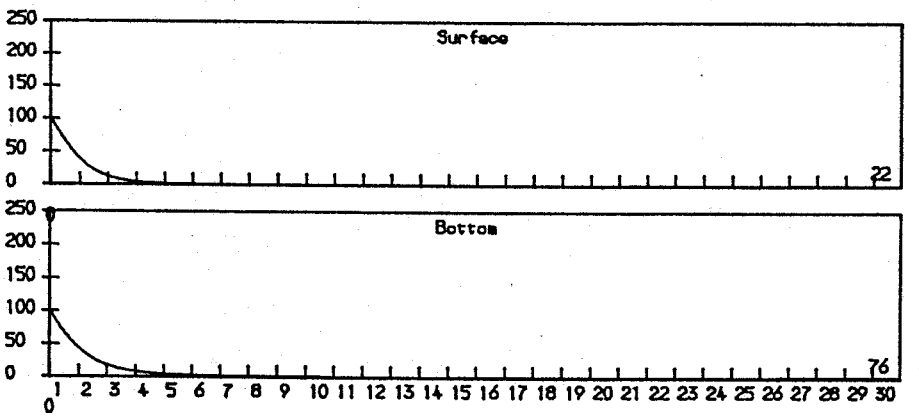


Fig 8c Simulated variation of Chlorophyll a segments 31, 36 and 42





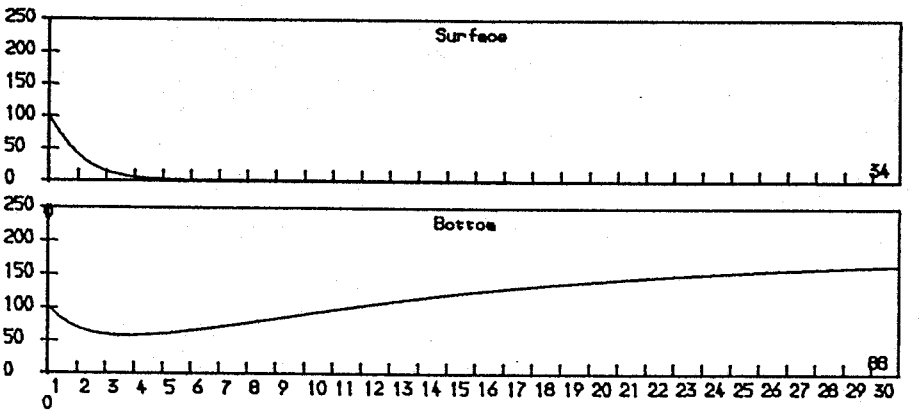
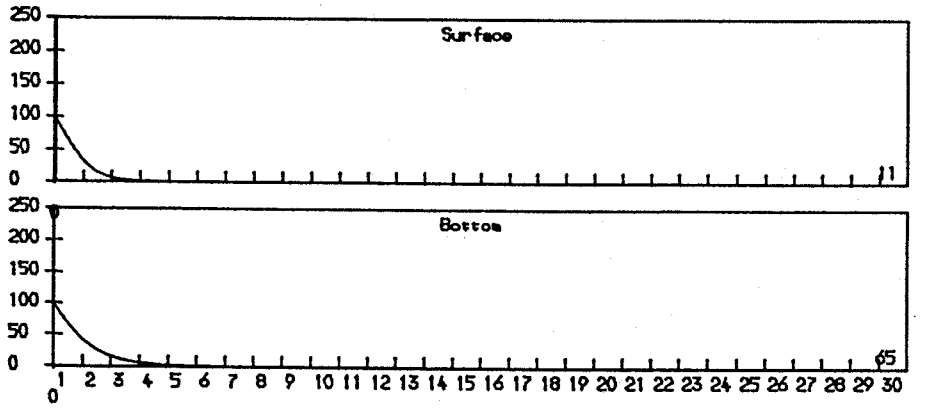
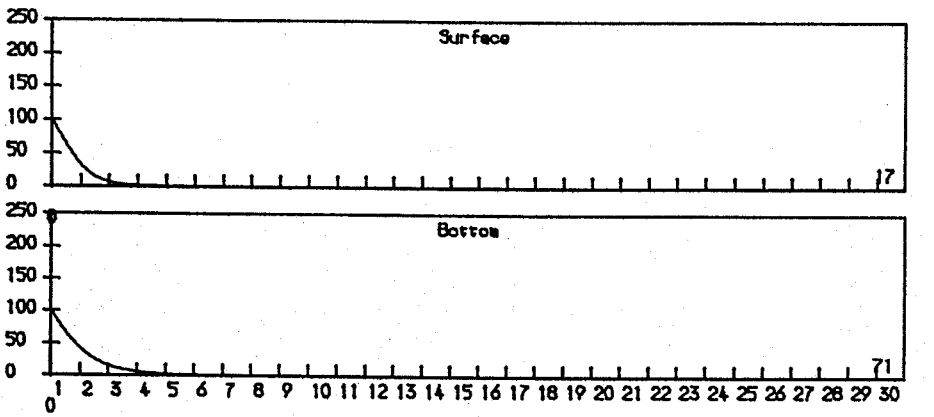


Fig 9a Simulated variation of adsorbed zinc segments 9, 22 and 34





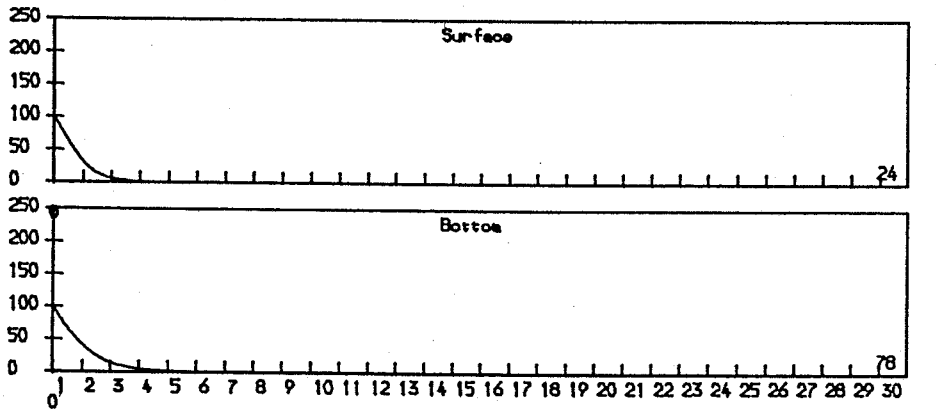
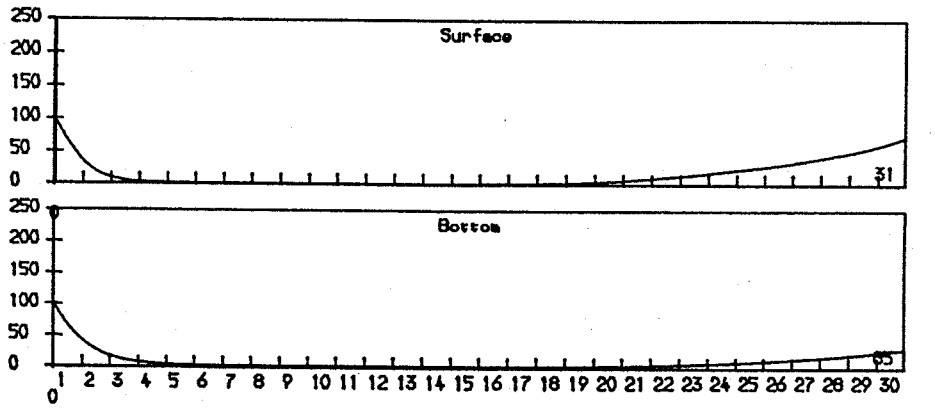
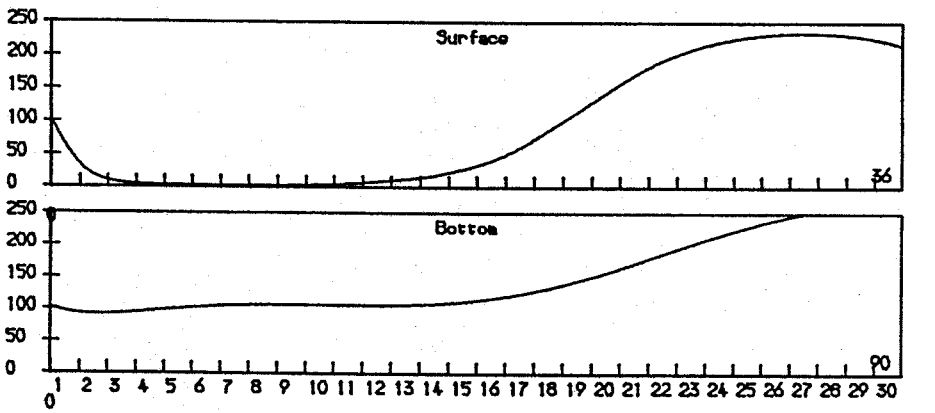


Fig 9b Simulated variation of adsorbed zinc segments 11, 17 and 24





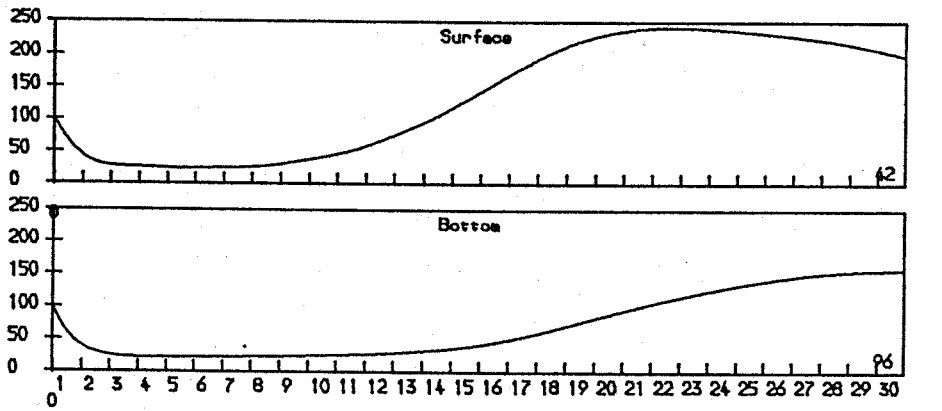


Fig 9c Simulated variation of adsorbed zinc segments 31, 36 and 42