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A REVIEW OF NUTRIENT SALT AND TRACE METAL DATA IN U.K. TIDAL WATERS

P.G.W. JONES

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A review of nutrient salt and trace metal data in UK tidal waters

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FOREWORD

This review has been written by Dr P G W Jones of the Ministry of Agriculture, Fisheries and Food's Directorate of Fisheries Research at the Fisheries Laboratory, Lowestoft, and the Directorate has undertaken its publication, but it is more than the work of just the author. It is the report of a Review Group set up by the Marine Pollution Monitoring Management Group of the Department of the Environment to make a selective and critical review of nutrient salt and trace metal data for United Kingdom tidal waters.

The comments, opinions and recommendations in this review are those of the Review Group, not just those of the author. A full list of members of the Review Group is to be found in Appendix 1 to this report.

A Preston
Director of Fisheries Research

1. Introduction

As part of the First Tactical Plan of the Department of the Environment (DOE) Marine Pollution Monitoring Management Group (MPMMG) a review was made of nutrient salt and trace metal monitoring programmes around the UK coastline based on the year 1975 (DOE, 1977). The general conclusion was that coverage in respect of nutrient salts was fair but that trace metal programmes were deficient both in their geographical distribution and reliability of data.

As part of the Second Tactical Plan a similar review was proposed but to be more comprehensive than the first and to include some assessment of the available data (DOE, 1979). The subject is of particular importance at the present time in view of the impending implementation of part 2 of the Control of Pollution Act (COPA) 1974 and the consequent responsibilities that will fall on Regional Water Authorities (RWAs) and River Purification Boards (RPBs). Thus a review group was established with terms of reference to make a selective and critical review of the available information on nutrient and metal levels in sea water around the UK. Membership consisted of representation from RWAs, RPBs, Government departments, the Natural Environment Research Council (NERC), industry, universities and other allied organisations (see Appendix 1). The report presented here is the result of the deliberations of this group.

Motivation for the measurement of the constituents listed in this review is important when considering the justification for such programmes. At present many of the exercises conducted by Government departments and RWAs/RPBs have been aimed at studying pollution but have not been subject to any statutory requirements. With the implementation of COPA part 2 this situation will change both at a national and at an international level. EC legislation requires such a national programme and the Act itself will confer a national statutory role on the relevant bodies in authorising and monitoring discharges to tidal waters. Thus a coordinated monitoring programme in the UK using proven analytical techniques, of which the measurement of nutrient salts and trace metals in water will only be a part, will assume even greater importance in future years.

The review group conducted its business mainly by correspondence but also met on two occasions to discuss tactics. Information for the review was collected mainly by means of detailed questionnaires. During the initial stages of the project it became apparent that the situation at the time of the first review still held in many respects: the quality of trace metal data seemed neither as good nor as extensive as that relating to nutrient salts. So it was decided that whereas a quantitative review of nutrient salt levels in UK coastal waters would be feasible, such treatment of trace metal data is still unrealistic. Thus the questionnaires asked for the submission of nutrient salt data but only rather more qualitative information on trace metals. The present review therefore separates these two constituents. Little attempt is made to make a detailed comparative evaluation of trace metal values whereas such treatment of nutrient salt data has proved possible.

There are several methods of listing the data. Information may be grouped according to the type of reporting organisation, e.g. RWA, Government department, university, etc., or a regional classification may be employed. The latter system has been selected because one of the main aims of the exercise is to review regional coverage of monitoring activities. Within the tables the data are generally arranged in a geographical sequence starting at the north-east coast of England and progressing in a clockwise direction around the British Isles: small deviations from this plan sometimes occur for the sake of simplicity. Data from 1970 onwards only are listed. If there are only observations prior to this for any locality, then repeat surveys are probably now due. Moreover, earlier trace metal data are probably unreliable.

The reported data are held in a variety of forms ranging from published papers through internal reports to raw data held by the organisation responsible for collection. The results of most projects undertaken by the more academically orientated organisations such as university departments tend to be in the open literature whereas much RWA/RPB data tend to be in raw form. However, all seem to be available subject to departmental approval.

In the presentation of data throughout this review, much variability will often be shown between one locality and another. It will not be the prime function of this review to provide environmental explanations for all such features but rather to assess the accuracy and extent of such data in order to verify the reliability of the observations.

The unit of measurement varies depending on the source and type of determinand. Most trace metals are reported as μg metal l^{-1}. However, nutrient salt measurements from the Harmonised Monitoring Scheme and some estuarine values are reported as mg N or P l^{-1} whereas marine values are usually recorded in μg atoms N or P l^{-1}. For comparison 1 mg N l^{-1} is equivalent to 71 μg atoms N l^{-1} and 1 mg P l^{-1} is equivalent to 32 μg atoms P l^{-1}.

2. Nutrient salts

The data are divided into three groups according to their relation to the Harmonised Monitoring Scheme, to estuarine profiles and to coastal waters. Information was requested between specific time periods wherever possible so as to make the data more comparable.

Data were sought on nitrogen and phosphorus. Although silicate is often also considered in the context of a nutrient salt, this constituent is unlikely to occur in the role of a major pollutant, so data for it are not included in this review. However, most of the organisations which reported on levels of nitrogen and phosphorus also measured silicate. Several laboratories measured total oxidised nitrogen (nitrate + nitrite) whereas others quoted one or both of the components separately. For the purpose of this review total oxidised nitrogen (TON) and nitrate are considered together: the amount of nitrate in any sample is generally in excess of an order of magnitude greater than that of nitrite and thus the two determinands, TON and nitrate, are roughly comparable.

2.1 Harmonised Monitoring Scheme data

RWAs and RPBs monitor a wide range of determinands in selected rivers in a programme controlled by the DOE, and data are reported for downstream as far as the tidal limits. Such information can be of considerable value when assessing estuarine pollution since it provides information on the freshwater inputs to such systems. All rivers with a mean annual flow in excess of 2 m^3 s^{-1} were included in the scheme unless it could be demonstrated that they were unpolluted, e.g., some in the more remote parts of Scotland. Significantly contaminated smaller rivers may also be monitored. Such decisions are based on the recommendation of the relevant RWA/RPB and are subject to DOE confirmation.

The data have been summarised for each RWA/RPB and are presented in Table 1. The overall mean value of each determinand for each Authority is presented together with the range of mean values gained from all sampling points at the tidal limits within the Authority's region. The data mainly cover the year April 1978 to March 1979. The method of classification gives a broad regional differentiation. It is apparent that for each constituent the overall range of mean values is generally in excess of an order of magnitude. Such a feature reflects broad regional variations in degrees of industrialisation and agricultural usage. Thus, the mean values reported by the Highland River Purification Board are generally low whereas such as those by the Thames Water Authority show much higher levels. Similarly, within each RWA/RPB there is a fair degree of variability reflecting local differences in land utilisation and industrialisation within river catchment areas. Thus, for example, a more detailed river-by-river analysis of the North West Water Authority data (Table 2) shows relatively high mean values for the Weaver and Mersey, whereas nutrient salts at the tidal limits of the Lune and other rivers further to the north are very much lower. The actual range of values throughout the 12-month period are also fairly great and reflect seasonal fluctuations in biological cycles in the water and in river flow.

2.2 Estuaries

Table 3 shows the coverage by those organisations that have measured nutrient salts in estuaries. It is immediately apparent that coverage around the British Isles is good. Nitrate, ammonia and phosphate have been and are measured at most localities and, in addition, nitrite was and is measured on several surveys. All the major "industrial" estuaries are being covered by on-going programmes, and the RWAs and RPBs play a prominent part in this respect. The Welsh Water Authority has undertaken a particularly comprehensive coverage of their regional estuaries where each system has been allocated a limited number of surveys, generally aimed at specific problems.

Most organisations contributing to this review have submitted nutrient/salinity-chlorinity profiles for estuaries. A selection are reproduced in Figures 1-4 covering the major industrial estuaries. All profiles relate to the period October-March and, where possible, the winter of 1978/79. Thus biological uptake should be minimal. The curves represent mean values drawn by visual examination of the data points. Thus the figures should be used to compare gross pollution loads rather than to determine detailed relationships.

In the majority of instances, the input of nutrient salts at the freshwater end of the estuary was considerably greater than at the seaward end, hence the characteristically high concentrations of oxidised nitrogen and phosphorus at lower chlorinities. In a situation of conservative mixing with no mid-estuarine inputs, a straight line would result between two end members. It is apparent that this situation does not prevail for most of the estuaries depicted in Figures 1 – 4. One may thus infer an input of nutrient salts from sources within the estuary or removal from the water phase during transportation. Both regimes would seem operative.

It is interesting to note that there is a wide variation in the specific concentration of nutrient salts at similar salinity points between one estuary and another, often to the extent of an order of magnitude difference. In the case of ammonia this range is even greater, with values in the Mersey Estuary being almost 70 times greater than in the Forth (Figure 3). The cause of the high input of ammonia to the Mersey is the large discharges of industrial and domestic effluent just upstream from the tidal limit. It is interesting to note that the profile of nitrate in the Mersey Estuary (Figure 1) shows a relatively low concentration at the low chlorinity end but rises to a peak at about 6 g Cl l^{-1}. The concentration of nitrite (Figure 2), although relatively high at the tidal limit, also shows a peak downstream. Both these features are considered to relate to the oxidation of ammonia during the passage down the estuary, firstly to nitrite and subsequently to the nitrate ion. The relatively high profiles for ammonia in the Clyde and Tyne both relate to the discharge of sewage effluents. The ammonia peak in the Humber at about 15 g Cl l^{-1} corresponds to domestic and industrial inputs from the Hull and Grimsby region.

Other features of interest are the high concentrations of nitrate and phosphate in the Thames Estuary (Figures 1 and 4). These relate to major inputs of sewage effluent coupled with run-off from agricultural land that has been treated with fertiliser. The ammonia peak (Figure 3) at about 5 g Cl l^{-1} in the same estuary coincides with discharges from several large sewage works in the vicinity.

Table 1 Overall mean values and range of mean values for nutrient salt data (mg l^{-1}) at tidal limits for each Regional Water Authority/River Purification Board. Number of observation points in parentheses

RWA/RPB	NO_3-N	NO_2-N	NH_4-N	PO_4-P	Total P
Northumbrian	2.39 (8) 0.52-4.95		0.28 (8) 0.09-0.93	0.26 (8) 0.02-0.77	0.38 (8) 0.09-0.97
Yorkshire	5.02 (6) 2.47-7.01	0.26 (6) 0.04-0.58	1.61 (6) 0.11-5.88	0.39 (6) 0.07-0.81	
Anglian	9.04 (13) 6.20-12.10	0.08 (9) 0.06-0.2	0.39 (13) 0.14-1.69	0.67 (13) 0.16-1.25	0.30 (2) 0.30-0.31
Thames	12.68 (3) 7.71-18.38	0.44 (2) 0.26-0.62	1.29 (3) 0.41-1.98	3.05 (3) 1.12-3.59	
Southern	5.19 (10) 2.59-6.75	0.07 (10) 0.03-0.11	0.18 (10) 0.10-0.29	0.70 (10) 0.16-2.16	
Wessex	5.01 (7) 3.7-6.9	0.11 (7) 0.03-0.24	0.31 (7) 0.07-0.97	0.47 (7) 0.09-0.92	
South West	2.59 (16) 1.50-4.35		0.10 (16) 0.02-0.58	0.15 (16) 0.02-0.41	
Severn Trent	7.50 (2) 6.10-9.00		0.30 (2) 0.20-0.40	1.10 (2) 0.70-1.50	
Welsh	1.53 (36) 0.23-4.25	0.04 (34) 0.001-0.28	0.19 (36) 0.02-1.69	0.10 (30) 0.01-0.90	
North West	3.4 (21) 0.4-10.1	0.19 (21) 0.01-0.56	1.68 (21) 0.06-8.85	0.77 (21) 0.01-5.74	
Solway	1.13 (7) 0.56-2.50	0.02 (7) 0.01-0.04	0.10 (7) 0.06-0.18	0.03 (7) 0.01-0.06	
Clyde	1.72 (12) 0.59-4.00	0.13 (12) 0.01-0.48	0.72 (12) 0.02-1.96	0.32 (12) 0.01-0.98	
Highland	0.43 (7) 0.10-0.98	0.01 (9) 0.01-0.01	0.07 (9) <0.01-0.20	0.01 (9) <0.01-0.01	
North East	2.69 (7) 0.33-5.75	0.03 (7) 0.01-0.06	0.11 (7) 0.07-0.21	0.06 (7) 0.02-0.14	
Tay	3.12 (6) 0.53-7.09		0.10 (6) 0.05-0.18	0.07 (6) 0.02-0.17	
Forth	2.03 (11) 0.31-4.35	0.07 (11) 0.01-0.18	0.39 (11) 0.05-1.33	0.40 (10) 0.10-0.58	
Tweed	2.23 (3) 1.96-5.51	0.03 (3) 0.02-0.04	0.08 (3) 0.06-0.08	0.23 (3) 0.21-0.23	

Table 2 Summary of nutrient salt data (mg l^{-1}) at the tidal limit for rivers within the North West Water Authority (Harmonised Monitoring Scheme), April 1978-March 1979: mean values with range

River	No. of observations	NO_3-N	NO_2-N	NH_4-N	PO_4-P
Weaver	48	5.7 1.5-8.3	0.57 0.35-1.3	8.86 4.3-21.0	0.28 0.10-0.80
Mersey	47	2.5 0.1-3.6	0.29 0.04-1.0	6.42 2.3-11.5	0.85 0.10-2.2
Alt	44	8.5 5.2-17.3	0.44 0.04-0.96	4.88 1.6-11.0	5.72 0.5-13.7
Douglas	25	3.8 0.3-7.9	0.35 0.04-0.84	2.79 1.0-7.5	1.56 0.45-4.5
Darwen	25	4.5 2.7-7.0	0.29 0.10-0.76	0.76 0.20-2.5	0.97 0.25-2.0
Ribble	49	6.4 1.8-23.0	0.09 0.01-0.31	0.34 0.05-1.9	0.34 0.05-0.85
Wyre	9	2.0 1.2-3.2	0.07 0.03-0.11	0.51 0.2-1.0	0.25 0.10-0.55
Lune	9	1.3 0.4-2.1	0.23 0.01-0.11	0.10 0.05-2.0	0.05 0.05-1.0
Bela	8	3.1 0.6-5.1	0.03 0.01-0.6	0.36 0.05-1.3	0.10 0.05-0.15
Kent	8	1.8 0.6-2.9	0.02 0.01-0.04	0.09 0.05-0.30	0.23 0.05-0.85
Leven	9	1.0 0.4-4.8	0.01 0.01-0.04	0.38 0.05-2.3	0.05 0.05-0.10
Derwent	7	1.1 0.4-1.6	0.02 0.01-0.03	0.06 0.02-0.13	0.02 0.005-0.46
Eden	8	2.1 1.3-3.1	0.04 0.02-0.07	0.11 0.04-0.17	0.14 0.03-0.33
Esk	9	0.8 0.1-2.0	0.01 0.01-0.02	0.06 0.01-0.18	0.02 0.005-0.08
Lyne	9	1.3 0.8-2.4	0.02 0.01-0.03	0.10 0.01-0.17	0.03 0.005-0.09

Table 3 Nutrient salts measured in estuarine waters of the UK

Organisation	Area	Frequency	Period	NO_3-N	NO_2-N	NH_4-N	PO_4-P
Northumbrian Water Authority	Tyne	8 surveys/ year	1970 →	x	x	x	
	Wear	4 surveys/ year	1976 →			x	
	Tees	6 surveys/ year	1970 →	x	x	x	
Humber Estuary Committee	Humber, Trent, Ouse	14 surveys/ year	1970 →	x	x	x	x
Anglian Water Authority	Witham	Monthly	1970 →	x	x	x	
	Welland, Nene	Quarterly	1970 →	x	x	x	
	Great Ouse, Yare, Waveney, Blyth, Orwell, Colne, Blackwater, Crouch, Roach	Quarterly	1970 →	x		x	x
Thames Water Authority	Thames	Weekly/ quarterly	1970 →	x	x	x	x
Southern Water Authority	Test, Southampton Water	Monthly	1976 →	x	x	x	x
	Wallington, Portsmouth Harbour	Monthly/ fortnightly	1974-76	x		x	x
Southampton University/ Central Electricity Generating Board	Test, Southampton Water	Various	1969-75	x	x	x	x
Marine Biological Association of the United Kingdom	Tamar	Monthly	1970 →	x		x	
Institute for Marine Environmental Research	Tamar	Approx. monthly	1977 →	x	x		x
	Dart	2 surveys/ year	1978 →	x	x	x	x
	Fal	1 survey	1978 →	x	x	x	x
Severn Estuary Survey and Systems Panel	Severn	Various	1975 →	x	x	x	x

Table 3 (continued)

Organisation	Area	Frequency	Period	NO_3-N	NO_2-N	NH_4-N	PO_4-P
Imperial Chemical Industries	Severn, Avonmouth to Oldbury	1 survey/ year	1972 →	x	x	x	
Welsh Water Authority	Wye	2 surveys	1978	x		x	
	Ebbw	Monthly	1980 →	x		x	x
	Usk	Fortnightly	1978, 1980 →	x		x	x
	Rhymney	2 surveys	1979	x		x	x
	Taff	2 surveys	1979-80	x	x	x	x
	Afan	1 survey	1979	x		x	x
	Ely	1 survey	1979			x	x
	Neath	2 surveys	1979			x	
	Towy	2 surveys	1979	x		x	x
	Loughor	4 surveys	1975-76	x		x	x
	Milford Haven	1 survey	1973	x			
	Mawddach	7 surveys	1974-75	x			
	Conwy	4 surveys	1975-78	x		x	x
	Dee	4 surveys	1975 & 1977	x	x	x	x
North West Water Authority	Mersey	Monthly	1970 →	x	x	x	x
	Ribble	2-4 surveys/ year	1975 →	x	x	x	x
	Wyre	Monthly	1978 →	x	x	x	x
	Lune	Monthly	1978 →	x	x	x	x
Imperial Chemical Industries	Wyre	Alternate years	1972 →	x	x	x	x
	Nith and Solway	2 surveys/ year	1972 →	x	x	x	x
Solway River Purification Board	Loch Ryan, Dee, Nith, Inner Solway	1-2 surveys/ year	1975 →	x	x	x	x
Clyde River Purification Board	Clyde	Monthly	1974 →	x	x	x	x
Forth River Purification Board	Forth	Monthly	1975 →	x	x	x	x
Imperial Chemical Industries	Forth	Yearly	1972 →	x	x	x	x

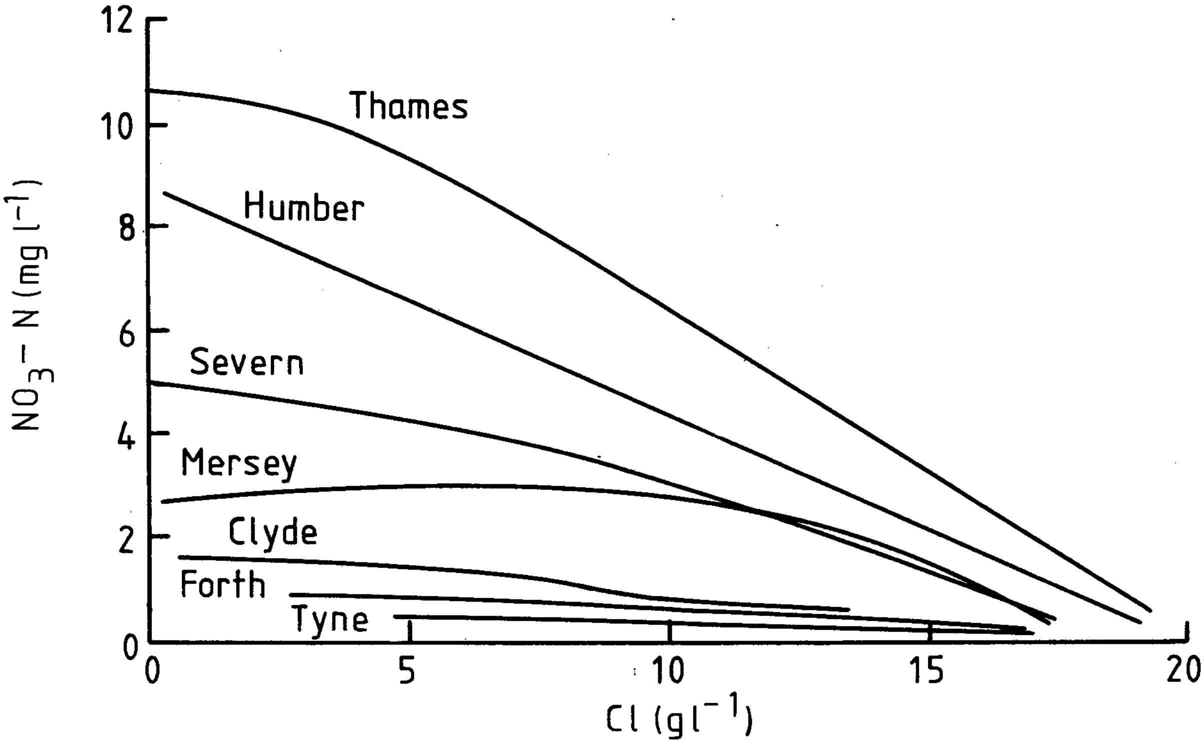


Figure 1. Nitrate – chlorinity profiles for selected estuaries.

Key:
Clyde – 21 surveys, Jan. 1978–Dec 1979;
Forth – 2 surveys, Neap and Spring tides, Jan.–Feb. 1979;
Humber – 3 surveys, Nov.–Dec. 1978, Mar. 1979;
Mersey – 6 surveys, Oct. 1978–Mar. 1979;
Severn – 31 surveys, 1975–1979;
Thames – 26 Surveys, Oct. 1978–Mar. 1979;
Tyne – 1 survey, Nov. 1978.

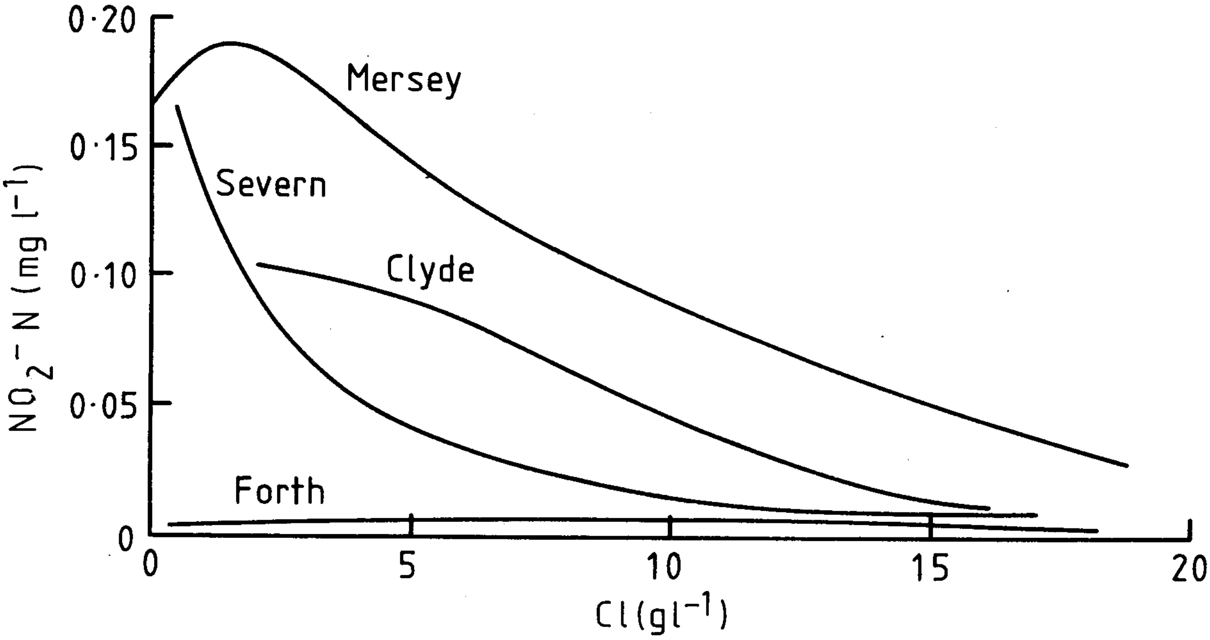


Figure 2. Nitrite – chlorinity profiles for selected estuaries (see Figure 1 for key).

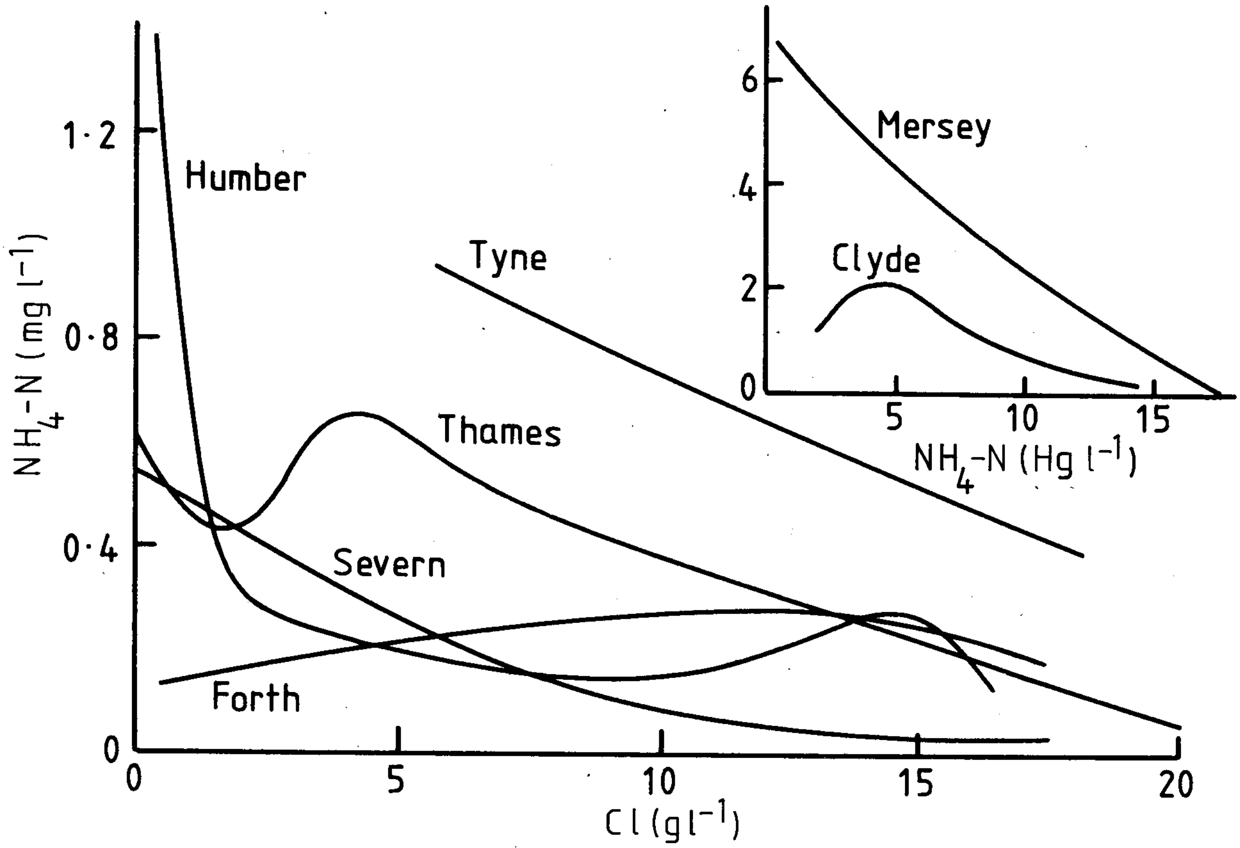


Figure 3. Ammonia – chlorinity profiles for selected estuaries (see Figure 1 for key).

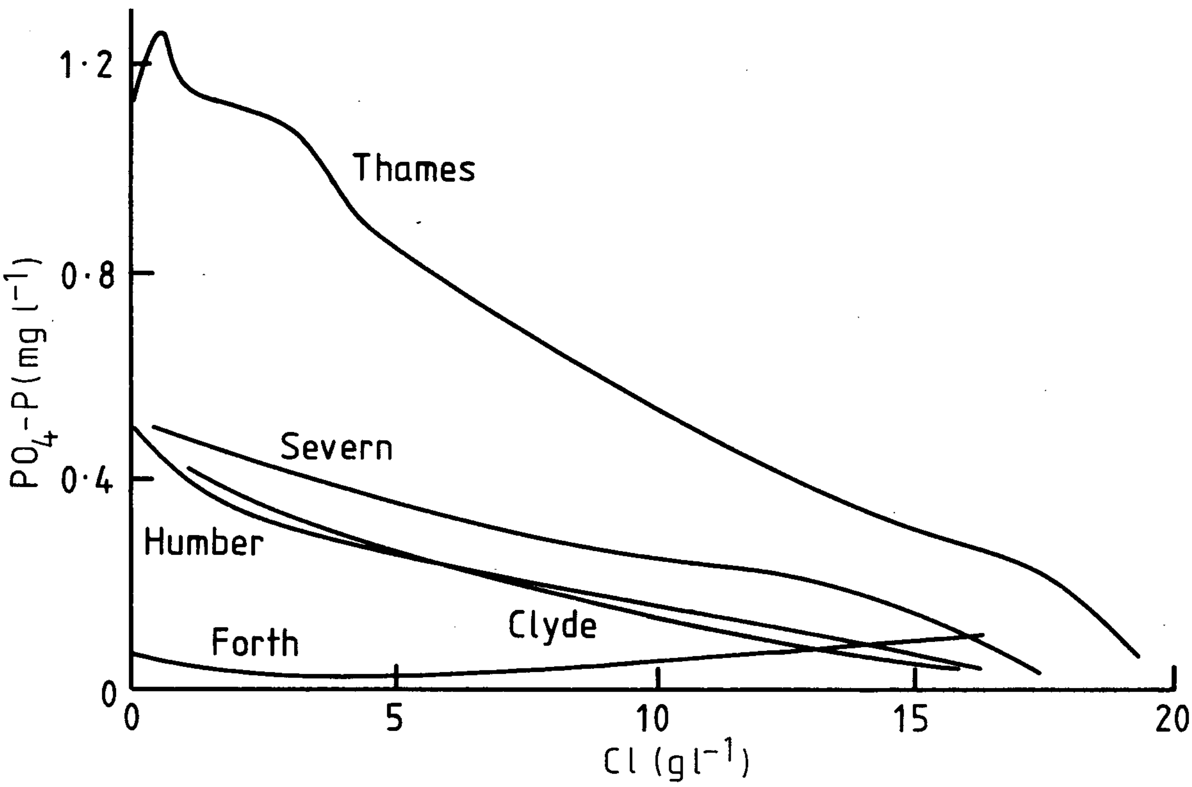


Figure 4. Phosphate – chlorinity profiles for selected estuaries (see Figure 1 for key).

In contrast, the generally low levels of all constituents in the profiles for the Forth relate to a freshwater input from a region of low population with little industrial discharge. The greatest nutrient salt input to this estuary occurs towards the more saline end and this feature is most clearly shown on the profiles for ammonia and phosphate (Figures 3 and 4).

nutrient salt profiles, although these two locations are not necessarily at the same geographical point. Table 4 compares those values for the principal UK estuaries. Considering that the mean values quoted were for different time periods, the data show a good degree of agreement. The relatively low levels of nutrient salts reported in the estuarine profiles of the Forth are confirmed by the values at the tidal limit.

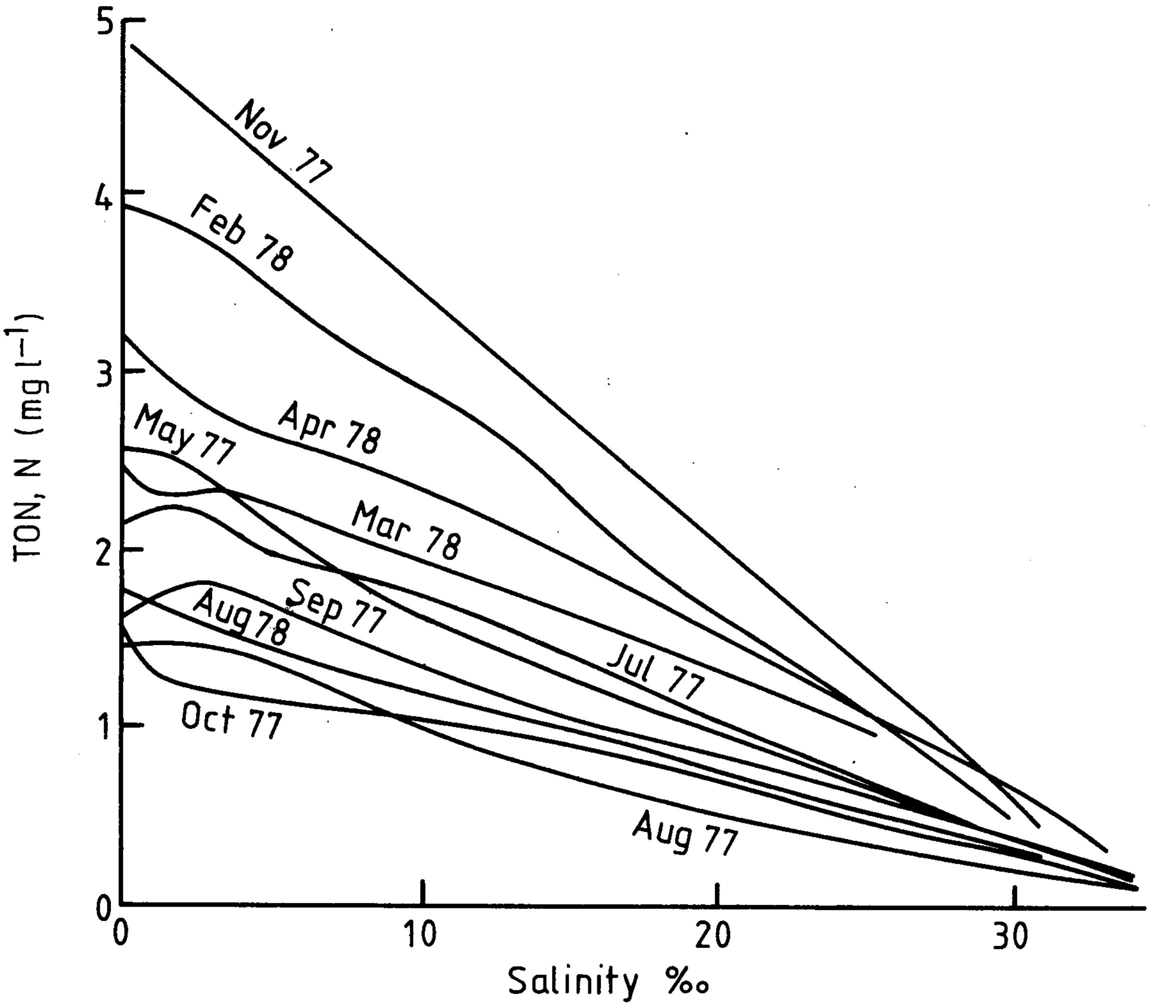


Figure 5. Total oxidised nitrogen (TON) relationships in the Tamar Estuary, obtained from the surveys between June 1977 and August 1978.

Figure 5 shows nitrate-salinity profiles for the Tamar Estuary for different months of the year. The data are presented to illustrate the degree of variability in such systems and also demonstrate that simple winter-summer-winter cycles do not necessarily always operate. There is a broad annual cycle based on fresh water input flow although there is a fair degree of detailed fluctuation superimposed.

Values recorded at the tidal limit as part of the Harmonised Monitoring Scheme theoretically should be broadly comparable with data at "zero" chlorinity from the estuarine

Similarly, the relatively high levels of ammonia in the Mersey are depicted in both sets of observations. The poorest agreement is for the Humber. The probable reason is that tidal limit locations occur in both the Ouse system and the Trent which feed into the Humber Estuary. The profiles depicted in Figures 1-4 used a mixture of data from both these tributaries at the low chlorinity end of the range. This feature coupled with a significant input of sewage and industrial waste between the tidal limits and the limits of saline intrusion has no doubt caused the discrepancy.

Table 4 Comparison of nutrient salt values (mg l^{-1}) at the tidal limit from the Harmonised Monitoring Scheme (HMS) with values at 'zero' chlorinity from estuarine profiles (EP)

Estuary			NH_4-N	NO_2-N	NO_3-N	PO_4-P
Humber	HMS	Trent	0.4		9.0	1.5
		Ouse	0.2		3.7	0.3
	EP		1.4		9.0	0.5
Thames	HMS		0.41		7.7	1.2
	EP		0.60		10.5	1.1
Severn	HMS		0.2		6.1	0.7
	EP		0.6		5.0	0.5
Mersey	HMS		6.4	0.29	2.5	
	EP		7.0	0.16	2.6	
Clyde	HMS		0.76	0.14	2.2	0.61
	EP		0.60	0.10	1.6	0.48
Forth	HMS		0.12	0.01	0.9	0.07
	EP		0.12	0.004	1.0	0.04

2.3 Coastal waters

Table 5 lists data available for coastal waters. In certain areas the division between estuarine and coastal waters is somewhat arbitrary. In general, if a set of data do not contain salinity values below 25^o/oo then they have been listed under coastal waters. Thus the Bristol Channel is listed as a coastal area whereas the adjacent Severn Estuary falls into the estuarine category. The range of constituents measured is similar to those in the estuaries. It is of interest to note that organic nitrogen and phosphorus have been measured in some west coast regions.

Coverage of the east coast of England is fairly good although few of these surveys are on-going. Similarly, Liverpool Bay is well catered for, with several organisations involved in continuing studies. However, some parts of the Scottish coast and west coast of Wales are less extensively surveyed.

Table 6 lists the nutrient salt content of selected coastal waters. All data refer to the winter period when biological uptake should be minimal. A mixture of surface samples and data at depth are presented. Vertical stratification, however, was small and insignificant compared with inhomogeneity typical of estuaries. The salinity data indicate that most values were above 30^o/oo. The range of mean values is not as great as between one estuary and another although nitrate levels almost span an order of magnitude. Of the areas listed, the north-east coast of England shows the lowest values with Liverpool Bay exhibiting the highest levels. It will be noted, however, that at each location a fairly wide range of values are reported. These observations may be biased towards localities expected to show elevated levels of nutrient salts, since such regions would receive preferential selection for survey.

3. Trace metals

Consideration was given by the review group to the collection and presentation of trace metal data in a similar manner to those of nutrient salts. However, the general consensus of opinion was that the smaller amount of data, together with doubts on the degree of accuracy of some of it, would make such a presentation difficult. Contributors were therefore requested to submit only qualitative information on the trace metal data in which they had reasonable confidence.

Table 5 Nutrient salts measured in coastal waters of the UK

Organisation	Area	Frequency	Period	NO_3-N	NO_2-N	NH_4-N	Organic N	PO_4-P	Organic P
Imperial Chemical Industries	NE coast England, Seaham to Donna Nook,	4 surveys	1974-75	x		x		x	
	Tees Bay	3 surveys/ year	1971-73 1976	x	x	x		x	
Ministry of Agriculture, Fisheries and Food	NE coast England, off Tees, Tyne	Various	1978 →	x	x	x		x	
	East coast England, Humber to Thames	1 survey/ winter	1974-79	x				x	
Southern Water Authority	Solent, east Isle of Wight	Monthly	1976 →	x		x		x	
Wessex Water Authority	Poole Harbour	Bimonthly	1976, 1977 & 1979	x	x	x		x	
Imperial Chemical Industries	Torbay and adjacent area	2 surveys	1978, 1979	x		x		x	
Institute for Marine Environmental Research	Bristol Channel	Various	1971-78	x	x	x		x	
Liverpool University	Bristol Channel	2 surveys	1971	x				x	x
	Liverpool Bay	4 surveys	1970/71	x				x	x
	Isle of Man-Morecambe Bay	Various	1970 →	x	x			x	
Welsh Water Authority	North Bristol Channel	6 surveys	1977	x	x	x		x	
	Swansea Bay	6 surveys	1976-77	x		x		x	
	Menai Strait	Various	1980 →	x	x	x		x	
	North Wales coast	Various	1979 →	x	x	x		x	
University College of North Wales	Menai Strait, Liverpool Bay	Various	1970 →	x	x	x		x	x

Table 5 (continued)

Organisation	Area	Frequency	Period	NO_3-N	NO_2-N	NH_4-N	Organic N	PO_4-P	Organic P
Lancashire and Western Sea Fisheries Joint Committee	Coastal-Menai Strait to Walney Island	Monthly	1971-76	x	x	x		x	
	Eastern Irish Sea	Monthly	1975 →	x	x	x	x	x	x
North West Water Authority	Liverpool Bay	Fortnightly	1974 →	x	x	x		x	
Imperial Chemical Industries	Irvine Bay	2 surveys/ year	1973 →	x	x	x		x	
Clyde River Purification Board	Outer Clyde, Ayr Bay to Bute Sound	Various	1973 →	x	x	x		x	
Scottish Marine Biological Association	Firth of Lorne and adjacent area	3 surveys/ year	1979 →	x			x	x	x
Department of Agriculture and Fisheries for Scotland	Outer Clyde	2-4 surveys/ year	1972-75	x		x		x	
	Sullom Voe	2-4 surveys/ year	1974 →	x		x		x	
	Outer Forth	2-4 surveys/ year	1975 →	x		x		x	
Highland River Purification Board	Cromarty Firth	1-2 surveys/ year	1976 →	x	x	x		x	
	Inverness and Beauly Firths	1-2 surveys/ year	1979 →	x	x	x		x	
	Loch Broom	1-2 surveys/ year	1979 →	x	x	x		x	
	Loch Linnhe and Loch Eil	1-2 surveys/ year	1978 →	x	x	x		x	
Forth River Purification Board	Firth of Forth (Edinburgh coastline)	Monthly	1980 →	x	x	x		x	

Table 6 Nutrient salt content (µg-atoms l^{-1}) of selected coastal waters. Mean values with range. (*Too many values below detection level)

Organisation	Area and time	No. of observations	NO_3-N	NO_2-N	NH_4-N	PO_4-P	S°/oo
Imperial Chemical Industries	NE coast England, Seaham to Saltburn (all depths) December 1974	96	4.6 2.8-7.9		* <7-11	0.56 0.35-0.65	34.0-34.5
Ministry of Agriculture, Fisheries and Food	Southern North Sea, Outer Thames (surface observations) January 1975	10	14.0 8.6-23.8	0.34 0.20-0.48		1.02 0.69-1.35	34.6 33.8-35.1
Imperial Chemical Industries	Torbay, south Devon (all depths) January 1979	36	10.3 7.1-12.5		3.3 1.7-8.9	0.79 0.48-1.29	34.7-35.5
Welsh Water Authority	Swansea Bay (surface observations) November 1977	70	32 0.71-70		4.3 0.2-97	0.87 0.06-5.71	30.1
Lancashire and Western Sea Fisheries Joint Committee	Lancashire and North Wales coast (surface observations) Mainly winter 1976/77	48	30 16.4-59.3	1.2 0.2-2.6	3.5 0.3-22.8	1.6 0.7-2.1	31.5 28.5-33.0
Clyde River Purification Board	Ayr Bay to Bute Sound (top 10 metres) Winter 1978/79	155	16.6 7.9-28.7	0.40 0.02-0.94	2.5 0.1-10.4	1.31 0.92-2.75	30.9 25.0-33.2
Department of Agriculture and Fisheries for Scotland	Outer Firth of Forth (all depths) December 1977	110	5.9 3.3-8.5			0.63 0.04-1.27	34.0 32.8-34.8

Trace metal analyses are made on samples collected at the tidal limits as part of the Harmonised Monitoring Scheme. However, a large number of values are at or below the detection limits of the methods used in this scheme even though the range of concentrations encountered in river systems is generally much higher than in sea water. So, in view of the limited value of such information, these data have been rejected. The remaining data are classified as estuarine or coastal. The quantitative results of a limited number of surveys are presented in order to broadly illustrate the range of trace metals measured in saline waters.

3.1 Estuaries

Table 7 shows the coverage by those organisations that have reported data on trace metal levels in estuaries. It is immediately apparent that the number of estuaries covered is considerably fewer than for nutrient salt measurements (Table 3). However, most of the main "industrial" systems have been surveyed although measurements in the Mersey have commenced only very recently. Many of the minor estuaries surveyed in respect of nutrient salts have not been sampled for trace elements. Most of the major potential pollutants have been measured apart from mercury for which there are fewer entries in Table 7 than for other important determinands.

3.2 Coastal waters

Table 8 lists observations in coastal waters. In contrast to the estuaries the extent of trace metal observation in coastal waters is greater than for nutrient salts. This feature probably reflects the current interest in trace metal chemistry by several marine institutes.

There are no major industrialised coastlines not included, although coverage of the English Channel coast is perhaps rather sparse since the Ministry of Agriculture, Fisheries and Food's surveys which are fairly extensive in most other areas are relatively infrequent in that region.

3.3 The distribution of trace metals in saline waters

The often dubious nature of comparisons of trace metal data between different organisations will be further dealt with later. However, measurements made by the same analytical unit can be of value in demonstrating trends and gradients. Three sets of data are presented in order to demonstrate such features.

Table 7 Trace metals measured in estuarine waters of the UK. (Method, where known: 1 = AAS direct injection; 2 = AAS solvent extraction; 3 = AAS ion exchange resin; 4 = electrochemistry; A = flame; B = graphite furnace, etc.)

Organisation	Estuary	Frequency	Period	As	Cd	Co	Cu	Cr	Fe	Hg	Mn	Ni	Pb	Zn	Method
Ministry of Agriculture Fisheries and Food	Humber	Yearly	1973-76		x		x			x		x		x	2, B
Thames Water Authority	Thames	Quarterly	1979 →		x		x			x		x	x	x	2
Southampton University	Southampton Water, Test and Beaulieu	Various	1970 →				x		x		x				2,3, A,B
Institute for Marine Environmental Research	Tamar	Various	1972 →		x	x	x		x		x	x	x	x	1,3, A,B
Marine Biological Association	Tamar	Various	1977 →	x					x		x				2,3,4
Westfield College	Cornwall-Restronguet	Various	1975-77	x	x		x							x	2
Imperial College	Cornwall-Restronguet and Helford	Various	1972-74		x	x	x		x		x	x	x	x	2
Imperial Chemical Industries	Severn	Yearly	1972 →			x	x				x	x	x	x	3
Severn Estuary Survey and Systems Panel	Severn	Various	1975 →		x		x				x	x	x	x	3
Welsh Water Authority	Usk	2 surveys	1978		x		x		x		x	x	x	x	3
	Loughor	4 surveys	1975 & 1976		x		x		x		x	x	x	x	3
	Milford Haven	Various			x		x		x		x	x	x	x	3
	Mawddach	6 surveys	1974 & 1975		x		x		x		x	x	x	x	3
	Conwy	1 survey	1975		x		x		x		x	x	x	x	3
	Lee	3 surveys	1975-77		x		x		x		x	x	x	x	3
University College of North Wales	Anglesey estuaries	Various	1970 →				x		x					x	1,2, A
Leeds University	Conwy	2 surveys	1973 & 1976		x		x				x		x	x	1,2
North West Water Authority	Mersey		1980 →	x	x		x	x		x		x	x	x	
	Ribble	2-4 surveys/year	1975 →											x	1
	Wyre	Monthly	1975 →				x			x				x	1
Imperial Chemical Industries	Wyre including Morecambe Bay	Alternate years	1972 →				x							x	3
	Nith and Solway	Twice yearly	1972 →		x	x	x				x	x	x	x	3
Clyde River Purification Board	Clyde	Occasional	1975-79		x		x					x	x	x	2, A
Imperial Chemical Industries	Forth	Yearly	1972 →				x			x				x	3

Table 8 Trace metals measured in coastal waters of the UK. (Method, where known: 1 = AAS direct injection; 2 = AAS solvent extraction; 3 = AAS ion exchange resin; 4 = electrochemistry; A = flame; B = graphite furnace, etc.)

Organisation	Region	Frequency	Period	Cd	Co	Cu	Cr	Fe	Hg	Mn	Ni	Pb	Zn	Method
Ministry of Agriculture, Fisheries and Food	North Sea, English Channel, Irish Sea	Various	1970 →	x		x			x	x	x		x	2, B
Imperial Chemical Industries	NE coast England, Seaham to Donna Nook	4 surveys	1974-75	x	x	x	x		x	x	x	x	x	3
Southern Water Authority	Solent	Monthly	1976 →	x		x				x	x	x	x	2, A
Institute for Marine Environmental Research	Bristol Channel	Various	1971-78	x	x					x		x	x	3
Welsh Water Authority	North Bristol Channel	6 surveys	1977	x		x		x		x	x	x	x	3
	Swansea Bay	6 surveys	1976-77	x		x		x		x	x	x	x	3
	South Wales coast - Bristol Channel to Aberaeron	2 surveys	1978-79	x		x		x		x	x	x	x	3
	Welsh coast - Wye to Dee	2 surveys	1979	x		x		x		x	x	x	x	3
Liverpool University	Bristol Channel, west coast of Wales, Liverpool Bay	Various	1971 →	x		x		x		x	x	x	x	3,4
Lancashire and Western Sea Fisheries Joint Committee	Liverpool Bay	Various	1976-78	x		x		x	x	x	x	x	x	3
Imperial Chemical Industries	Irvine Bay	Twice yearly	1973 →			x						x	x	3
Clyde River Purification Board	Middle and outer Firth of Clyde and adjacent sea lochs	Occasional	1978 →	x		x					x		x	2, A
Department of Agriculture and Fisheries for Scotland	Outer Firth of Clyde and outer Firth of Forth	Twice yearly	1975-79	x		x			x			x		4

Abdullah and Royle (1974) measured the trace metal content of the water in the lower non-tidal sections of selected rivers discharging into the Bristol Channel, using a method of sufficient sensitivity for such samples. Some of the data are shown in Table 9. The pattern is similar to that of the levels of nutrient salts at the tidal limits (Table 2) with each element showing a wide range of values from one river to another and the ratio of one metal to another within each river being also variable. This reflects variations in drainage and discharges from both natural and anthropogenic sources.

Figure 6 shows metal salinity profiles down the Clyde Estuary, measured by the Clyde River Purification Board. It is apparent that, for all the metals depicted the levels at the marine end are lower than at the head of the estuary. However, the profiles depicted all show an input of trace metals at about 13°/oo salinity and this point corresponds to a major sewage discharge. Such profiles thus show similar relationships to those of nutrient salts (Figures 1-4).

Table 9 Distribution of trace metals ($\mu g\ l^{-1}$) in the water of the lower non-tidal sections of selected rivers discharging into the Bristol Channel, November 1971 (Abdullah and Royle, 1974)

River	Cd	Cu	Ni	Pb	Zn
Taf	2.44	2.02	1.47	0.39	27.49
Loughor	1.00	5.24	0.72	3.93	1.63
Tawe	0.79	1.84	27.08	0.47	30.96
Parret	3.21	3.33	1.01	1.53	88.44
Washford	0.07	7.02	0.02	67.7	1.68
Umber	0.01	0.50	0.02	0.45	2.87

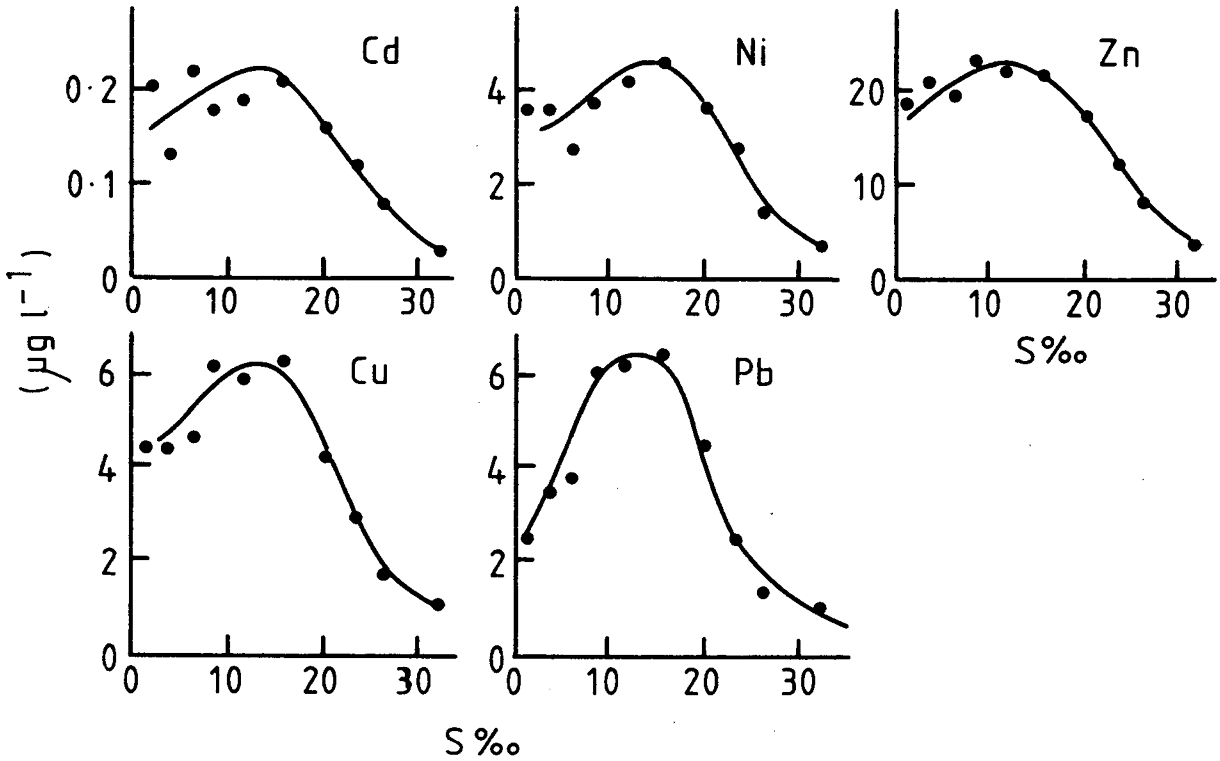


Figure 6. Clyde metal-salinity profiles, 6 April 1979.

Figure 7 shows the mean distribution of selected trace metals in the water of UK shelf seas measured during a variety of surveys by the Ministry of Agriculture, Fisheries and Food. It is apparent that elevated levels occur in coastal water, particularly near estuaries. The low concentration of trace metals recorded in open waters such as the northern North Sea were near the limits of detection for the tecnique used and probably represent levels approaching uncontaminated oceanic water.

4. Discussion

Of prime importance when reviewing chemical data of any kind is a consideration of its accuracy and comparability between one set of analyses and another. To achieve a satisfactory standard, participation in intercalibration exercises is of primary importance. All organisations were asked to provide information on such activities together with the data submitted.

The situation in respect of nutrient salts is reasonably satisfactory. Most institutes had participated in intercalibration programmes and indeed such exercises are an integral part of the Harmonised Monitoring Scheme. Moreover, the techniques of nutrient salt analyses are now well proven. With the exception of nitrate, similar methods are used for both fresh and saline waters with only minor modifications to take account of the different concentration ranges encountered in the two environments. Both manual and automatic procedures were reported: both methods have similar degrees of precision, although the latter clearly permits a greater throughput of samples in a given time.

The good agreement between the nutrient salt data at the tidal limit compared with the low salinity estuarine profile levels (Table 4) was particularly encouraging since within each RWA and RPB these two sets of measurements were generally made by different analytical teams using techniques best suited to freshwater or saline media.

One may infer that the nutrient salt data submitted by the various institutes are comparable and can be assembled into a composite picture of their distribution around the British Isles. However, this does not permit any relaxation in stringent quality control exercises which are an on-going necessity for any monitoring programme.

The situation in respect of trace metals is unfortunately much less satisfactory. Tables 7 and 8 show that most trace metal analyses are performed by atomic absorption spectroscopy (AAS) but that a variety of procedures are adopted. It has been known for some time that AAS analytical techniques suitable for freshwater are often not satisfactory for saline waters owing to the interference of salt. Such errors are particularly accentuated by the relatively low levels of metal in sea water which may easily be masked if fresh water methods are applied directly to such samples.

Topping *et al.* (1980) recently reviewed the distribution of trace metals in waters of the Atlantic including the shelf seas. The aims of this exercise were very similar to those of the present review. The main conclusion was that, at present, data from different areas measured by different analysts cannot be compared owing to the diversity of methods for sample collection and analysis, and to inadequate intercalibration.

A full international intercalibration programme for trace metals in sea water has recently been conducted under the auspices of the International Council for the Exploration

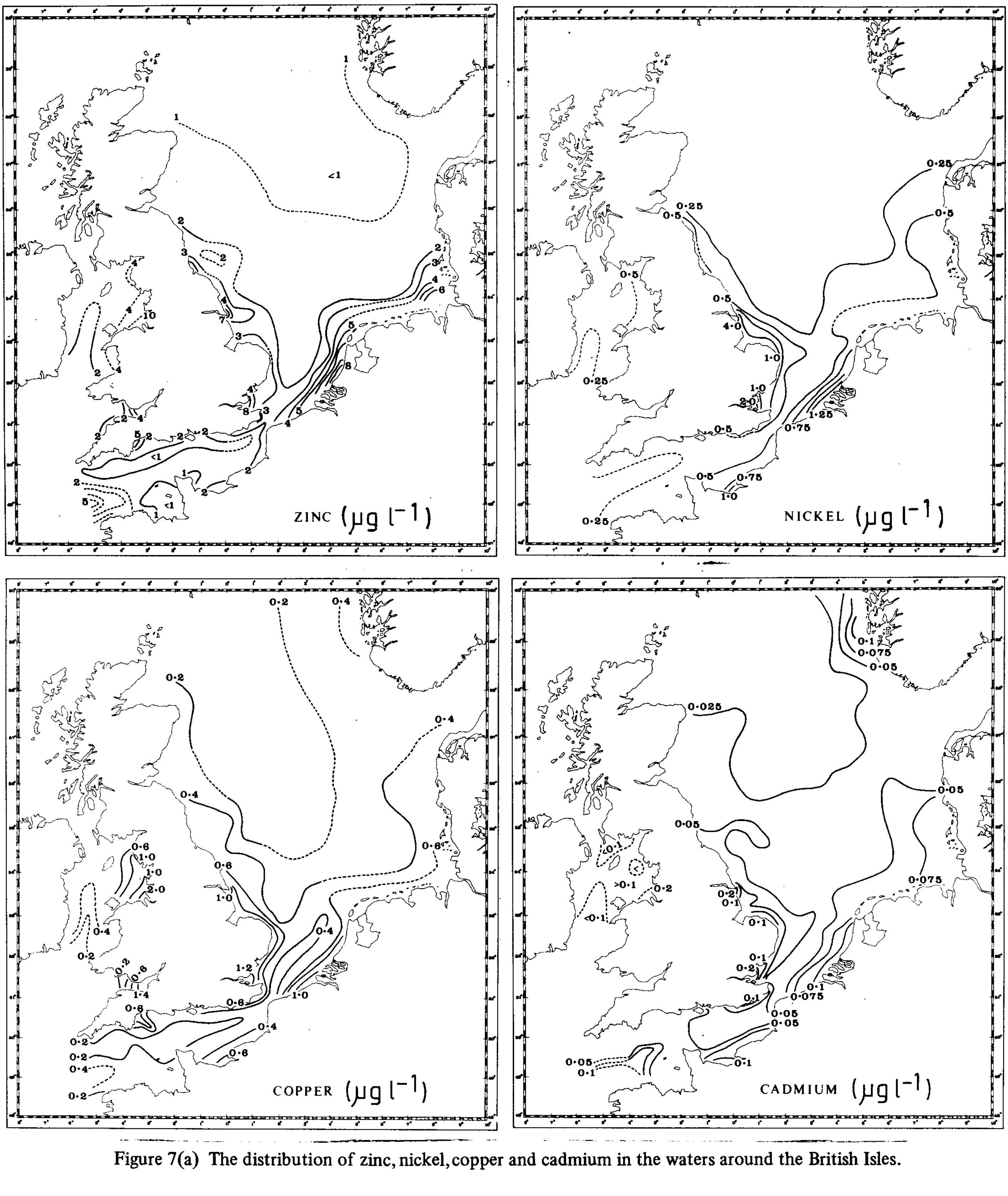
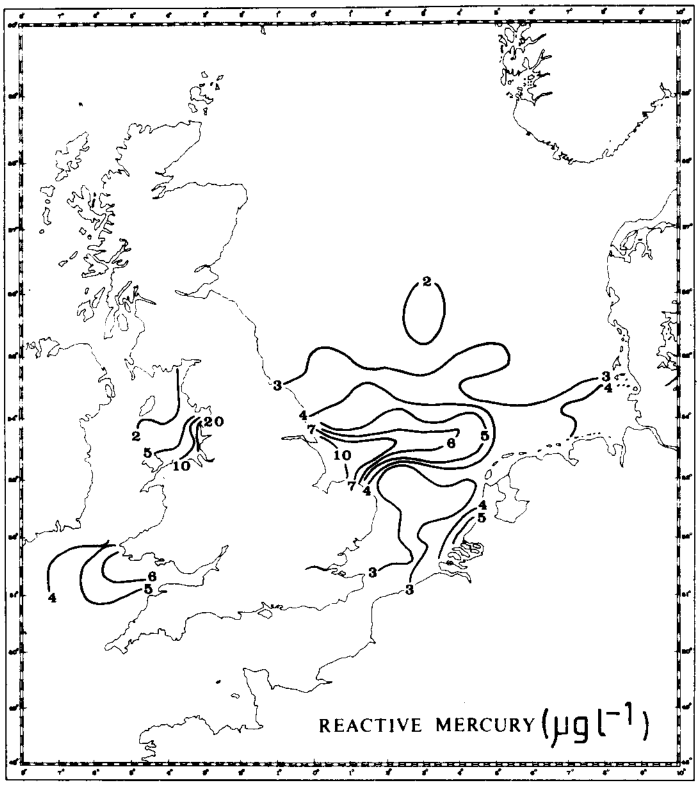


Figure 7(a) The distribution of zinc, nickel, copper and cadmium in the waters around the British Isles.



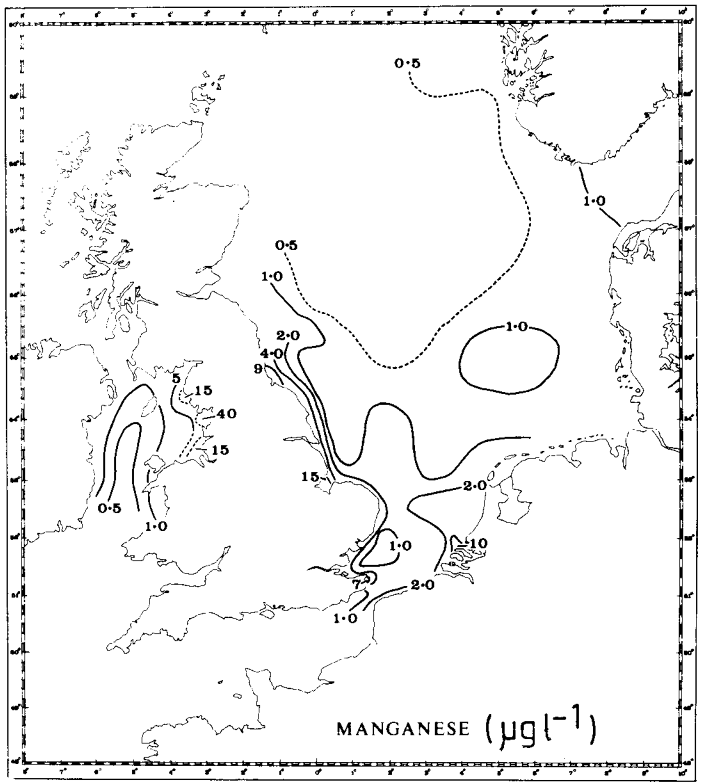


Figure 7(b). The distribution of reactive mercury and manganese in the waters around the British Isles.

of the Sea (ICES). Components of the programme covered standard solutions (Jones, 1976), mercury (Ólafsson, 1978) and sea water (Jones, 1977; Bewers *et al.*, 1979). In addition, the Joint Monitoring Group of the Oslo and Paris Commissions requested ICES to conduct an intercalibration for the analysis of cadmium and mercury in sea water. This programme was carried out during 1979 and has been reported by Thibaud (1981) for cadmium and Ólafsson (1981) for mercury. Whereas considerable diversity in reported levels of trace elements was recorded during all the exercises, the later stages showed a better degree of agreement among many participants. Future proposed exercises will be orientated towards methods of sample collection and preservation (Bewers *et al.*, 1980).

Several, but not all of the contributors to the present review, have participated in the above ICES exercises. However, these programmes were mainly orientated towards relatively low levels of trace metals encountered in offshore waters and are thus not entirely suited to the range of concentrations found in estuarine waters of variable salinity. Jones (1978) has reviewed our knowledge of trace metals in estuaries. In addition to illustrating the complexity of the systems present in the environment, he draws attention to the importance of intercalibration exercises. Thus, there is a strong case for a UK coordinated exercise paying particular attention to estuarine samples and covering concentration ranges most likely to be encountered in estuaries and coastal waters.

When evaluating the geographical coverage of any monitoring programme consideration must be given to the aims of such a programme. Requirements will vary from one locality to another and will depend largely on the degree and type of pollution involved. It has been shown in this review that most of the "hot" areas are already monitored, particularly in respect of nutrient salts. Some expansion, however, will be needed if the extent of trace metal monitoring is to be raised to an equal standard: since an adequate programme in respect of nutrient salts already exists, the logistics of sample collection should present little problem. Any monitoring programme should relate to a specific need. Thus the geographical coverage of such exercises will, to a large extent, reflect the distribution of "hot spots" where there is known or suspected pollution. The locations of these will largely be governed by the patterns of industrial discharges, and sampling logistics will become increasingly manageable after the implementation of COPA part 2. One will thus look to the RWA/RPB to take a central role in this programme.

It has already been shown that data submitted are from a wide range of organisations. Much of the material is held by the more academically-orientated bodies such as university departments and NERC-supported laboratories as part of research projects and cannot be considered in the context of monitoring. Such information, however, plays an important role in the overall scenario, since its collection is directed towards a study of environmental processes. Within recent years our knowledge of the behaviour and speciation of trace metals in water has advanced considerably from such research projects. Ultimately mere numbers for determinands in water are of little value if they cannot be assessed for their significance and impact on the marine environment. In this context the review group wishes to emphasise the need for a full understanding of the distribution of pollutants in all the marine compartments such as sediment, suspended particulate material, biota and water. Thus, monitoring must not be confined to just the water but should cover all the above compartments. The basis for pollution control is to prevent discharges being harmful to man and damaging the environment into which they are released. In order to fully understand the effects of a discharge such complex relationships must be known. Routine monitoring provides the essential raw data which can be fed into appropriate models.

Monitoring programmes benefit from liaison between participating organisations. Such instances are listed in the present review. The Severn Estuary Survey and Systems Panel is a group composed of the relevant RWAs, representatives of NERC and the Confederation of British Industries, and other participants. Similarly, the Humber Estuary Technical Working Party consists of the RWAs, the Water Research Centre (WRC), NERC, Government departments, etc. In addition, a number of other informal liaisons have developed on an *ad hoc* basis and such activities are to be encouraged.

At present there is no overall coordination of monitoring programmes. The truly monitoring activities are concentrated in those areas with a potential pollution problem and are largely controlled by the local regional authorities. With the implementation of COPA part 2, the RWAs and RPBs will have an increasing degree of responsibility in such matters. The more fundamental investigations need not have this regional constraint and may thus be more cosmopolitan in extent. There would, however, seem to be some merit in a form of overall coordination. This need not take the form of statutory control but would be merely to provide regular updated information on the type of activities reviewed here, so that individual organisations are aware of all programmes. It would help to avoid duplication, pinpoint areas inadequately covered and provide an interface between the routine and more academic programmes. Such a liaison body may also assume responsibility for the coordination of intercalibration programmes. In spite of the demise of the WRC Estuaries (Chemistry) Section, the parent WRC still retains an active interest in the programmes of the RWAs and may thus exercise such a function within this group of organisations. The MPMMG itself may be considered as already providing the wider service advocated above. However, there would still seem to be merit in having a more detailed, regular and on-going, in-depth coordination embracing all the types of activities reported here.

Most of the data presented in this review refer to surface observations, both in respect of nutrient salts and trace metals. In the context of pollution monitoring such samples will be of most importance since industrial/sewage discharges will often be made in a low saline medium. However, settlement of suspended particulate material may occur from discharges and a high density matrix may sink below the surface of the receiving water. Consideration should therefore always be given to the depth of sampling when inaugurating monitoring programmes.

Much of the nutrient salt data quoted in this report refers to the winter months when the dissolved levels of these constituents are maximal. It is thus recommended that the majority of measurements be made at this time of year. However, observations at other times of year should not be entirely neglected, since in some locations factors such as reduced freshwater flow coupled with high discharge rates could lead to elevated levels. There is now some evidence that in sea water many trace metals may undergo similar seasonal biological cycling to nutrient salts, although in coastal waters such a phenomenon is unlikely to be detectable, if indeed it occurs.

Some attention to the measurement of total nitrogen and phosphorus as a routine procedure may be worthwhile in some circumstances. If a discharge having a high organic component is being monitored, then such analysis may provide important information.

5. Conclusions and recommendations

1. The programmes reviewed here have been carried out for a variety of purposes. Those projects conducted by the more academically orientated institutes have generally been designed primarily to investigate fundamental processes. On the other hand, many monitoring activities carried out by Government departments and RWAs/RPBs have often been aimed at measuring the degree of pollution in specific locations. We wish to emphasise the importance of relating all such programmes to specific needs rather than indiscriminately measuring a long list of determinands at a variety of locations.

2. We are of the opinion that activities in respect of nutrient salt monitoring are reasonably satisfactory.

3. Trace metal programmes require urgent expansion in relation to intercalibration and training. In particular, the analytical techniques employed in the Harmonised Monitoring Scheme should be improved in order to provide data of comparable sensitivity to those obtained for coastal areas. The implementation of COPA part 2 may require a geographical enlargement of sampling programmes but the logistics should already be available in respect of nutrient salts.

4. We place much importance on an understanding of the behaviour of pollutants through all compartments of the marine environment and potential pathways back to man. A knowledge of levels in water alone is of limited value.

5. We recommend some overall coordination in respect of the types of programmes reviewed in order to improve the general degree of awareness between the many organisations involved.

6. The above conclusions and recommendations must relate primarily to those bodies involved in statutory control. However, we recognise the importance of the more fundamental investigations and hope that a healthy liaison will be maintained in the future between all types of organisation covered by this review.

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Appendix 1

Membership of the Review Group of Nutrient Salts and Trace Metal Data in Tidal Waters.

Member	Representing
Dr P Jones (Chairman)	Ministry of Agriculture, Fisheries and Food
Mr E Butler	Marine Biological Association of the United Kingdom
Dr D Burton	University Departments
Mr M Colley	Northumbrian Water Authority
Mr B Dale	South West Water Authority
Mr R Furley (part time)	Thames Water Authority
Dr J Gardiner	Water Research Centre
Mr W Halcrow (part time)	River Purification Boards
Dr P Head	North West Water Authority
Dr T Leatherland	River Purification Boards
Mr P Long	Southern Water Authority
Dr A Morris	Natural Environment Research Council Institute for Marine Environmental Research
Dr A Nelson (part time)	Thames Water Authority
Dr C Pattinson (part time)	Welsh Water Authority
Mr C Saunders	Wessex Water Authority
Mr D Sayers	Anglian Water Authority
Mr M Stockley	Yorkshire Water Authority
Dr J Stoner (part time)	Welsh Water Authority
Dr R Thompson	Industry
Dr G Topping	Department of Agriculture and Fisheries for Scotland
Dr C Vivian	Lancashire and Western Sea Fisheries Joint Committee
Mr G Woodward	Severn Trent Water Authority