

FINAL VERSION 02.01.91

NRA BASELINE ESTUARY AND COASTAL WATERS MONITORING PROGRAMME

1. Background

This programme is a first step in the process of producing a national standard monitoring protocol for estuaries which will ultimately seek to rationalise existing monitoring programmes undertaken by the various NRA regions. It incorporates recommendations by Marine Pollution Monitoring Management Group arising out of their review of the UK marine monitoring programme. It also forms part of the Monitoring Master Plan of the North Sea Task Force (NSTF); it is the ultimate intention that NRA will be responsible for monitoring NSTF sampling locations in major estuaries and out to three miles. The opportunity has been taken to bring these requirements together and institute a common programme which will meet the needs of the North Sea Task Force and go some way towards establishing a baseline programme for major estuaries which fall within the responsibilities of the NRA. The present proposals will need to be modified subsequently in the light of future NRA requirements, particularly in terms of frequency and intensity of sampling. The present, very low sampling frequency is largely determined by the needs of the North Sea Task Force. This programme is not a substitute for more intensive programmes (such as those on the Humber and Mersey) which are necessary to meet local requirements but represents a minimum scheme which must be achieved.

2. Objectives

- a) To provide baseline information on the quality of coastal waters and major estuaries in England and Wales and to develop standard sites which can be used for trend analysis*.
- b) To provide data which can be used to make quantitative comparisons between major estuaries.
- c) To fulfil monitoring obligations arising out of North Sea Task Force (North Sea Task Force Monitoring Plan JMG 15/8/2-E, Jan 1990).
- d) To fulfil monitoring obligations arising from Joint Monitoring Programme of the Oslo and Paris Commissions.

*NOTE (i) This programme is not a substitute for the more intensive sampling programmes presently underway in some estuaries. Standardisation of the techniques adopted in these surveys will be necessary at a later date.

(ii) The range of determinands included in the programme may need to be changed subsequently to reflect future national and international concerns.

3. Sampling Sites

3.1 Estuarine Sites

Tyne	Southampton Water
Tees	Tamar
Wear	Severn
Humber	Dee
Wash	Mersey
Thames	



Three sites per estuary need to be selected, representative of salinity regimes 0-10, 10-20, 20-30 ppt. Sites should be located within the main channel for water quality monitoring. It may be necessary to go outside the main channel for biological and sediment sampling in order to obtain a representative sample because of local factors such as dredging operations and also for reasons of practicality and ease of access. Once a sampling site has been chosen, all future sampling should be at the same sampling location under the same tidal conditions.

3.2 Intermediate (Coastal Waters) Sites

11 sites (see attached diagram Appendix 1) located at the edge of the estuary plume (i.e. limit of estuarine influence) with one exception in Cardigan Bay. Exact location to be agreed in discussion with MAFF. Where possible these sites should be identical to existing JMP sites.

4. Routine survey of Physico-chemical determinands

4.1 Determinands and Matrices

Determinand	Matrices to be analysed	Component of NRA Programme	Some Matrices form a Component of NSTF Programme
Salinity	2 ^m	/	/
Temperature	2 ^m (insitu)	/	/
Oxygen	2 ^m (insitu)	/	/
NH ₄ -N	1 ^m	/	/
NO ₄	1 ^m	/	/
NO ₃ -N	1 ^m	/	/
Orthophosphate-P	1 ^m	/	/
SiO ₂ -Si	1 ^m	/	/
*Total P	1 ^m	/	/
*Total N	1 ^m	/	/
Suspended Solids	2 ^m	/	/
Chlorophyll <u>a</u>	2 ^m	/	/
Secchi-depth	2 ^m (insitu)	/	/
Cd	1, 3 ^m , 5, 6	/	/
Cu	1, 3 ^m , 6	/	/
Pb	1, 3 ^m , 5, 6	/	/
Zn	1, 3 ^m , 5, 6	/	/
Ni	1, 3 ^m , 6	/	/
Hg	1, 3 ^m , 5, 6	/	/
Cr	1, 3 ^m , 6	/	/
As	1, 3 ^m , 6	/	/
DDT (ppDDE, ppDDT, ppTDE, opDDE, opDDT)	2, 3 ^m , 5	/	/
HCBD	2, 5	/	/
PCB (on an individual basis cogener numbers 28, 52, 101, 118, 153, 138, 180)	2, 3 ^m , 5	/	/
✓ - HCH	2 ^m , 5	/	/
× - HCH	2 ^m , 5	/	/
HCB	2, 3 ^m , 5	/	/
Dieldrin	2, 3 ^m , 5	/	/
Aldrin	2, 3 ^m , 5	/	/
Endrin	2, 3 ^m , 5	/	/

CHCl ₃	2,5	/	
CCl ₄	2,5	/	
PCP	2,5	/	

* Further clarification is being sought from NSTF on these determinands and no samples should be taken at this time.

Matrices to be analysed

Code used above.

- 1 - filtered water sample
 - 2 - unfiltered water sample
 - 3 - surficial sediment
 - 4 - shellfish tissue as defined by NSTF
 - 5 - bioaccumulation organism consistent with recommendations of proposed NRA bioaccumulation protocol (Appendix 4); preferably molluscs for organics and molluscs and seaweed for metals from estuarine sites
 - 6 - surficial sediments, <63 µm size fraction to be analysed; analysis of sediments must include measurement of particle size distribution/composition to aid normalisation.
- m - mandatory determinand within NSTF programme; matrix and sample preparation/analysis must be consistent with the requirements of NSTF. Data collection should begin for NSTF programme during 1990/91.
- v - voluntary determinand within NSTF programme; matrix and sample preparation/analysis must be consistent with the requirements of NSTF.

4.2 Method of Collection and/or Analysis

Where appropriate the field method of analysis is identified in Appendix 2. Alternatively Appendix 2 also identifies which NRA laboratories will supply suitable sample containers and undertake the various analyses on behalf of individual Regions; Regions should liaise directly with the appropriate laboratory manager. DO NOT use routine river water sampling bottles for this programme as they may be inappropriate. Laboratory Managers will ensure that the analytical techniques employed on NSTF samples are consistent with the requirements of this programme as defined in Appendix 3 which is based on Annex 2 of 15th Meeting of the Joint Monitoring Group 23/26th January 1990.

4.3 Analytical Quality Control

Whenever appropriate Laboratories must participate in 'Aquacheck' until alternative recommendations are forthcoming from the Laboratory Managers Group. For sediments and bioaccumulation analyses the appropriate standard materials should be used.

5. One-off survey of Physicochemical determinands

There is a requirement under the NSTF and NRA programmes to undertake a one-off programme to identify levels of a range of substances in a variety of matrices. In view of the complexity of the routine

programme and the burden this places upon the laboratories at this time it has been agreed that the ONE-OFF SURVEY WILL NOT PROCEED AT THIS TIME ON A NATIONAL BASIS. The situation will be reviewed later. However should individual Regions wish to obtain data on some or all of the substances they should do so, whenever possible in a manner consistent with the overall programme at sites and at times which form part of the routine programme.

Determinands for One-Off Survey

Determinand	Matrices to be analysed	Component of NRA Programme	Some Matrices form a Component of NSTF Programme
Polynuclear aromatic hydrocarbons (Benx[a]anthracene, Benzo[a]pyrene, Benzo[b]fluorathene Benzo[e]pyrene Benzo[ghi]perylene, Chrysene, Fluoranthene, Ineno [1,2,3-cd]pyrene, Phenanthrene, Pyrene)	2,3 ^v ,5	/	/
Polybrominated biphenyls (flame retardants)	2,5 (NSTF matrix to be specified)	/	/
Dioxins	2,3 ^v ,5	/	/
Atrazine	2 ^v ,5	/	/
Simazine	2 ^v ,5	/	/
Toxaphene	2,3 ^v ,5	/	/
Chlordane (Cis-Chlordane Trans-nonachlor, Trans-chlordane, Oxychlordane)	2,3 ^v ,5	/	/
Methyl mercury	4 ^v		
TBT	3 ^v ,4 ^v		/

Matrices to be analysed

Code used above.

- 1 - filtered water sample
 - 2 - unfiltered water sample
 - 3 - surficial sediment, size fraction to be defined by NSTF.
 - 4 - shellfish tissue as defined by NSTF
 - 5 - bioaccumulation organism consistent with recommendations of proposed NRA bioaccumulation protocol (Appendix 4); preferably molluscs for organics and molluscs and seaweed for metals from estuarine sites
 - 6 - surficial sediments, <63 µm size fraction to be analysed; analysis of sediments must include measurement of particle size distribution/composition to aid normalisation.
- m - mandatory determinand within NSTF programme; matrix and sample preparation/analysis must be consistent with the requirements of NSTF. Data must be collected for NSTF programme during 1990/91.

v - voluntary determinand within NSTF programme; matrix and sample preparation/analysis must be consistent with the requirements of NSTF.

6. Microbiological Determinands

6.1 Determinands

E. Coli

Total Coliforms

Faecal Streptococci

These determinands do not form part of NSTF programme.

6.2 Analysis

The sample bottles, analytical techniques etc are identical with those employed for the bathing water programme; the laboratories from which sample bottles can be obtained and to which individual regions should direct their samples for analysis are summarised in Appendix 2.

7. Mandatory Biological Determinands

7.1 Benthic Samples

Estuarine samples should be recovered from areas of the estuary broadly consistent with the salinity regimes specified in Section 3.1 and should be representative of each of the different substrate types present in the estuary. Samples should also be recovered from the intermediate site. These analyses are a mandatory component of the NSTF programme as well as part of the NRA programme; data must be collected for NSTF programme, preferably starting in 1990/91 using approved NSTF methods. Organisms will need to be identified to species level after sieving through a 0.5 mm sieve. A separate sample at the same location will be required for granulometric analysis, determination of redox potential (Eh) at 1 cm intervals to a depth of 10 cm at least and for elemental analysis of carbon and nitrogen to provide an estimate of organic enrichment (the presence of coal should be identified where appropriate).

7.2 Oyster embryo bioassay.

These analyses are a mandatory component of the NSTF programme as well as part of the NRA programme; The bioassay should be undertaken on water samples recovered from the three estuarine sites and the intermediate site. MAFF undertook the analysis of NRA samples in 90/91 to meet the NSTF requirement. If sites were not sampled in 90/91 MAFF should be contacted. Analyses in subsequent years will have to be funded by NRA and contracted out. Regions should make their own arrangements.

8. Optional Biological Determinands ††

†† NOTE

These optional determinands are only likely to be included where they are already present in existing programmes and for which there is sound local justification for their presence. They are not part of the NSTF programme.

8.1 Mussel scope for growth. Sampling protocol to be defined following discussions with WRC but only likely to be undertaken on estuary samples.

8.2 Fish population assessment (only within estuary).

8.3 Fish pathology on samples recovered from 7.2.

9. Sampling Frequency

9.1 Estuarine Sites

9.1.1 Physicochemical determinands

Routine water column determinands four times per year corresponding to seasons. Bioaccumulation samples once per year in accordance with NRA Bioaccumulation protocol, sediments once per year, probably at the same time as the benthic sampling.

9.1.2 Microbiological determinands.

Four times per year corresponding to seasons.

9.1.3 Benthic sampling

Once per year November - February inclusive.

NOTE Ideally sampling at all sites within a single estuary should be undertaken on the same day on each occasion although this is not essential if there are sound practical reasons for not doing so.

9.1.4 Oyster Embryo Bioassay

Once per year as close as possible to the Benthic sampling period but recognising the availability of oyster embryos.

9.2 Intermediate Sites

9.2.1 Physicochemical determinands.

Routine determinands once per year November - February inclusive.

9.2.2 Benthic sampling

Once per year November - February inclusive.

9.2.3 Oyster Embryo Bioassay

As for 9.1.4.

9.3 Liaison with Laboratory

In view of the complexity of the determinand suite it is imperative that there is close liaison between sampling staff and the Laboratory Managers over the choice of mutually convenient sampling dates.

10. Tidal State

Estuarine water samples should be recovered at or around highwater preferably on or around neap tides, unless worst case conditions expected at other times due to local circumstances or there are sound practical reasons for sampling at other times. Neap tides are also preferred for intermediate sites.

11. Depth in Water Column

Water samples should be recovered at about 1m below the surface. Where significant stratification occurs it may be more appropriate to specify other depths to obtain a representative sample.

12. Bioaccumulation Sample Collection

For those determinands which form part of NSTF programme, first choice bioaccumulation shellfish species is mytilus edulis; number 50±10%, size 2-6cm with a mean of 4-6cm, analysing whole soft tissue. Second choice in NSTF programme is Crassostrea gigas; number 10±10%, size 9-14cm (2 years of age), analysing whole soft tissue. Otherwise, sampling, treatment and preservation must be consistent with guidance given in the Bioaccumulation protocol included as Appendix 4. Samples will almost certainly be collected from the margins of the estuary at locations largely dictated by the distribution of suitable organisms.

13. Organisational Responsibility for sampling sites

13.1 Estuarine Sites

National Rivers Authority:-

<u>Estuary</u>	<u>Region</u>
Tyne, Tees, Wear	Northumbrian
Humber	Humber Estuary Group (Anglian)
Wash	Anglian
Thames	Thames
Southampton Water	Southern
Tamar	South West
Severn	Severn Estuary Management Group (Welsh)
Dee	Welsh
Mersey	North West

13.2 Intermediate Sites

For the purposes of the North Sea Task Force, responsibility for individual sites should be agreed between NRA and MAFF having regard particularly to the availability of suitable sampling vessels and associated safety considerations. Whenever possible the NRA should assume responsibility particularly in the longer term. Location is to be agreed in discussion with MAFF. NRA regions will assume responsibility for intermediate sites associated with individual estuaries as per 13.1, Welsh Region will be responsible for the Cardigan Bay site.

14. Duration of Programme

14.1 NRA baseline programme

Ongoing with a review and update of determinand suite every five years.

14.2 North Sea Task Force Programme

Routine programme to commence 1990; duration subject to review. Timing of one-off survey to be advised in due course following discussions with DOE over funding arrangements.

14.3 Joint Monitoring Programme

Ongoing.

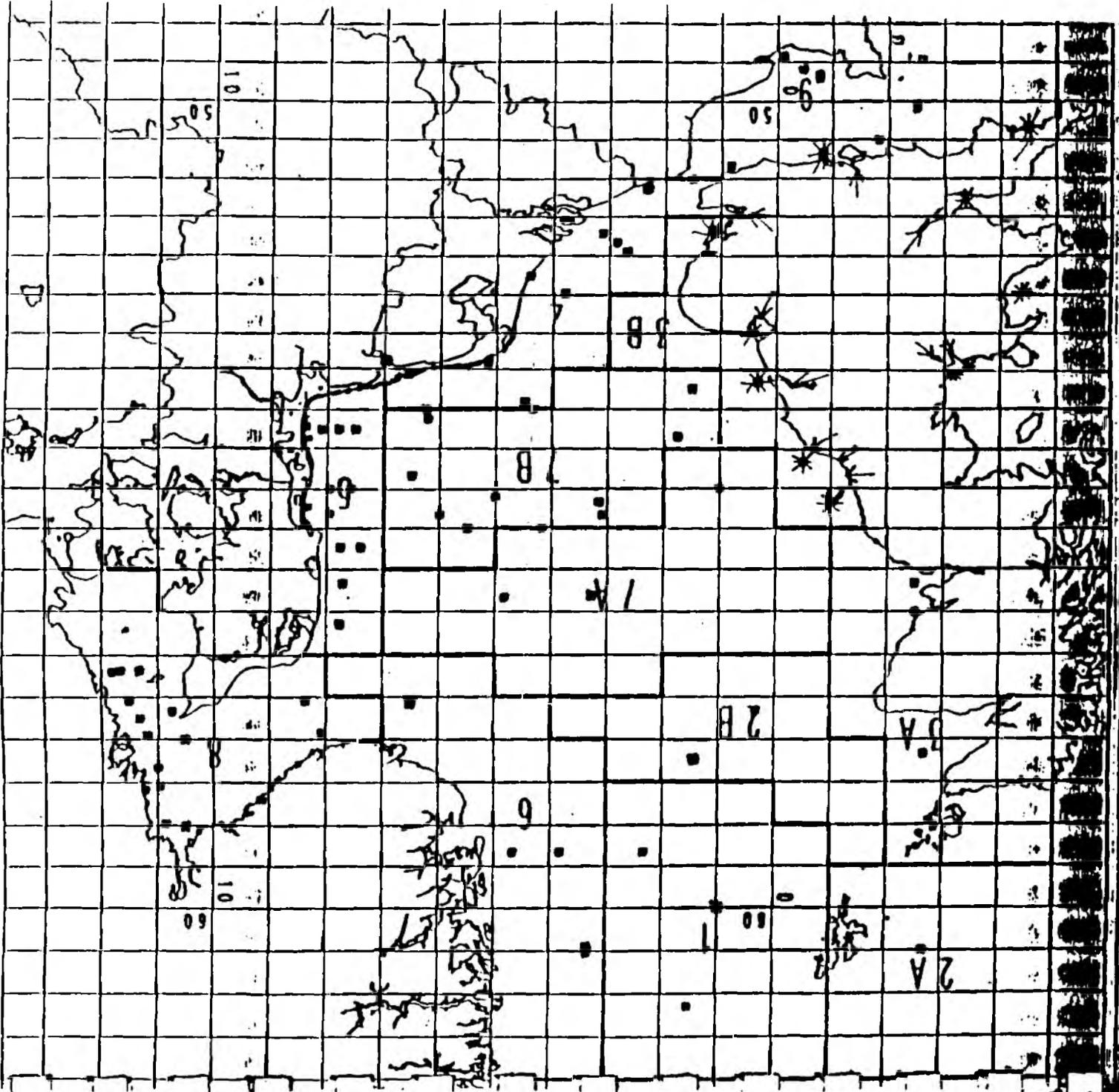
PL/EAM/M2jmm
20.03.90.

DATA PROCESSING & CARTOGRAPHY
CONTIN - SEC. OF NAVY 11/81

DATA PROCESSING & CARTOGRAPHY
CONTIN - SEC. OF NAVY 11/81

LEGEND:
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NORTH SEA TASK FO
MONITORING MASTER PLAN (00)
Location of main monitoring sta
according to the NATO Sub-Sea



AVAILABILITY OF ANALYTICAL METHODSNSTF BASELINE STUDIES

Region	Determinand					
	Salinity 1	Temp 2	Do 3	Ammonia 4	Nitrate 4	Nitrate 4
Anglian	Field	Field	Field	Welsh NRA initially - until own low level system established		
Northumbrian	"	"	"	Welsh NRA initiall. (Then in-house)		
North West	"	"	"	Welsh NRA initially. (Then in-house)		
Severn Trent	"	"	"	Not required at present - will set up if required		
Southern	"	"	"	Welsh NRA initially (Then in-house)		
South West	"	"	"	Welsh NRA initially (Then in-house)		
Thames	Salinity meter not used (Chloride in lab)	"	"	Welsh NRA initially (Then in-house)		
Welsh	Field	"	"	Welsh NRA low level saline method		
Wessex	"	"	"			
Yorkshire	"	"	"	Welsh NRA initially (Then in-house)		

NSTF Baseline Studies

Region	Determinand					
	Ortho phosphate 4	Silicate 4	Total N	Total P	SS 5	Chloro phyll <u>a</u>
Anglian	Welsh NRA until own system established		Not required at present		Anglian NRA	Anglian NRA
Northumbrian	Welsh NRA initially (Then in-house)		"	"	N'brian	N'brian (Methanol)
North West	Welsh NRA initially (Then in-house)		"	"	N. West	N. West (Acetone)
Severn Trent	Set up if required		"	"	Severn Trent	Severn Trent (Cold Acetone)
Southern	Welsh NRA initially (Then in-house)		"	"	Southern Science (NRA S. Region later)	Southern Science (Methanol)
South West	Welsh NRA initially (until systems established)		"	"	Welsh NRA initially until estab'd	South West Water plc
Thames	Welsh NRA initially (Then in-house)		"	"	Thames	Thames (Acetone)
Welsh	Welsh NRA low level saline method		"	"	Welsh NRA	Welsh NRA (Acetone)
Wessex	As for S. West					
Yorkshire	Welsh NRA initially (Then in-house)		"	"	Yorkshire	Yorkshire (Acetone)

NSTF Baseline Studies

Region	Determinand					
	Secci Disc 6	Dissolved Cu,Pb,Ni in water 7	Hg in Water	Cr(Dissol) in Water	As in Water	Organo Chlorine Pesticide in water 8
Anglian	Field	Anglian	Anglian	-	Anglian	Anglian Red List Method
Northumbrian	"	N'brian	N'brian	-	Severn Trent	Yorks NRA initially Then in-house
North West	"	N. West	N. West	-	N. West	N. West
Severn Trent	"	Not capable at present			Severn Trent	Severn Trent NRA
Southern	"	Welsh NRA init. (Then in-house)		-	Welsh NRA initially (then in house)	Ang'n NRA initially (then in- house)
South West	"	? No method (Welsh NRA)	Welsh NRA		?	Other NRA Region (Welsh? Severn T)
Thames	"	Thames	Thames		Thames	Severn Trent NRA (then in- house)
Welsh	"	Welsh NRA	Welsh NRA	Welsh NRA	Welsh NRA	Welsh NRA As Red List
Wessex	As for S. West					
Yorkshire	"	Yorks NRA	Yorks NRA		Yorks NRA	Yorks NRA

NSTF Baseline Studies

Region	Determinand				
	CHCl ₃ CCl ₄ in waters	PCP in waters	Sediments		
			<63µm fraction Cu,Pb,Cd,Zn,Hg Ni,Cr	<63µm fraction as	Total Sediment Cu,Pb,Dc,Zn, (HF digest or equivalent)
9	10	11	11	12	
Anglian	Anglian NRA Red List Methods		Anglian NRA	Anglian NRA	<u>Not</u> HF Anglian NRA
Northumbrian	Yorks NRA initially (Then in-house)		Northumbrian	Northumbrian	<u>Not</u> HF Northumbrian
North West	N. West	N. West	N. West	N. West	N. West? <u>Not</u> NF
Severn Trent	Severn T NRA			Severn T	Severn T NRA Have HF Technique Operational
Southern	Anglian NRA initially (Then in-house)]		Welsh NRA initially then in-house		
South West	Other NRA labs Welsh? Severn Trent?		Welsh NRA initially	Welsh NRA initially	<u>NOT</u> HF
Thames	Severn Trent NRA initially (Then in-house)		Thames	Thames	Thames <u>NOT</u> HF
Welsh	Welsh NRA As Red List		Welsh NRA	Welsh NRA	Welsh NRA
Wessex	As for S. West				
Yorkshire	Yorks	Yorks		Yorks	Yorks

NSTF BASELINE STUDIES

	Determinand					
	Sediments				Biological Tissues	
	PCBs+HCB Sediments 13	Particle Size 14	CHN 15	Redox 16	Pb,Cd,Zn, Hg 17	Organics 17
Anglian	Anglian NRA	Welsh NRA	Welsh NRA	Field	Anglian NRA	Anglian NRA
Northumbrian	N'brian	Welsh NRA	Welsh NRA	"	N'brian	N'brian
North West	N. West	Welsh NRA	Welsh NRA	"	N. West	Welsh NRA?
Severn Trent	Severn T.	Welsh NRA	Welsh NRA	"	Severn T.	Severn T.
Southern	Anglian NRA initially then in- house	Welsh NRA	Welsh NRA	"	Welsh NRA	Anglian NRA initially then in- house
South West	Welsh NRA	Welsh NRA	Welsh NRA	"	Welsh NRA	Welsh NRA?
Thames	Thames	Welsh NRA	Welsh NRA	"	Thames	Severn T
Welsh	Welsh NRA	Welsh NRA	Welsh NRA	"	Welsh NRA	Welsh NRA
Wessex	As for S. West			"	As for S. West	
Yorkshire	Yorks	Welsh NRA	Welsh NRA	"	Yorks	Yorks

NSTF BASELINE STUDIES

Region	Determinand	
	Micro Bio Determ 18	Biology
Anglian	Anglian NRA	In House
Northumbrian	N'brian	"
North West	N. West	"
Severn Trent	Severn T NRA	"
Southern	In house Southampton Univ.	"
South West	As Bathing Water Samples	"
Thames	As Bathing water samples	"
Welsh	Welsh NRA	"
Wessex	As Bathing Water Samples	"
Yorkshire	Yorks	"

- Notes
1. Meter must be properly calibrated at regular intervals before use in the field, preferably against a bench salinometer. Results should be recorded as parts per thousand salinity.
 2. Meter must be property calibrated at regular intervals before use in the field.
 3. Field calibration techniques must be checked initially for reliability against laboratory calibration, preferably Winkler. DO meter must be salinity compensated.
 4. Nutrient samples must be filtered in the field immediately after collection. Filtration equipment, bottles and detailed instructions for preservation must be obtained from Ron West, Laboratory Manager, Welsh Region.
 5. Analytical method must recognise need to wash out salt from solid residue prior to weighing.
 6. Details of secchi disc measurement provided in Appendix 5. Results should be recorded in metres.
 7. Saline method to be used or samples filtered through 0.45 m membrane filter or equivalent. Lab managers will advise on sample containers and preservation.
 8. 'Organo chlorine pesticides' includes the following determinand suite:- DDT, HCBd, PCB, γ -HCH, α -HCH, HCB Dieldrin, Aldrin and Endrin.
 9. Lab Managers will advise on sample containers and preservation techniques.
 10. Lab managers will advise on sample containers and preservation techniques.
 11. Prior to analysis it is recommended that sediments are freeze dried and dry sieved to obtain <63 μ m fraction. Lab Managers will advise on amount of sediment required, sample containers and preservation prior to sieving.
 12. Laboratory Managers will identify suitable analytical technique in lieu of HF digest but it is likely to be aqua-regia/microwave digest. Lab Managers will advise on amount of sediment required, sample containers and preservation prior to digestion.
 13. Laboratory Managers will advise on sample containers and preservation techniques.
 14. Recommended that all regions use the Welsh Region Laser Particle sizer for this programme; ca 50mls samples stored in plastic bags prior to analysis.
 15. Ca 50mls sample stored frozen in glass bottles prior to analysis. All samples should be examined microscopically for presence of coal - if coal present or likely to be present do not send for CHN (total carbon, hydrogen, nitrogen) analysis.

16. Redox measurements should be undertaken in the field at 1cm intervals to a depth of at least 10cm in an undisturbed sediment core. The method is described in ref:- Whitefield, M (1969) Limnal and Oceanogr 14 P547-558. 'Eh as an operational parameter in estuarine studies'.
17. Samples should be collected and cleansed prior to analysis in accordance with the guidance provided in Appendix 4.
18. Collection and analysis as per 'Bathing Water Directive' samples. If practicable initial phases of analysis should be carried out onboard the sampling vessel.

LIST OF SELECTED REFERENCES OF THE MOST RECENT GUIDELINES
FOR THE CONDUCT OF THE JOINT MONITORING PROGRAMME

General

1. Monitoring Strategies. Report of the ICES Advisory Committee on Marine Pollution, 1988, (Section 4), Coop. Res. Rep. No. 160.
2. Advice on the most appropriate matrices for use in monitoring for the purposes of assessing risk to human health, assessing spatial distribution and assessing temporal trends. Report of the ICES Advisory Committee on Marine Pollution, 1989 (Section 6), Coop. Res. Rep. No. 167.

Seawater

3. Guidelines for the sampling and analysis of trace metals in seawater under the Joint Monitoring Programme. Tenth annual Report on the Activities of the Paris Commission (1989), Annex 24.
4. Trace metals in seawater. Sampling and storage methods. ICES Techniques in Marine Environmental sciences, No. 2, 1987.
5. Suspended particulate matter: Collation methods for gravimetric and trace metal analysis. ICES Techniques in Marine Environmental Sciences (in press).

Sediments and Suspended Particulate Matter

6. Guidelines for the sampling and analysis of sediments under the joint Monitoring Programme. Twelfth Annual Report on the Activities of the Oslo Commission (1987), annex 11.
7. Guidelines on normalisation in the use of sediments in monitoring. Report of the ICES Advisory Committee on Marine Pollution, 1989, (Section 14), Coop. Res. Rep. No 167.
8. The potential role of sediments in pollution monitoring. Report of the ICES Advisory committee on Marine Pollution, 1983, (Annex 2), Coop. Res. Rep. No. 124.
9. Methods for sampling and analysis in studies of contaminants in sediments. Report of the ICES Advisory Committee on Marine Pollution, 1984, (Annex 2), Coop. Rep. No. 132.
10. Guidelines for the use of sediments as a monitoring tool for studies of contaminants in the marine environment. Report of the ICES advisory Committee on Marine Pollution, 1984, (Section 150, Coop. Res. Rep. No. 142.

11. Sediments and suspended particulate matter: Total and partial methods of digestion. ICES Techniques in Marine Sciences (in press).

Biota (Fish and Shellfish)

12. Guidelines to be followed for sample collection, preparation and analysis of organisms in the context of the Joint Monitoring Programme. Eighth annual Report on the activities of the Oslo Commission (1984), Annex 9.
13. Amendments to the Agreed Guidelines for sampling and pretreatment of samples and reporting of results under the Joint Monitoring Programme. (OSPAR 7/12/1. Annex 6).
14. ICES Guidelines for Monitoring Contaminants in Fish and shellfish and in Sediments. Six Year Review of ICES Co-ordinated Monitoring Programmes, 1984, Coop. Res. Rep. No. 126. pp. 96-100.
15. Guidelines for Temporal trend Analysis of Data on Contaminants in Fish, Report of the ICES Advisory Committee on Marine Pollution, 1986, (Annex 1), Coop. Res. Rep. No. 142.

Biological Monitoring (Phytoplankton. Zooplankton. Primary Production)

- 16 Primary Production: Guidelines for measurement by ¹⁴C incorporation. ICES Techniques in Marine Environmental Sciences, No. 5, (1987).

Biological Effects Techniques

Benthos Studies

17. Procedures for the Monitoring of Benthic communities around Point Source Discharges. Report of the ICES Advisory Committee on Marine Pollution, 1988, (Section 7), Coop. Res. Rep. No. 160.
18. Examples of the application of ICES Guidelines for the monitoring of benthic communities around point source discharges. Report of the ICES Advisory Committee on Marine Pollution, 1989, (Annex 1), Coop. Res. Rep. No. 167.
19. Soft bottom macrofauna: Collection and treatment of samples. ICES Techniques in Marine Environmental Sciences, (in press).

Fish Disease Studies

20. Methodology of Fish Disease Surveys. (1989) Coop/ Res. Rep. No. 166.

Miscellaneous

21. Guidelines for Monitoring Methods to be used in the Vicinity of Platforms in the North Sea, Paris Commission, 1989.
22. Control procedures: Good laboratory practice and quality assurance. ICES Techniques in Marine Environmental Sciences, No. 6, (1987).

23. ICES Intercalibration reports published in the Coop. Res. Rep. Series. Report of the ICES Advisory Committee on Marine Pollution, 1989, (Annex 2), Coop. Res. Rep. No. 167.
24. Helsinki Commission, 1988. Guidelines for the Baltic Monitoring Programme for the Third Stage, Part B, Physical and Chemical Determinands in sea Water, Baltic Sea Environment Proceedings No. 9, pp. 1-10.

FINAL VERSION
25/10/90

GUIDELINES FOR A BIO-ACCUMULATION
PROGRAMME FOR THE MONITORING OF PERSISTENT
CONTAMINANTS IN ESTUARIES AND COASTAL WATERS

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1. OBJECTIVES

- i) To propose a scheme for monitoring trends in the levels of persistent contaminants in the marine and estuarine environments.
- ii) To provide a coherent framework for coordinating bioaccumulation work in the N.R.A.
- iii) To present a protocol for the provision of data in connection with the North Sea Task Force.
- iv) To present a protocol for the provision of data in connection with the requirements of the Oslo and Paris Commission programmes (J.M.P.).
- v) To present a protocol for the provision of data in connection with various E.C. Directives.
(Black List, Grey List, Red List, TiO₂).

2. INTRODUCTION

Fundamental Considerations

Biological material offers several benefits over other materials for the assessment and monitoring of persistent contaminants (p.c.'s) in the marine/estuarine environment:

1. Levels are time-averaged or integrated over an extended period of time.
2. Results generally reflect the biologically available levels of p.c.'s.
3. The phenomenon of 'bio-magnification' usually provides concentrations of p.c.'s which are amenable to analysis by readily available routine techniques/procedures.

These advantages have led to the widespread adoption of bioaccumulation work in pollution monitoring and environmental appraisal programmes both in the U.K. and internationally. (The most universally cited example being the global "mussel-watch" approach. ⁵).

Specific Considerations

Any bio-accumulation programme requires careful planning and execution particularly with respect to the selection of 'target' species and the rigour and consistency of the methods. Many species are totally inappropriate because they are too scarce, too difficult to handle or because they regulate the body-burden of contaminants in some way. Indeed, it is generally recognised that no one species is capable of acting as a universal "indicator". The criteria for the selection of suitable species have been listed and discussed by several authors (2,4,6,7). Furthermore, for each appropriate target organism various biological factors must be taken into account and standardised. The principal factors are the number of specimens required to 'smooth out' variation between individuals, and the influences of size/weight/age,

and time of year, all of which relate to variability associated with the growth and reproductive state of the organism. (For a more detailed discussion see 8). This document sets out practical guidelines which will minimise the influence of the numerous complicating factors which can otherwise distort or completely invalidate the results generated.

3. SELECTION OF TARGET SPECIES

It must be recognised that different types of organism will reflect levels of p.c.'s in different ways, according to the pathways by which accumulation takes place. For example, seaweeds tend to respond to ambient dissolved concentrations of chemicals, whilst deposit feeding animals will generally relate to the levels of p.c.'s associated with sediments. Consequently, a comprehensive programme must include species which indicate the availability of p.c.'s in the dissolved, particulate and sedimentary phases. These are summarised in Table 1.

TABLE I

Target Species	Environmental Compartment (phase)
<u>Fucus vesiculosus</u> (Bladder wrack) <u>Fucoid algae</u>	Dissolved constituents
<u>Mytilus edulis</u> (Mussel) <u>Ostrea edulis</u> (Native oyster) <u>Cerastoderma edule</u> (Cockle)	Dissolved and particulate p.c.'s
<u>Patella vulgata</u> (Limpet) <u>Littorina littorea</u> (Common Winkle)	Dissolved and detrital constituents
<u>Macoma balthica</u> (Baltic tellin) <u>Nereis diversicolor</u> (Ragworm)	P.c.'s present in sediments
<u>Limanda limanda</u> (Dab) <u>Platichthys flesus</u> (Flounder)	Dissolved constituents (and dietary sources)

In addition to the two species of flat-fish listed above, *Pleuronectes platessa* (Plaice) may be considered for locations where the preferred species are absent.

The minimum sampling programme must include a species from each of the first 2 groups so that the dissolved and particulate phases will be monitored, together with one of the flatfish species, preferably Dab.

The latter are included for consistency with international monitoring commitments and because of the range of p.c.'s accumulated (see Section 6).

4. SAMPLING CONSIDERATIONS

The major criteria for sampling each of the target species are summarised below in Table II.

TABLE II

Target species	No. of specimens*	Size (range) mm	Time/Season for collection	Tidal/shore position
<u>F. vesiculosus</u>	25-30	250-300	February	Mid-shore
Furoid algae (A)	25-30	200-300	February	Mid-shore
<u>M. edulis</u>	50(1)	25-45(1)	Mid. Jan-Mid. Mar	Mid-shore
<u>O. edulis</u>	25	60-100	Jan-Mar	Shallow sub-tidal
<u>C. edule</u>	50	25-40	Jan-Mar	Mid-shore
<u>M. balthica</u>	25+	12-18	Jan-Mar	Mid-shore
<u>N. diversicolor</u>	100?(2)	N/A(3)	Aug/Sept?	Mid-shore
<u>P. vulgata</u>	50	ca. 40 (Diameter)	Mar-May	Mid-shore
<u>L. littorea</u>	30	ca. 20	Aug/Sept-Nov.	Mid-shore
<u>L. limanda</u>	30**	200-300(4)	Late June-Sept	Shallow areas
<u>P. flesus</u>	30**	150-300(5)	Late June-Sept	Shallow areas

* Number of individuals comprising one 'batch' sample for analysis, except in the case of flatfish.

** Analysed individually (or pooled samples comprising 5 specimens)

Notes:

(A) Where F. vesiculosus cannot be obtained, other furoid algae may offer a satisfactory substitute, but a mixture of species should NOT be used in any one sample. F. serratus should be collected as the first choice alternative on open coasts.

- (1) Based on ICES criteria
- (2) Uncertainties exist over sample size for this species. This number may therefore be an over-estimate - subject to revision.
- (3) In practice, small worms (less than ca.50mm) will be difficult and unduly onerous to collect. Unusually large specimens (ca.200mm) should be avoided. Size does not appear to have much influence on accumulation.
- (4) 200-250mm for North Sea.
- (5) 250-300mm for North Sea.

In general it is advisable to take more than the stipulated number of specimens to allow for subsequent loss or rejection of unsatisfactory material. Where readily available, consideration should be given to collecting a second sample batch at the same location either to facilitate duplicate analysis if resources permit, or for storage/archiving. Within the specified size ranges every effort should be made to collect material of the same size, and this size group should be adopted as the specification for subsequent sampling at that location. Appropriate field observations should be recorded at the time of sampling to provide information on any visual evidence relating to possible contamination (e.g. beached chemical containers) and to add the capacity for assessment of aesthetic quality considerations (Litter). Samples should be returned to the laboratory in cooled containers (but NOT frozen). Each sample should be placed in a clearly labelled plastic bag or clean polythene bucket with seal-tight lid. In the case of sediment dwelling organisms (Cerastoderma, Macoma and Nereis) a small amount of sediment from the sampling site should be included in the package.

Collection methods:

- a) Seaweed, mussels and the gastropod molluscs can be simply collected by hand from the rock surfaces on which they live, although limpets will require the use of a stout blade to prize them off.

- b) Cockles, Macoma and Nereis will need to be dug for using a fork or small spade, depending on the nature of the sediment and picked out from the sediment by hand or with plastic forceps.
- c) Flatfish can be collected by use of a push-net, or small beam trawl deployed from a boat.

5. SAMPLE PREPARATION

It is essential to remove extraneous matter from all samples so as to measure only the contaminants in the tissues. This is achieved by external cleansing and/or depuration of gut contents to remove superficial or ingested sediment, and food material. Furthermore, in many cases only selected tissue or tissues are appropriate for particular analyses and dissection is therefore necessary to obtain the relevant material. For example, the shells of molluscs must be removed prior to analysis. The main facets of sample preparation for each target organism are summarised in Table III.

SUMMARY OF TISSUE PREPARATION PROCEDURES AND REQUIREMENTS - TABLE III

Target Species	Storage prior to cleansing/preparation	Cleansing	Depuration	Storage prior to dissection	Tissue Selection	Storage prior to analyses	Reference for further details
<u>F.vesiculosus</u>	Refrigeration (up to 10 days)	Scrubbing and washing	N/A	No	Old thallus only	Refrigeration Analyse a.s.a.p.	(1), 3
<u>Fucus spp.</u>	"	"	N/A	No	"	"	
<u>M.edulis</u>	No	Scrape off growth on shells and scrub clean	48 hrs in clean water	(Deep frozen)	Remove shells	Can be frozen but best analysed immediately	
<u>O.edulis</u>	"	"	"	"	"	"	
<u>C.edule</u>	Kept cool and in sediment (up to 24 hrs)	Scrubbing and washing	3 to 4 days in clean water	(Deep frozen)	"	"	3
<u>M.balthica</u>	"	"	7 days in clean water	(Deep frozen)	"	"	3
<u>N.diversicolor</u>	"	Gentle washing (in fine sieve)	6 days in acid-washed sand 1 day in clean water only	(Deep frozen)	N/A (Whole animals)	Equivalent to storage prior to dissection	11
<u>P.vulgata</u>	No	Thorough washing in clean water	-	(Deep frozen)	Remove shells	Can be frozen but best analysed immediately	3
<u>L.littorea</u>	No	"	-	()* (Deep frozen)	Remove shells after boiling for 1 min or steaming	"	3
Flatfish (<u>L.limanda</u>) (<u>P.flessus</u>)	Refrigeration (up to 24 hrs)	Thorough washing and gentle scrubbing, remove mucilage and attached matter	-	(Deep frozen)	Remove white muscle tissue - dorsal fillet, RHS. Remove liver (for hydrocarbon analyses)	"	

* Not recommended

Notes: (To Table III)

Washing may usually be carried out with tap water, although clean sea water (if available in sufficient quantities) is probably better. Where cleansing is not followed by depuration, material should be shaken to remove surplus water, or blotted dry.

Depuration should be carried out using water of appropriate salinity according to the area of collection.

Long-term storage is best carried out prior to dissection since losses from whole animals are probably much less than those from cut tissues especially when these have been previously frozen.

If material has not been stored prior to dissection prepared tissue may be stored for an extended period prior to analysis.

The effects of storage have not been well researched, and the recommendations in Table III and accompanying notes are therefore only general guidelines. The U.S. EPA have suggested that material may be stored deep-frozen (-20°C) for 6 months to a year, although where tissue is analysed for mercury a period of 1 month has been proposed.

Footnote to Section 5.

Bulked samples may provide an unmanageable quantity of material for analysis. In such instances, all tissue should be homogenised and a suitable size of sub-sample withdrawn for analysis. Sub-sampling by selection of individuals from within a batch should NOT be utilised as this defeats the purpose of the minimum batch size specified in Table II. It is recommended that initially three sub-samples are taken and analysed, but if satisfactory repeatability is demonstrated from early results this may subsequently be reduced to one sub-sample, although duplicates are preferable.

6. ANALYSIS/DETERMINANDS

Details of analytical procedures will be provided elsewhere, and a full list of chemical determinands is given in the Estuaries and Coastal Waters monitoring programme. This section seeks to identify those determinands which can be most effectively monitored by the various target organisms and to identify those determinands which are not satisfactorily estimated by particular species. In addition, relevant biological determinands required e.g. wet weight are also tabulated. The available information is summarised in Table IV. It must be emphasised that assessments are related to indicator reliability for each environmental compartment (phase) as identified in Table I.

TABLE IV

Target Species	Determinands efficiently accumulated/monitored	Determinands NOT reliably monitored	Biological Determinations
<u>F.vesiculosus</u>) <u>Fucoid algae</u>)	As, Cd, Co, Cu, (Hg), Ni, (Se) (Sn) Zn Fe?	Cr, Pb,	Dry wt. General condition
<u>P.vulgata</u>	Cd, Cu (Ag), (Hg), (Pb)	As	Wet wt.- shell Dry wt.- shell
<u>L.littorea</u>	Ag, (As), Cd, Pb (Hg)	Co, Ni, (Cr), (Mn) (Fe) (Zn)	"
<u>M.edulis</u>	Cd, (Co) Cr, (Hg), Pb, (Se) (Sn)	Cu, Zn, As, Ag	Wet wt.+ shell Dry wt.- shell
<u>O.edulis</u>	Cu, Zn, and probably most other metals		"
<u>C.edule</u>	(Ag), (As), (Ni) (Cd)	Cu, Zn	"
<u>M.balthica</u>	Ag, As, (Cr), Hg, Se	Cu, Zn?	Wet wt.- shell Dry wt.- shell
<u>N.diversicolor</u>	Co, Cu, (Ag), (Hg)	Zn, Fe, Mn	Wet wt., Dry wt.
Flatfish * <u>(L.limanda)</u> <u>(P.flessus)</u>	Hg(1), Organic compounds, [Pesticides, PCB's etc] (2), Cd(2) (1) In white muscle (2) In liver tissue	Most metals	Sample wet wt., Dry wt. Length Sex Lipid content

Notes: () in column 2 denote moderate efficiency

() in column 3 denote poor reliability

Metals not identified in either column may be taken to have some relationship between environmental levels and concentrations in the target organism, although the strength of the relationship is probably not as good as might be considered desirable.

* Analyses and measurements on individual specimens for metals/white muscle analyses. Pooled samples of 5 (or more if small) livers will be needed for hydrocarbon determinations and associated lipid content. (All other organisms pooled to constitute one sample). Determinations of whole animal wet weights should be made prior to freezing.

N.B. Results for fish tissues are conventionally reported on a wet weight basis.

Each set of analyses should be accompanied by analysis of a standard reference material.

It may be noted that for some p.c's in certain compartments, there is no recommended organism which acts as a reliable monitor, e.g. Zn in sediments.

Accumulation of heavy metals has been well researched, but little or no information exists on the effectiveness of most of these organisms in accumulating organic compounds. Petroleum hydrocarbons have been 'monitored' in mussels, but it has been suggested that the levels present only reflect very recent exposure to these compounds (10). Flatfish (livers) are probably the best biological media for monitoring hydrocarbons because of their high lipid content, and the lipophilic nature of many organic substances. Clearly the efficacy of using bioaccumulation to monitor persistent organic contaminants requires urgent research.

7. DESIGN OF A NATIONAL PROGRAMME

i) Spacing of sampling sites:

It is recommended that for *Fucus* spp and invertebrates a minimum of one monitoring point should be established for each 150km section of coast in addition to the proposed baseline sites in each major estuary. Fish collection areas may be more appropriately spaced at greater intervals, particularly where coastal topography results in a considerable length of coastline surrounding a single water body (embayment).

ii) Selection of sampling sites:

Wherever practicable, a monitoring point should be established at locations where the maximum number of the designated target species can be obtained from the same site. Target species not present at the principal location should be collected from the nearest appropriate habitat within the 150km section. In regions of fairly uniform coastal topography where a number of suitable sites exist it is strongly recommended that an initial, more intensive, screening survey be undertaken to assist in the identification of the most appropriate monitoring point. Point source discharges should be avoided if possible.

iii) Selection of target species:

As an absolute minimum, one species accumulating from the dissolved phase plus one species accumulating from the particulate/dissolved phase (see Table I), together with flatfish (for hydrocarbon contamination) must be collected from each monitoring point/sector. It is also highly desirable that the second species listed for each category is also collected and analysed.

It is likely that in certain sectors some species will be absent or not present in sufficient numbers (or not compatible with the specified size criteria), and there is every possibility that a species collected on one occasion will be absent on a future occasion or occasions. The second species therefore represents a 'back-up' for the main species. Furthermore, since levels of p.c. in one species are not comparable with levels in other species, even for the same environmental 'compartment', the apparent duplication is necessary to maximise spatial and temporal comparison. Such a 'safety-net' procedure could be reviewed after the early years of monitoring data have been collated and appraised.

iv) Frequency:

Samples should be collected annually at the appropriate time of year (see Table II). Where a range of collection times is given it is recommended that the month selected for sampling in the first survey is established as the collection time for subsequent sampling.

v) Intercomparability Exercises:

It is strongly recommended that intercomparability exercises are undertaken by all contributing laboratories to ensure compatibility of methods and results. This will be especially vital during the first few years of the programme.

8. GENERAL CONSIDERATIONS

The information and guidelines set out in the preceding sections are based on the best data currently available and are therefore subject to modification in the light of continuing research.

There is certainly scope for the introduction of "new" monitoring species, and early returns may demonstrate the need for adopting a programme of transplanting target species to overcome regional variations.

Local investigations -

The programme proposed in Section 7 is intended to fulfill the requirements of a national programme, which should be viewed as the minimum commitment for each Region. Local problems, especially areas receiving appreciable quantities of domestic and/or industrial waste will require more comprehensive investigation. The criteria established here should be incorporated into regional programmes and every attempt should be made to ensure that localised investigations are compatible with national monitoring to facilitate comparison of data. Local programmes will require much greater geographical coverage, and indeed the identification of point source discharges may require sampling intervals of only a few km. (9), although the annual sampling frequency should be adequate for monitoring purposes.

Existing Regional Programmes -

It is appreciated that in some regions relatively comprehensive bioaccumulation programmes already exist and in some cases these have been continuing for a number of years. It is recommended that insofar as possible these programmes be incorporated into the broader framework.

They should therefore be continued at least for a sufficiently long period of time to allow calibration of existing data with that generated for the national programme, in cases where different species have been used, or sampling has been carried out at times of the year other than those listed here. (Data submitted for the national programme must comply with the specifications in this document to ensure the validity of comparisons).

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10. OTHER REFERENCE MATERIAL

The following documents are not referred to in the text, but have been used in the preparation of this paper.

- a) Investigations into the methodology of bioaccumulation studies.
Unpublished report: Welsh Water Authority, Directorate of Scientific Services, Tidal Water Section, Tremains House, Coychurch Road, Bridgend. Tidal Waters Report No. TW 82/4.

- b) The concentration of metals, organochlorine pesticide and PCB residues in marine fish and shellfish.
MAFF Directorate of Fisheries Research; Aquatic Environment Monitoring Report NO.16. 1987.

- c) Draft Recommendations of 'Joint Monitoring Group/North Sea Task Force' joint monitoring workshop. November 1989.

Chapter 5

$$I_d = I_0 e^{-kd}$$

where I_d is the light intensity at depth d , I_0 is the light intensity at the surface and k is the extinction coefficient, which varies with the wavelength of light. The value of k also depends on the chemical composition of the water, and on its particle content and composition. In estuaries, k is predominantly determined by the suspended load, which can be determined as follows:

2.2 - *Gravimetric determination.* The amount of material in suspension in the water column can be measured by filtering a known volume of water through a pre-weighed filter using the procedures described by Strickland and Parsons (1972).

2.3 - *Turbidity meters.* See Chapter 2, Section 2.2.3.

2.4 - *The Secchi disc.* The Secchi disc is one of the oldest techniques in oceanographic and limnological research. It provides a very crude measurement of water turbidity but it can be very useful in studies of phytoplankton production. A white disc is lowered into the water and the depth at which it is no longer visible (called the Secchi disc depth, SD) is measured. Normally, a disc of 30cm diameter is attached to a line marked in metres with a heavy weight suspended below the disc so that the rope hangs vertically in the water with the disc at right angles to the rope. The point at which the disc disappears from view may be easier to distinguish if a black zig-zag band is painted on the white disc but this is a matter of personal preference. A value of three times the Secchi disc depth is commonly taken as the 1% light level (Holmes, 1970).

Several factors have been suggested to convert Secchi disc readings into extinction coefficients. Poole and Atkins (1929) suggested that $k = 1.7/SD$; Jones and Willis (1956) suggested $k = 2.1/SD$. Perhaps the most appropriate factor for estuarine studies was derived by Holmes (1970) who suggested that $k = 1.44/SD$. Clearly, there is a very large range in these values and this highlights the imprecision of the Secchi disc technique. It is susceptible to many experimental errors, not least of which is operator error. An example of the variation obtained between two observers has been given by Holmes (1970).

Despite the limitations of the method, it is possible to obtain good agreement between the Secchi disc reading and other indicators of water turbidity, such as gravimetric determination. Figure 4.1 illustrates the relationship between Secchi disc readings and gravimetric determination in the Bristol Channel in 1973 and 1974; the correlation coefficient is 0.91, significant at $P < 0.001$ and the equation of the line is:

$$SD^{-1} = 0.10 + 0.040P,$$

where P is the gravimetric particulate load expressed in units of mg/l.

2.5 - *Light meters.* The most appropriate estimate of light in studies of phytoplankton production is obtained by using a submersible light meter. The amount of photosynthetically available light at any depth can be measured if an underwater quantum sensor is coupled with another at the surface. The surface sensor measures any fluctuation occurring in solar radiation during the measurement, and the difference