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International Council for the Exploration of the Sea

C.M.1975/E:31 Fisheries Improvement Committee Ref: Hydrography Cttee



# WORKING GROUP ON POLLUTION BASELINE AND MONITORING STUDIES IN THE OSLO COMMISSION AND ICNAF AREAS

Sub-Group on Contaminant Levels in Sea Water

(Chairman : Dr Diether Schmidt)

Report of the First Meeting Charlottenlund, 21 - 22 May 1975

### 1. Introduction

1.1. The Chairman welcomed those present and briefly referred to the activities of the parent Working Group on Pollution Baseline and Monitoring Studies in the Oslo Commission and ICNAF areas, which established the present sub-group on contaminant levels in sea water.

- 1.2. Mr Smed welcomed those present on behalf of ICES.
- 1.3. The Chairman proposed a timetable for the meeting and intimated that its business may be completed within 2 days.
- 1.4. Members of the sub-group present (ANNEX 1) then briefly indicated their chief interest in relation to the subject matter of the meeting.

1.5. Prof. I. Elskens (Belgium) had previously asked Dr P. Jones to act on his behalf at this meeting. Dr G. Topping (Scotland) was unable to attend owing to injury; however, he had sent a telex (which was read by the Chairman) giving in detail his ideas relevant to the agenda of this meeting.

### 2. Terms of Reference

2.1. The Chairman outlined the terms of reference of the sub-group (ANNEX 2). Although the nature of pollutants was not specified, it was decided to confine discussion to trace metals during the present session.

2.2. The Chairman referred to the ICES Cooperative Research Report Number 39 on the activities of the original North Sea Pollution Working Group, from which the enlarged North Sea and North Atlantic Group had emerged.

#### 3. Adoption of Agenda

3.1. The provisional agenda was adopted without alteration (ANNEX 3).

### Appointment of Rapporteur

4.1. Dr Jones was appointed rapporteur of the meeting.

### 5. Review of Trace Metals in the Water of the North Atlantic

5.1. This review was prepared by Dr Jones at the request of the ICES Advisory Committee on Marine Pollution (ICES Coop.Res.Rep.No.43, para. 6.1) and copies were distributed to members of the sub-group prior to the meeting.

5.2. The metals reviewed were Hg, Pb, Zn, Cu, Cd, Ni, Mn and Co and the area covered was the whole of the North Atlantic excluding continental shelves. Some metals such as cadmium showed reasonably good agreement between different surveys but the levels of other metals such as manganese and mercury ranged over several orders of magnitude between different investigations. Some variation may have been real, but there was evidence that much of the discrepancy was attributable to the techniques of sample collection, storage and analysis.

5.3. A discussion followed in which members of the sub-group quoted from experience information relevant to the subject matter of the review. Mr Olafsson reported generally low levels of mercury in oceanic waters around Iceland and that U.V. irradiation of samples showed a sizeable fraction of the mercury to be presumably in organic form. Dr Kremling had observed high metal levels in upwelled water off northwest Africa. He also reported on data collected between Iceland and Faroes during the ICES Overflow '73 Survey. Metal levels were in general agreement with those in Dr Jones' review.

5.4. The importance of the surface film was discussed in relation to the sampling of surface water for trace metal analysis and also in relation to the more fundamental aspects of the exchange of metals at the air/water interface. Dr Jones reported on a UK project being carried out at AERE, Harwell, to study this subject and several members reported similar interests within their own institutes. The sub-group recommended that this type of investigation be encouraged.

### 6. Reports on National Programmes

6.1. Members reported, either verbally or by distributing duplicated reports, on their national programmes of metal investigation in the area under consideration.
All those present agreed to submit a final written report on their national programme for inclusion in the minutes of the meeting (ANNEX 4).

6.2. The absence of a representative from the USA was noted with regret since a report on the activities of the GEOSECS project would have been highly relevant to the business of the sub-group.

6.3. After the presentation of national programmes there followed a discussion on problems of sampling and analytical techniques raised during the presentation of Dr Jones' report. Problems of filtration were discussed in relation to contamination from laboratory air supplies and in relation to particulate material that may be forced through membranes under pressure. The type of bottle most suitable for sample storage was discussed. Quartz glass was generally preferred to polyethylene since the danger of contamination from the former material was very low. Teflon bottles were also considered to be suitable. Storage by acidification and deep freezing was discussed. Dr Kremling compared the analyses of cadmium in sea water by AAS and ASV. Data by the former technique showed a greater scatter of results compared with results by the latter method. This feature was attributed to laboratory contamination during the manipulative processes of extraction. Dr Walton reported a progressive reduction in lead values analysed by his institute. He attributed this trend to improvements in the analytical environment of the laboratory.

### 7. Feasibility of Routine Monitoring of Metals in the North Sea

7.1. Existing national programmes involving the measurement of trace metals in the water of the North Sea were examined in relation to the possible establishment of a routine monitoring programme. Coverage of the southern North Sea and the German Bight was good but the northern part of the area was less well surveyed.

7.2. Several existing projects would be able to feed suitable data into a routine monitoring programme. However, some investigations are at present designed to study the more basic scientific processes and may not be readily adaptable for incorporation into a monitoring exercise.

7.3. It was unanimously agreed that for a routine programme to have any value, data provided by participants must be comparable. This could only be achieved by either the standardisation of sampling, storage and analytical techniques or by understanding the nature of any discrepancies in the data between participants and making the necessary adjustments. The meeting considered that at present neither of these ideals are feasible and that it is therefore not realistic to propose and organise such a routine monitoring programme in the North Sea.

7.4. In spite of the absence of such a co-ordinated programme, several national projects will measure metals in the water of the North Sea (ANNEX 4), thus metal levels will continue to be reported for several areas of the North Sea.

7.5. The meeting decided prior to the establishment of a monitoring programme, an expanded intercalibration project is necessary and must cover all aspects of sample collection, storage and analysis. Since such a project is also highly relevant to a baseline survey of metals in the North Atlantic, it was decided to discuss this topic (agenda item number 10) before considering the baseline exercise (agenda item number 9).

### 8. Intercalibration Programme

8.1. Dr Jones opened the discussion by outlining the results of a metal intercalibration exercise conducted between laboratories in Belgium, the
Netherlands and the United Kingdom. Tests were confined mainly to a comparison of analytical techniques. Reasonable agreement was reported when similar methods were compared, but discrepancies were often observed between different basic techniques. It is hoped to present a critical report on this exercise at the forthcoming ICES Annual Meeting in Montreal.

8.2. During the discussion which followed, the possible causes of discrepancies between analytical techniques were considered. It was agreed that different basic methods may selectively measure different species of the same metal.
Dr Kremling reported interference by mercury in the measurement of copper by ASV resulting in copper values too high.

8.3. Many members quoted evidence of contamination by a variety of metals from the walls of containers. The nature and pore size of filter membranes were also considered to be relevant to the metal content of filtered sea water. The sub-group therefore considered it vital that techniques of sample collection and storage be intercalibrated in addition to analytical techniques.

8.4. A lengthy discussion followed on the best way to conduct an intercalibration programme in order to include all possible variables. It was decided that such an exercise should take place in 3 stages:-

- a) A concentrated multi-element standard in acid solution will be circulated to all participants. The standard will be prepared from commercially available reagents manufactured specifically for AA analysis and will contain Hg, Cd, Zn, Co, Ni, Mn, Fe, Pb, Cu and Cr. The sample will undergo a simple dilution prior to analysis and will provide a means of intercalibrating the standards used by each participant. Dr Jones agreed to undertake the organisation of this exercise. The samples will be distributed during the autumn of 1975, the results of the analysis should be available not later than April 1976 and a report on the exercise will be prepared by the summer of 1976.
- b) The second stage of the exercise will involve the distribution of sea water samples. It was proposed that 2 samples of North Sea water be collected and filtered. One sample will contain a relatively high metal level and the other will have a low metal content. Each sample will be contained in plastic bottles provided by the organiser. Additional sub-samples may be contained in bottles specially provided by each participant. All samples will be deep-frozen and distributed by air-freight to participants at the national expense of each recipient.

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Samples will be analysed for those metals which participating laboratories measure as part of their programme. Dr Jones agreed to investigate the feasibility of his undertaking this exercise.

- b.2) It was realised that the intercalibration of mercury poses special problems. The storage of samples may be different than for other metals and a separate sample will generally be required for the analysis of this element. Mr Olafsson agreed to organise the intercalibration exercise for mercury.
- c) It was proposed that the final stage of the intercalibration exercise should take the form of an international project inviting the participation of as many research vessels as possible. The exercise should be based on the ICES intercalibration of nutrient salts held in Copenhagen during the autumn of 1966. Emphasis should be placed on the methods of sample collection and treatment as well as analysis. It was appreciated that for some institutes participation by a research vessel may prove difficult. In these instances individual analysts would be urged to attend, preferably with their own equipment.
- c.2) It was agreed that the Chairman of the sub-group should request the Chairman of the ICES Working Group on Chemical Analyses of Sea Water to publicise the proposal for the workshop outlined above and to invite comment from members of his Working Group concerning the organisation of such a project.

8.5. All countries represented at the meeting agreed to participate in the first 2 stages of the intercalibration exercise (8.4.a. and 8.4.b. above). The following figures in parentheses refer to the number of institutes in each country which may take part:-

Canada (1); Denmark (1-2); Federal Republic of Germany (1); Greenland (1); Iceland (1); Netherlands (1-3); Norway (2-3); and the United Kingdom (2-3).

8.6. Other member countries not present at the meeting should be informed of the proposed exercise via the ICES Secretariat and invited to participate.
Although not a member of the sub-group, the Soviet Union should also be invited to take part in the exercise since they report metal levels from the North Atlantic. The Chairman agreed to approach the Chairman of the Baltic group of analysts in order to effect such liaison.

8.7. The cadmium and mercury standard solutions prepared by Professor Sugawara of the Sagami Chemical Research Centre, Japan, were discussed in relation to the proposed intercalibration exercise. The general opinion of the meeting was that the metal levels in these standards were rather high in relation to levels normally found in sea water. However, the concept of preparing such trace metal standards should be encouraged. It is to be hoped that Professor Sugawara will prepare standards with lower levels of cadmium and mercury and also eventually include other metals.

8.8. In addition to the above proposals concerning the intercalibration of analytical techniques, the meeting was of the opinion that much basic research into methodology is still required. Several lines of investigation, such as selecting the most suitable solvent and complexing agent for methods involving solvent extraction, are best carried out by single research teams. Institutes more concerned with fundamental research not having large applied commitments are urged to undertake such investigations.

#### 9. Baseline Survey of Metal Levels in the North Atlantic

9.1. Existing national programmes and those planned for the near future (ANNEX 4) involving the measurement of trace metals in water of the North Atlantic were examined in the light of a possible amalgamation into a unified baseline survey. However, the coverage was considered inadequate to provide a comprehensive base-line survey of the ICNAF/NEAFC region.

9.2. After considerable discussion the meeting came to the conclusion that in order to plan such a baseline study the area covered by some national programmes would need to be extended further offshore. In addition, the cooperation of the USA would be essential in making available GEOSECS data and in actively participating in future surveys.

9.3. For the reasons stated in the above paragraph and because of the present unreliability of comparing data from different sources, it was decided that the time was not yet ripe to plan an international baseline survey of the North Atlantic. Such a programme may be more feasible next year when some of the above problems may be resolved.

9.4. Existing national programmes involving the measurement of trace metals in the water of the North Atlantic should be encouraged to continue and other countries not yet participating urged to inaugurate such investigations. Proposed plans for such surveys as well as the results obtained after completion, should be made freely available to other members of the sub-group.

#### 10. Date of Next Meeting

10.1. The date of the next meeting will be decided after the second meeting of the parent working group at present scheduled for April 1976.

# 11. Any Other Business

11.1. Dr Walton expressed concern over the possible lack of communication between the large number of national and international organisations at present involved in pollution studies and he asked what channels were available to exchange information. Other members of the sub-group endorsed this concern. On behalf of ICES Mr Smed said that copies of relevant documents formally accepted by the Council were circulated to other organizations that might be interested.

11.2. The Chairman then thanked those present for their participation in the meeting and expressed appreciation for the amenities provided by ICES. There being no further business, the meeting was concluded at 1800 hours on 22 June.

#### ACTION

ALL MEMBERS: who have not already done so, to send to the Chairman a final version of their national programme (6.1).

#### CHAIRMAN:

1. To contact the Chairman of the ICES Working Group on Chemical Analyses of Sea Water regarding a multi-vessel trace metal workshop (8.4.c.2)). 2. To contact the Chairman of the ICES Baltic group of analysts regarding Soviet participation in the metal intercalibration exercises (8.6).

DR P. JONES:

- 1. To organise a metal intercalibration exercise involving the distribution of a concentrated multi-element standard (8.4.a)).
- 2. To investigate the feasibility of a metal intercalibration exercise involving the distribution of frozen sea water samples (8.4.b.1)).

MR J. OLAFSSON:

To organise a mercury intercalibration exercise (8.4.b.2)).

ICES SECRETARIAT:

To publicise the proposed metal intercalibration exercises among members of the parent Working Group on Pollution Baseline and Monitoring Studies in the Oslo Commission and ICNAF Areas.

### List of Participants .

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J. Olafsson

C. Vagn Olsen

A. Walton

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Deutsches Hydrographisches Institut.

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Marine Research Institute, Skúlagata 4, Reykjavik, ICELAND

Danmarks Fiskeri- og Havundersøgelser, Charlottenlund Slot, 2920 Charlottenlund, DENMARK

Bedford Institute of Oceanography, P.O. Box 1006, Dartmouth, N.S., CANADA

ICES Hydrographer, ICES, Charlottenlund Slot, 2920 Charlottenlund, DENMARK

# Terms of Reference

 To examine in the light of knowledge gained in the course of the baseline investigations of metal levels in sea water in the North Sea area, whether or not routine observations of these contaminants are yet appropriate in a monitoring context.

- a) If they are, to draw up recommendations for such observations in the North Sea area and to supervise their conduct and prepare a draft report on the results for consideration by the parent Working Group;
- b) If they are not, to draw up plans for further development work so that at an early stage routine observations can be conducted.

2. In the light of knowledge gained in the course of the baseline studies of metals in sea water in the North Sea area, and as a preparatory to any possible monitoring operations in an extended area, to plan and conduct a baseline survey of metal levels in sea water for the remainder of the NEAFC and relevant parts of the ICNAF areas and to prepare a draft report of the results for submission to the parent Working Group.

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# Agenda

- 1. Opening of meeting.
- 2. Composition of the membership.
- 3. Terms of Reference of the sub-group.
- 4. Adoption of the Agenda.
- 5. Appointment of Rapporteur.
- 6. Review of metal levels in sea water (Dr P. Jones).
- 7. Reports on national programmes and results for trace metals in sea water in the North Sea and parts of the North Atlantic.
- 8. Consideration of the feasibility of routine observations, in a monitoring context, of trace metal levels in sea water in the North Sea area.
- 9. Planning of a baseline survey of metal levels in sea water for relevant parts of the North Atlantic.
- 10. Necessary intercalibration programmes.
- 11. Date of next meeting.
- 12. Any other business.

INVENTORY OF NATIONAL PROGRAMMES INVOLVING THE MEASUREMENT OF TRACE

METALS IN THE WATER OF THE NORTH SEA AND NORTH ATLANTIC

- a) Canada
- b) Germany, Federal Republic of
- c) Greenland
- d) Iceland
- e) Netherlands
- f) Norway
- g) United Kingdom

### a) <u>Canada</u>

#### Canadian Programs of Trace Metal Investigations in West Atlantic Regions

- 1. The principal Canadian laboratories performing trace metal investigations are as follows:
  - (i) Bedford Institute of Oceanography, Dartmouth, Nova Scotia.
  - (ii) Department of Oceanography, Dalhousie University, Halifax, Nova Scotia.
  - (iii) Marine Sciences Institute, McGill University, Montreal, Quebec.
  - (iv) Department of Oceanography, Université du Québec à Rimouski, Rimouski, Quebec.

<sup>\*</sup>Within the Bedford Institute there are three individual laboratories engaged in these studies.

Atlantic Oceanographic Laboratory (A.O.L.): Dr J.M. Bewers Atlantic Geoscience Centre (A.G.C.): Mr D. Buckley Marine Ecology Laboratory (M.E.L.): Dr D.H. Loring

Additional research in other geographical locations (principally the Pacific Ocean) is carried out by the Fisheries and Marine Service laboratories in Vancouver/Victoria. For further information on these regions contact can be made through:

Dr M. Waldichuk, Pacific Environmental Institute, Fisheries and Marine Service, W. Vancouver, British Columbia, Canada

and

Dr C.S. Wong, Marine Chemistry Division, Fisheries and Marine Service, Victoria, B.C., Canada

2. Some results of trace metal studies in ocean waters conducted to date are reported in the attached bibliography.

### 3. Program of the Atlantic Oceanographic Laboratory

a) Preliminary work on trace element studies began in 1971 with the first major suite of water samples being collected in 1972 from the Gulf of St. Lawrence. Details of procedures and results are to be found in

> Macaulay, I.D. and J.L. Barron (1973) McCormach, C.E. and S.F. Hartling (1973) Bewers, J.M., W.W. Hall and I.D. Macaulay (1974) Bewers, J.M., I.D. Macaulay and B. Sundby (1974) Bewers, J.M. and A. Walton (1974).

b) The last publication discusses in broad terms the justification for the program in the Gulf of St. Lawrence and also outlines an anticipated additional coastal studies program which has, in fact, begun in 1974. Data from the latter investigations are as yet only available in draft manuscript form.

The study involves profile investigations along a line of stations extending from Halifax across the Scotian Shelf to the edge of the Continental Shelf with the deepest samples being taken at >1000 m in the Central Atlantic Water. In this study four distinct water masses are recognised from the T-S structure - namely Surface Shelf Water, Deep Shelf Water, Slope Water and Central Atlantic Water.

c) Further work is continuing in the Gulf of St. Lawrence with the emphasis being geographically centred in the St. Lawrence River Estuary between Quebec and the Saguenay Fjord River System. The intention of this work is to elucidate the "inputs" of the St. Lawrence River to the Gulf and subsequently to the N. Atlantic. It can be taken as a Canadian contribution to the RIOS program presently being developed under the auspices of SCOR in WG 46.

(The region mentioned is one of rapidly changing salinity and is characterised by a local zone of high turbidity. Trace element behaviour is being examined in solution, suspended matter and sediments from the fresh water through to salinities of 28%.)

#### REFERENCES

- 1. THOMSON, J. and A. Walton, 1972. "Natural Radioactive Decay Series Elements in the Oceans and Sediments", Proc. Roy. Soc. (Edinburgh), (B), 72/73: 167-182.
- 2. FITZGERALD, R.A., D.C. Gordon, Jr. and R.E. Cranston, 1973. "Total mercury in seawater in the northeast Atlantic Ocean. Deep-Sea Res. 21: 139-144.
- 3. GORDON, D.C., Jr. and A. Walton, 1973. "Marine Pollution Research", Ocean Science Reviews, Biennial Review 1971/72, Bedford Institute of Oceanography, 67-74.
- 4. MACAULAY, I.D. and J.L. Barron, 1973. "Lithium, Magnesium, Calcium, Strontium and Fluoride in the Gulf of St. Lawrence: Analytical Results and Data Logging System", Data Series/BI-D-73-2/March 1973.
- 5. McCORMACK, C.E. and S.F. Hartling, 1973. "Data on Some Trace Elements in the Gulf of St. Lawrence", Data Series/BI-D-73-8/June 1973.
- 6. BEWERS, J.M., I.D. MACAULAY and B. SUNDBY, 1974. "Intercalibration as an aid to Quality Control", Report Series/BI-R-74-5/June 1974.
- 7. BEWERS, J.M., W.W. Hall and I.D. Macaulay, 1974. "A Modified Niskin Bottle for Trace Element Sample Collection", Report Series/BI-R-74-2/February 1974.
- 8. BEWERS, J.M., I.D. Macaulay and B. Sundby, 1974. "Trace metals in the Waters of the Gulf of St. Lawrence", Can. J. Earth Sciences <u>II</u>, 939-950, 1974.
- 9. BEWERS, J.M. and A. Walton, 1974. "Monitoring the Quality of Canada's Coastal Zone - A Proposed National Plan", Science Forum, <u>V38</u>, 26-28, 1974.
- 10. MACAULAY, I.D., 1974. "Pilot Intercalibration I: Trace Metals in Freshwater and ' Seawater", Report Series/BI-R-74-1/February 1974.

#### b) Federal Republic of Germany

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#### Program for Research and Monitoring of Trace Heavy Metals in Sea Water

<u>Area</u>	:	Southeastern North Sea, 22 stations (German Bight); Western Baltic, 18 stations (see attached maps).	
Frequency	:	Once per year for each area.	
Sampling	:	Research Vessel "Gauss". PVC-coated wire, 1.7 l plastic samplers "Hydrobios", 3 - 6 depths. Temperature/salinity - probe.	
<u>Sample</u> <u>Treatmen</u> t		Vacuum filtration : 0.4 µm "Nuclepore" membrane filters. Particulat residue on filter preserved. Filtered and unfiltered water samples (500 ml each) in SiO <sub>2</sub> -glass bottles. Rapidly frozen (within less than 30 min) at 200 - 220 K using specially designed apparatus. Samples transported and stored deep-frozen at 250 K until analysis.	

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### Analysis:

1) Atomic Absorption Spectrometry:

Acidification. Liquid / Liquid - Extraction (1 ml, 1 : 1) with APDC / MIBK.

AAS flameless technique, Perkin - Elmer model 300, graphite furnace HGA 74, D<sub>o</sub> background correction, gas-stop, Ar.

Metals: Cd, Cu, Fe (fully operative); Ni, Mn (II) introduced now; more elements considered for inclusion later in the program.

### 2) Anodic Stripping Voltammetry:

"Princeton Applied Research" Polarographic Analyzer model 174 with Automated Electroanalysis Controller model 315; "Metrohm" cell with thermoregulated Si0<sub>2</sub>-glass vessel.

Metals: Zn, Pb, Cd, Cu.

Analysis program just begun.

### 3) Neutron Activation Analysis:

Research and Development project for future monitoring applications to be started in 1975/76.

#### Results

First data available for Cd, Cu, Fe in Western Baltic, VFS "Gauss" cruise, October 1973 (publ. in prep.).





### c) <u>Greenland</u>

# Programme for Research and Monitoring of Trace Metals in Sea Water at West Greenland

At West Greenland two areas have been sampled for measuring trace metal levels in sea water (see attached map).

One area is the Kangerdluarssuk fjord in South Greenland near the town of Narssarssuaq Sampling started in the summer of 1974 and is continuing during 1975. Sea water samples are to be analysed for at least Zn, Cd, Pb, Cu and Hg.

The other area is the fjord system adjacent to a zinc lead mine and mill on the west coast of Greenland in Umanak district. The tailings from the mine production are discharged into the sea. Sampling in this area has been done twice before the mining operation started, in order to determine natural levels of metals in sea water and selected organisms. Since late 1973, when the mining operation started, sampling in the fjord system has been carried out 3 times and the sampling is going to continue twice a year. Sampling includes sea water and selected organisms. The results suggest sea water to be a proper medium for monitoring the pollution resulting from the disposal of the solid waste.

Analyses of sea water are made by the Geological Survey of Greenland by means of optical spectroscopy after concentrating on chelex 100 ion exchanger, neutron activation, anodic stripping voltammetry, and flameless atomic absorption.



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### d) <u>Iceland</u>

#### Report on Icelandic Measurements of Trace Metals in Sea Water

#### Existing Programmes

A multidisciplinary programme starts in 1975 on a coastal region in Faxabay, which received sewage effluents. Trace metals in solution and suspension will be determined as well as other chemical parameters.

Sea water samples for trace metal analyses will be collected in late 1975 from typical water masses that are encountered near Iceland.

An investigation is being carried out on particulate iron and aluminium in coastal waters.

Measurements of mercury in sea water will continue in 1975.

#### Analysis

Liquid-liquid extraction with APDC/MIBK is employed, followed by atomic absorption measurement on Techtron AA5 using either air-acetylene flame or Model 63 Carbon Rod.

Iron and aluminium are determined by colorimetry using ferron and 0-phenanthroline.

Mercury is determined by flameless atomic absorption after concentration and isolation by amalgamation on gold.

#### Published Results

OLAFSSON, J., 1974. Determination of nanogram quantities of mercury in sea water. Anal. Chim. Acta, <u>68</u>, 207-211.

OLAFSSON, J., 1975. Volcanic influence on seawater at Heimaey, Nature 255, 138-141.

# e) <u>Netherlands</u>

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Program Water Quality Monitoring Dutch Coastal Waters 1975 (mainly surface waters)

Period: 12 May - 31 December 1975. Taking of Samples: Directie Noordzee. Analyses: RIZA or elsewhere.

	Parameters	Sampling Points	Frequency
1.	pH Oxygen Chloride Temperature Secchi depth	all	Every 14 days (December once)
2.	Silicate Orthophosphate Total Soluble Phosphate Nitrate Ammonia	all	
3.	Total Phosphate Kjeldahl nitrogen	Half of the points	Every month
4.	Chlorophyl Total organic carbon	all	Every 14 days (December once)
5.	Suspended matter residue after ignition of the susp. matt.	all	11
6.	Total iron	all	11
7.	Mercury ) Cadmium ) Chromium )	A,T,N	Every 14 days (December once)
	Copper ) Total and Lead ) dissolved Zinc ) Arsenic )	S,C,R	Every 2 months

### Metal Analysis in Dutch Coastal Waters

#### Note on some Analytical - Chemical Aspects

- 1. Analysis will be done in surface waters (total and dissolved) of: mercury, arsenic, copper, zinc, cadmium, lead and chromium.
- 2. Dissolved metals will be determined after N<sub>2</sub> pressure filtration by a 0.45  $\mu$ m filter of Sartorius (nr. SM- 111.06, low contaminated cellulose acetate, especially made for limnologists).



The filter-holder is of teflon, the pressure - container is of polypropylene. Filtration will take place on the sampling-ship. All samples will be stored in high-pressure polypropylene bottles, acidified  $(pH \approx 2)$  and deep-frozen. Digestion will proceed by oxidation with bromium. For mercury the cold-vapor atomic absorption spectrometric method will be used. .6. For arsenic the "arsine-generation method" will be used (after bromiumoxidation for destruction of possible methylated forms of arsenic). For copper, zinc, cadmium and lead MIBK-APDC extraction will in principle be used, although extraction with xylene seems to have the advantage of much lower solubility of xylene in water. The extracts will be brought directly into the graphite furnace. For chromium, direct determination in the furnace has not been successful so far. Extraction has, however, the disadvantage of strong variable yields (50 - 80%). These procedures will be in operation during 1975 (12 May - 31 December 1975).

f) Norway

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The only Norwegian laboratory engaged in studies of heavy metals in seawater is the Institute of Marine Biology and Limnology, University of Oslo.

The area of study involves profile investigations along a line of stations extending from the city of Oslo to the outermost part of the Oslofjord. No data have been ished yet, but will be presented as a doctor thesis in the near future.

Further studies related to those given above, but in the shallow near-shore waters of the Oslofjord are now carried out. This investigation includes also analyses of sediment and seashore fish.

Other surveys have been primarily of a biological nature.

#### g) United Kingdom

Report on UK Measurements of Trace Metals in the Water of the North Sea and North Atlantic

Ministry of Agriculture, Fisheries and Food (Lowestoft)

The results of published surveys are:-

- DUTTON, J.W.R., Folkard, A.R., Jefferies, D.F. and Jones, P.G.W., 1973. Trace metals in the North Sea. Mar. Poll. Bull., 4: 135-138.
- ICES (1974) Report of Working Group for the international study of the pollution of the North Sea and its effects on living resources and their exploitation. Coop. Res. Rep., No.39.
- JONES, P.G.W., Henry, J.L. and Folkard, A.R., 1973. The distribution of selected trace metals in the water of the North Sea 1971-1973. ICES, C.M.1973/C:5.
- PRESTON, A., Jefferies, D.F., Dutton, J.W.R., Harvey, B.R. and Steele, A.F., 1972. British Isles coastal waters: the concentrations of selected heavy metals in sea water, suspended matter and biological indicators - a pilot survey. Environ. Pollut., <u>3</u>: 69-82.

In addition to the above, surveys have also been made by the Fisheries Laboratory, Lowestoft as follows, the data not having yet been published:-

#### 1973-74

January 1974	Thames estuary to Hook of Holland
March 1974	Southern North Sea
September 1974	Thames estuary to Hook of Holland
November 1974	Northern North Sea (by RV "Meteor")
August 1974	English Channel
September-October 1	973 N.E. Atlantic, west of Scotland
July 1974	Shelf west of Scotland - Irish Sea - SW approaches(49°N - 59°N).
November-December 1	974 Shelf west of Ireland to SW approaches (48°N - 54°N).

#### <u> 1975</u>

The attached chart shows the areas in the North Atlantic over which trace metals have been/will be sampled during 1975. The tracks indicate approximate areas only. The survey of the southern region during September to October will be devoted entirely to trace metal sampling. Other surveys are primarily of a biological nature and trace metals will be sampled as opportunity permits.

In addition to the above, metals were sampled in the water of the southern North Sea during January and May; in the Thames Estuary during January and in the Humber Estuary during May.

#### Institute of Oceanographic Sciences (Wormley)

Trace metals have been analysed in parts of the eastern Atlantic near the Bay of Biscay. No data have been published yet. This institute does not plan any further extensive measurements of metals in water, but intends to study the behaviour of metals across the water/sediment interface in detail.

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