

C.M. 1980/C:24

Strategy for the study of sea-air exchanges
in the Belgian coastal zone

H. DEDEURWAERDER, M. DEJONGHE, F. DEHAIRS
Laboratorium voor Analytische Scheikunde
Vrije Universiteit Brussel, Belgium

Strategy for the study of sea-air exchanges in the Belgian coastal zone

H. DEDEURWAERDER, M. DEJONGHE, F. DEHAIRS
Laboratorium voor Analytische Scheikunde
Vrije Universiteit Brussel, Belgium

Abstract

In order to assess the contribution of the sea to the global atmospheric circulation of heavy metals in the North Sea area, we have started the study of the chemical composition of the sea-surface microlayer and of the marine aerosol.

Introduction

Sea-air exchange processes must be studied when looking for processes able to induce enrichment of heavy metals in the marine aerosol. Indeed, the air-sea interface appears to consist of a complex microenvironment which influences strongly and differentially the exchange of elements through it.

As well the chemical species of the elements as the relative amounts exchanged between the sea and the atmosphere can be affected by the composition of the microlayer itself.

Setting of the problematics

For several heavy metals (Cu, Fe, Zn, V, Pb, Cd, ...) the study of the marine aerosol has revealed a strong enrichment, which was not *a priori* expected when considering seawater and crustal material as sole sources (Piotrowicz et al., 1972). Furthermore, such strong enrichments are also

observed in remote, unindustrialized areas, such as the Antarctic continent, although absolute concentrations are smaller by a few orders of magnitude (Duce *et al.*, 1975 ; Maenhaut *et al.*, 1979). Due to the smallness of tropospheric exchange between the northern and southern hemisphere, anthropogenic influence is but poorly sensed in the southern hemisphere (Duce *et al.*, 1975). Therefore, natural processes are generally invoked (Piotrowicz *et al.*, 1972 ; Duce *et al.*, 1975 ; Hunter, 1977). Of these, high and low temperature volatilisation processes (resp. vulcanism and biological methylation) and extraction processes in the sea-air interface are considered (Duce *et al.*, 1975 ; Szekiolda *et al.*, 1972 ; Lantzy and Mackenzie, 1979). We will discuss the latter process with more detail.

An enrichment of heavy metals in the sea-surface microlayer has been observed (Piotrowicz *et al.*, 1972 ; Szekiolda *et al.*, 1972 ; Duce *et al.*, 1972 ; Pattenden and Cambray, 1977 ; Hunter, 1977). There exists evidence that this enrichment is induced as a result of the accumulation of surface active organometal complexes at the sea-air interface (Piotrowicz *et al.*, 1972 ; Duce *et al.*, 1975 ; Hunter, 1977).

Through the bursting of air bubbles at the sea surface, microtomal sections of the enriched surface microlayer are expelled into the atmosphere together with water droplets (Duce *et al.*, 1975 ; Piotrowicz, 1977 ; Fasching *et al.*, 1974 ; Buat-Menard *et al.*, 1979). Such a mechanism could provide highly enriched marine aerosols. A more detailed description of the marine aerosol formation is given in Figure 1.

The study of the element enrichment in function of the aerosol size allows a distinction of the aerosol sources. Small particles (*i.e.* sizes $< 1 \mu\text{m}$) appear to be produced mainly by evaporation/condensation processes, which can result as well from natural as from anthropogenic processes. Typical marine particles are generally found in the sizes $> 1 \mu\text{m}$ (Hunter, 1977 ; Duce *et al.*, 1976). As a result of their relatively large size such particles can remain only for a few days suspended in the atmosphere (Pattenden and Cambray, 1977 ; Cambray *et al.*, 1975). However, in coastal areas these large, typically marine aerosols can reach the continent and contribute in a significant way to the global aerosol composition (Rossknecht *et al.*, 1973).

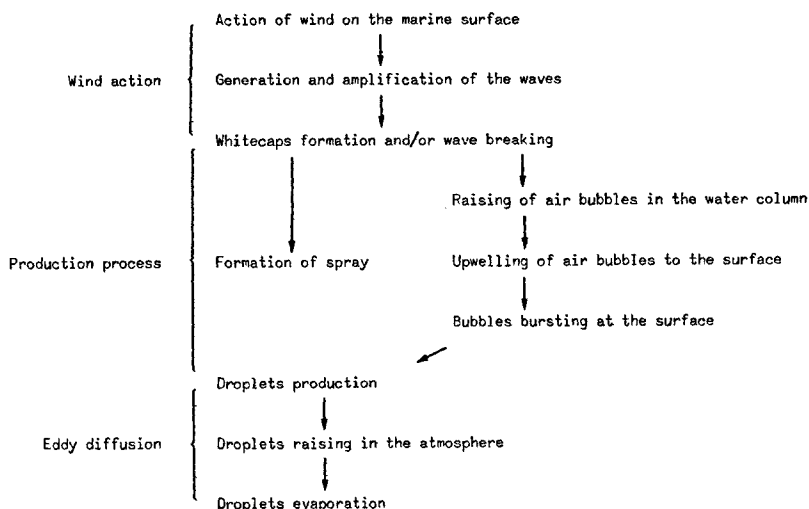


fig. 1.

(After Resch, 1978)

Proposed study

Both the composition of the sea-surface microlayer and of the marine aerosol will be studied.

1.- THE SEA-SURFACE MICROLAYER

The surface microlayer is sampled with the Garrett-screen technique (Garrett, 1965). The screen framework is all plexiglass and nylon mounted and stretches a nylon screen with openings of 400 by 400 μm and a fabric thickness of 440 μm .

The sampling is done aboard a small rubber boat, away from possible contamination by the research vessel.

The operator, wearing rubber gloves, immerses the screen vertically into the water and retrieves it horizontally. By surface tension a film of water, including the surface microlayer, is captured between the meshes of the screen. The thickness of the film sampled approximates the thickness

of the screen fabrics (i.e. ~ 0.4 mm). Successive samples are drawn into polyethylene containers. Bulk seawater is sampled at 20 to 30 cm below the surface, by immersing a polyethylene container.

Since we are mainly interested in the occurrence of organo-metal complexes, the samples were deep-frozen, immediately after return aboard the research vessel, without addition of any preservative. According to Wangersky and Zika (1978), this is the most reliable method in cases where the dissolved organic component must be stored with as small as possible changes in its composition. It is possible that this method goes at the expense of a good conservation of the dissolved inorganic heavy metal species.

In the laboratory ashore samples are rapidly thawed and filtered on Millipore membrane filters of $0.45 \mu\text{m}$ pore size. Samples are then split up according to the molecular size of the dissolved species. This is performed by ultrafiltration on 500 to 1000 Dalton membranes in a large volume (2 litre) cell. Heavy metal analyses are done on both the filtrate and the concentrate. Preconcentration of heavy metal in the filtrate is done by conventional APDC-MIBK complexation and Chelex ion-exchange techniques. The dialysed concentrate is analysed directly for heavy metal content, by AAS (flame or flameless technique).

Further studies involve the separation of the concentrate according to molecular weight of the dissolved organic materials present. This is performed by injection of a small aliquot of the concentrate on a Sephadex gel filtration column.

Since most microlayer sampling techniques induce a too large dilution of the microlayer with bulk seawater the extent of the heavy metal enrichment is difficult to assess. This emphasizes the need to study the microlayer as a discrete unit. The freezing and PVC-spray technique (Hamilton and Clifton, 1979) look very promising in avoiding this too large dilution. These techniques are also interesting since the microlayer with associated particulates is trapped onto a substrate suitable for analysis with the photonic and electronic microscope and electron microprobe.

2.- MARINE AEROSOLS

Sampling of marine aerosols is performed aboard a light vessel anchored at 20 miles from the Belgian coast on the West-Hinder Bank (Figure 2). The vessel moves freely around the anchor point as guided by tide currents. A high volume sampler ($30 \text{ m}^3/\text{hour}$) pumps the air through a Whatman 41 cellulose filter. Up to 300 m^3 of air are sampled per

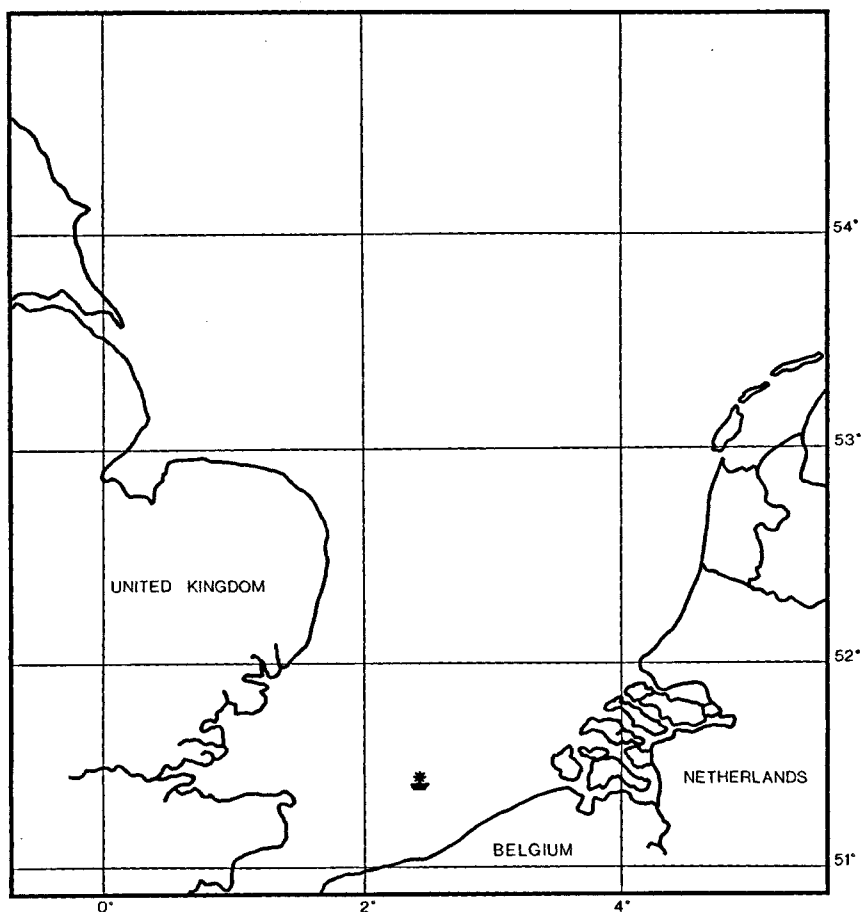


fig. 2.

Geographical location of the marine aerosol monitoring station
(West-Hinder light vessel) in the North Sea

filter. The volume of air sampled is measured with a gas-meter. The air filtration unit is all PVC mounted and is located at about 10 m above sea level, away from possible contamination by the vessel.

The sampling is automatically steered by a wind-direction and wind-speed monitor, obeying to preset boundary conditions. Sampling is performed only for wind blowing from the bow of the vessel in an angle of max. 60° and exceeding a speed of 3 knots. Aerosol sampling in function of particle size is performed with a 5 stage Sierra cascade impactor fitted with slotted Whatman 41 substrates. This allows for the aerosol size separation in the following size classes : .0 to .6 μm ; .6 to 1.3 μm ; 1.3 to 1.7 μm ; 1.7 to 4.9 μm ; 4.9 to 10.0 μm and 10.0 to > 10.0 μm . Microscopical analysis of the sampled particulates can be performed by positioning small Nuclepore membrane strips onto the Whatman 41 substrates of each stage (Buat-Ménard *et al.*, 1979 ; C. Lambert pers. comm., 1980). The Nuclepore membrane offers a suitable substrate for analysis with the scanning electron microscope and electron microprobe. Parallel to the sampling system for heavy metal analysis a filtration unit is mounted for the study of particulate carbon and airborne bacteria, resp. by using glass fiber (Whatman GF/F) and Millipore membrane (0.45 μm pore size) filters.

Preliminary results

1.- THE MICROLAYER

Presently we have not started the systematic analysis of heavy metal content in the microlayer and the bulk seawater. Nevertheless, preliminary measurements and laboratory tests have led to the following observations :

- Enrichment of heavy metal in the microlayer is not clearly demonstrated. This is most probably the result of a too large dilution of the microlayer, inherent to the sampling technique used. This urges the need for sampling techniques collecting more specifically the surface layer of the sea (*vide supra*).
- Humates are an important component of the dissolved organic load in the sea (Hunter, 1977; Baier *et al.*, 1974; Sieburth *et al.*, 1976; Sieburth

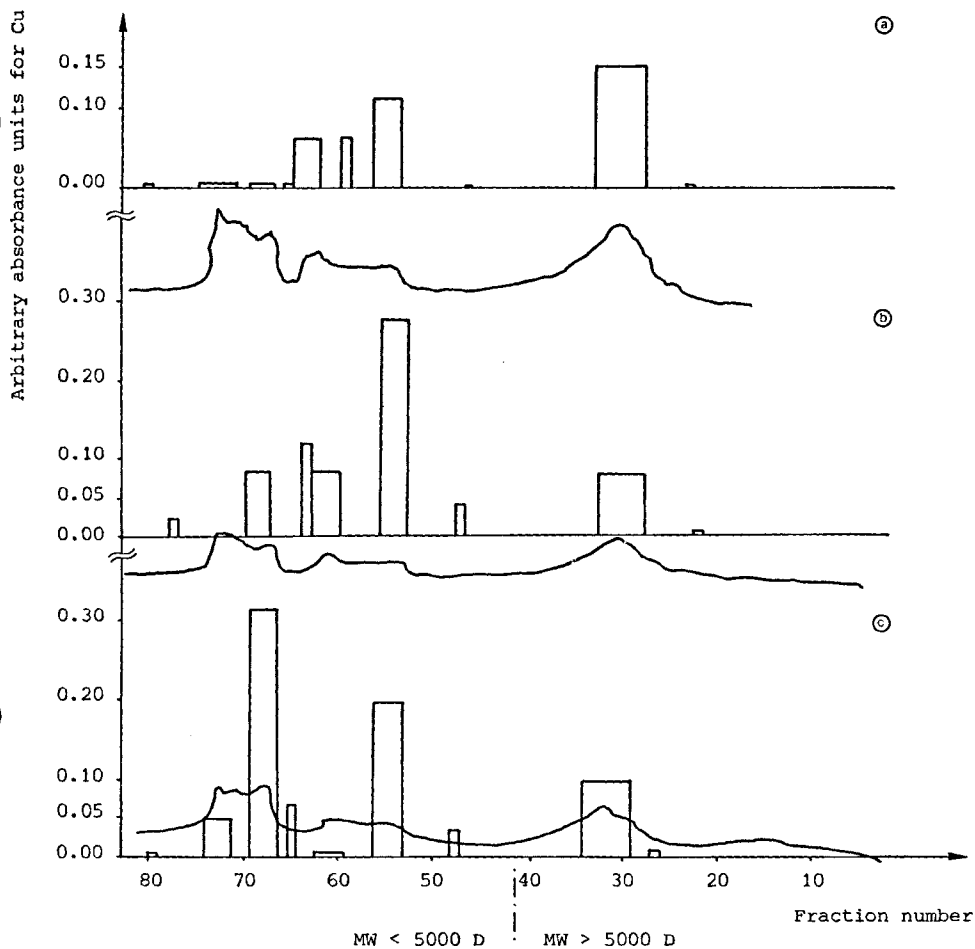


fig. 3.

Sephadex G-25 elution profiles for concentrate-fraction of samples ultrafiltered through a 1000 D membrane. Profile represents U.V. absorbance (at 254 nm) by the eluted fraction (each 10 ml). Profile-shapes are typical for humates. Histograms: Cu-content of some of the eluted fractions as measured by flameless AAS; bar-width = sample volume.

(a) Bulk seawater collected 04-03-80, location 51°08'04" N - 2°33'04" E.

(b) Microlayer collected 04-03-80, location 51°08'04" N - 2°33'04" E.

(c) Bulk seawater collected 05-03-80, location 51°23' N - 2°26' E (West-Hinder Bank).

and Jensen, 1968 and 1969; Nissenbaum and Kaplan, 1972) and are efficient heavy metal complexants (Pillai et al., 1971). The efficiency of ultrafiltration membranes of different pore sizes to concentrate humates was tested by analysing the retained concentrate with the fluorescence spectrophotometer (excitation at 319 nm; detection at 425 nm). From this study it resulted that membranes of 500 or 1000 dalton must be used to concentrate successfully the humates.

- Sephadex gel-filtration of the ultrafiltration concentrate : 5 ml of the concentrate were applied onto a G-25 (5000 dalton exclusion) Sephadex gel column (I.D. : 5 cm; height : 40 cm). This sample was eluted with twice deionized water. Fractions of 10 ml were collected after U.V. absorbance measurement at 254 nm for detection of fenol groups. Figure 3 represents elution profiles for two bulk seawater and one microlayer sample. The eluted fractions were analysed for Cu by flameless AAS (Figure 3). For Cu, preliminary analyses of a bulk seawater sample (location : Calais, 50°58'N - 1°24'E) revealed that of a total concentration of 1.6 ppb Cu, 0.8 ppb or 50% occur as organometal complexes.

2.- MARINE AEROSOLS

Aerosol composition is monitored routinely. Since January 1980, 33 filters were analyzed for the concentration of Al, Fe, Mn, Pb, Cu, Zn and Cd, with AAS, after wet oxydation with Suprapur HNO_3 and HClO_4 in teflon beakers.

The first conclusions we can draw are :

1. The concentrations are ranging between 15 and 703 ng/m^3 for Al, 98 and 2283 ng/m^3 for Fe, 3 and 250 ng/m^3 for Mn, 35 and 487 ng/m^3 for Pb, 1.5 and 88 ng/m^3 for Cu, 5 and 1460 ng/m^3 for Zn and between .5 and 10 ng/m^3 for Cd.
2. If we plot the concentrations of heavy metals in function of the wind direction, significant differences are observed between "marine air" (wind blowing from the sector North-West to North-East) and "continental air" (wind blowing from the sector South-West to East). For "marine air" the mean concentrations (arithmetic mean of 9 samples) are 200 ng/m^3 for Fe, 7.2 ng/m^3 for Mn, 160 ng/m^3 for Pb, 11 ng/m^3 for Cu, 64 ng/m^3 for Zn and 1.3 ng/m^3 for Cd.

For "continental air", the mean concentrations (arithmetic mean of 19 samples) are 1056 ng/m³ for Fe, 72 ng/m³ for Mn, 276 ng/m³ for Pb, 22 ng/m³ for Cu, 332 ng/m³ for Zn and 4.2 ng/m³ for Cd.

The higher mean concentrations for continental air are mainly due to emissions from punctual sources : the heavy industrial zone of Dunkerque and the triangle Zeebrugge - Brugge - Oostende.

3. With a single sampling equipment in operation it was not possible up to now to differentiate between the different aerosol sources (natural or anthropogenic). In order to resolve this problem, the elemental composition of the aerosols will be studied in function of particle size (use of a cascade impactor). The sampling of particles in function of their sizes will allow to study the influence of the wind velocity on the sea-air extraction process. Indeed, the greater the wind velocity the greater the efficiency of the heavy metal extraction from the microlayer by bursting bubbles. In the sample this will result in a greater relative contribution of the larger (> 1 µm) particles and in their greater enrichment in heavy metals. Furthermore, the study of the aerosol particle size distributions will inform us about their residence time in the atmosphere and therefore about the distance they covered.
4. Up to now, we do not measure the concentration of mercury in the atmosphere. According to Fitzgerald and Gill (1979), 96% of the Hg in the marine atmosphere is present in the vapor phase. Presently, a sampling method for Hg in the gas phase (with preconcentration on a Au-column) and the use of a furnace technique to obtain volatilisation of Hg in particulate samples are tested in our laboratory by G. Decadt and M. Dejonghe. It is our intention in the near future to monitor the Hg concentration routinely aboard the light-vessel West-Hinder.

Acknowledgments

This work was done in the framework of a National Research and Development Program. We thank the Ministry of Science Policy for financial support.

We also thank the crew of the West-Hinder light vessel for technical assistance.

References

- BAIER, R.E., GOUPIL, D.W., PERLMUTTER, S. and KING, R., (1974). Dominant chemical composition of sea surface films natural slicks and foams, *J. Rech. Atm.*, 8, 571.
- BUAT-MENARD, P., LAMBERT, C.E., EZAT, E., FONTUGNE, M. and CHESSELET, R., (1979). Preliminary data from electron microscopy and carbon isotopes mass spectrometry related to the sea-air exchange processes, *Searex Newsletter*, 2, 11-22.
- CAMBRAY, R.S., JEFFERIES, D.F. and TOPPING, G., (1975). An estimate of the input of atmospheric trace elements into the North Sea and the Clyde Sea (1972-3) AERE report, 7733, 26 pp.
- DUCE, R.A., HOFFMAN, G.L. and ZOLLER, W.H., (1975). Atmospheric trace metals at remote northern and southern hemisphere sites, pollution or natural?, *Science*, 187, 59.
- DUCE, R.A., QUINN, J.G., OLNEY, C.E., PIOTROWICZ, S.R., RAY, B.J. and WADE, T.L., (1972). Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, *Science*, 176, 161.
- DUCE, R.A., RAY, B.J., HOFFMAN, G.L. and WALSH, P.R., (1976). Trace metal concentrations as a function of particle size, *Geophys. Res. Letters*, 3, 339.
- FASCHING, J.L., COURANT, R.A., DUCE, R.A. and PIOTROWICZ, S.R., (1974). A new surface microlayer sampler utilizing the bubble microtorne, *J. Rech. Atm.*, 8, 649.
- FITZGERALD, W.F. and GILL, G.A., (1979). Subnanogram determination of mercury by two-stage gold amalgamation and gas phase detection applied to atmospheric samples, *Anal. Chem.*, 51, 1714.
- GARRETT, W.D., (1965). Collection of slick-forming materials from the sea surface, *Limnol. Oceanogr.*, 10, 602.
- HAMILTON, E.I. and CLIFTON, R.J., (1979). Techniques for sampling the air-sea interface for estuarine and coastal waters, *Limnol. Oceanogr.*, 24, 188.
- HUNTER, K.A., (1977). *Chemistry of the sea surface microlayer*, Ph. D. Thesis, University of East Anglia, G.B.
- LANTZY, R.J. and MACKENZIE, F.T., (1979). Atmospheric trace metals: global cycles and assessment of man's impact, *Geochim. Cosmochim. Acta*, 43, 511.
- MAENHAUT, W., ZOLLER, W.H., DUCE, R.A. and HOFFMAN, G.L., (1979). Concentration and size distribution of particulate trace elements in the South Polar atmosphere, *J. Geophys. Res.*, 84, 2421.

- NISSENBAUM, A. and KAPLAN, I.R., (1972). Chemical and isotope evidence for the *in situ* origin of marine humic substances, *Limnol. Oceanogr.*, 17, 570.
- PATTENDEN, N.J. and CAMBRAY, R.S., (1977). Investigations into the sea-surface enrichment of trace elements and its effect upon the atmospheric aerosol, Natural Environment Research Council, Intern. report.
- PILLAI, T.N.V., DESAI, M.V.M., MATHEW, E., GANAPATHY, S. and GANGULY, A.K., (1971). Organic materials in the marine environment and the associated metallic elements, *Current Science*, 40, 75.
- PIOTROWICZ, S.R., (1977). *The sea to air transport of trace metals*, Ph. D. Thesis, University of Rhode Island, USA.
- PIOTROWICZ, S.R., RAY, S.J., HOFFMAN, G.L. and DUCE, R.A., (1972). Trace metal enrichment in the sea-surface microlayer, *J. Geophys. Res.*, 77, 5243.
- RESCH, F., (1978). Incidence des activités humaines sur les cycles atmosphériques à l'échelle globale, Ecole Européenne d'été d'environnement, Peyresq, septembre.
- ROSSKNECHT, G.F., ELLIOTT, W.P. and RAMSAY, F.L., (1973). The size distribution and inland penetration of sea-salt particles, *J. Appl. Meteor.*, 12, 825.
- SIEBURTH, J.Mc.N. and JENSEN, A., (1968). Studies on algal substances in the sea. I. Gelbstoff (humic material) in terrestrial and marine waters, *J. Exp. Mar. Biol. Ecol.*, 2, 174.
- SIEBURTH, J.Mc.N. and JENSEN, A., (1969). Studies on algal substances in the sea. II. The formation of Gelbstoff (humic material) by exudates of phaeophyta, *J. Exp. Mar. Biol. Ecol.*, 3, 275.
- SIEBURTH, J.Mc.N., WILLIS, P., JOHNSON, K.M., BURNEY, C.M., LAVOIE, D.M. HINGA, K.P., CARON, D.A., FRENCH, F.W., JOHNSON, P.W. and DAVIS, P.G., (1976). Dissolved organic matter and heterotrophic microneuston in the surface microlayers of the North Atlantic, *Science*, 194, 1415.
- SZEKIELDA, K.H., KUPFERMAN, S.L., KLEVAS, V. and POLIS, D.F., (1972). Element enrichment in organic films and foam associated with aquatic frontal systems, *J. Geophys. Res.*, 77, 5278.
- WANGERSKY, P.J. and ZIKA, R.G., (1978). The analysis of organic compounds in sea water, Nat'l Rech. Council. Canada Rep., 3, 177 pp.